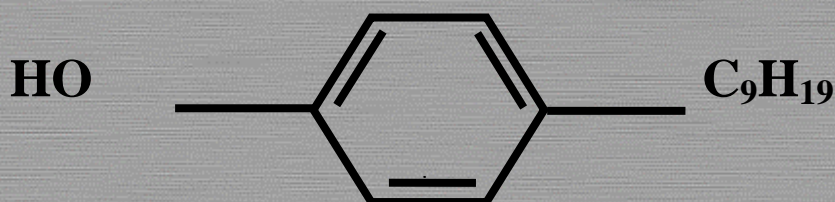


# European Union Risk Assessment Report

CAS Nos: 84852-15-3  
25154-52-3

EINECS Nos: 284-325-5  
246-672-0

## 4-nonylphenol (branched) and nonylphenol





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CAS Nos: 84852-15-3 and 25154-52-3

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### **RISK ASSESSMENT**

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**4-NONYLPHENOL (BRANCHED)  
AND  
NONYLPHENOL**

CAS Nos: 84852-15-3 and 25154-52-3

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**RISK ASSESSMENT**

*Final report, 2002*

United Kingdom

This document has been prepared by the UK rapporteur on behalf of the European Union. The scientific work on the environmental part was prepared by the Building Research Establishment (BRE) Ltd, under contract to the rapporteur.

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<b>Date of Last Literature Search :</b>	<b>1996</b>
<b>Review of report by MS Technical Experts finalised:</b>	<b>1999</b>
<b>Final report:</b>	<b>2002</b>

(The last full literature survey was carried out in 1996. Use data were added up to 1997, with some specific information more recent than this. Toxicity data have been added up until 1999.)

## Foreword

We are pleased to present this Risk Assessment Report which is the result of in-depth work carried out by experts in one Member State, working in co-operation with their counterparts in the other Member States, the Commission Services, Industry and public interest groups.


The Risk Assessment was carried out in accordance with Council Regulation (EEC) 793/93<sup>1</sup> on the evaluation and control of the risks of “existing” substances. “Existing” substances are chemical substances in use within the European Community before September 1981 and listed in the European Inventory of Existing Commercial Chemical Substances. Regulation 793/93 provides a systematic framework for the evaluation of the risks to human health and the environment of these substances if they are produced or imported into the Community in volumes above 10 tonnes per year.

There are four overall stages in the Regulation for reducing the risks: data collection, priority setting, risk assessment and risk reduction. Data provided by Industry are used by Member States and the Commission services to determine the priority of the substances which need to be assessed. For each substance on a priority list, a Member State volunteers to act as “Rapporteur”, undertaking the in-depth Risk Assessment and recommending a strategy to limit the risks of exposure to the substance, if necessary.

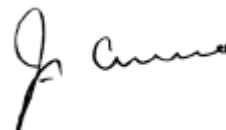
The methods for carrying out an in-depth Risk Assessment at Community level are laid down in Commission Regulation (EC) 1488/94<sup>2</sup>, which is supported by a technical guidance document<sup>3</sup>. Normally, the “Rapporteur” and individual companies producing, importing and/or using the chemicals work closely together to develop a draft Risk Assessment Report, which is then presented at a Meeting of Member State technical experts for endorsement. The Risk Assessment Report is then peer-reviewed by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) which gives its opinion to the European Commission on the quality of the risk assessment.

If a Risk Assessment Report concludes that measures to reduce the risks of exposure to the substances are needed, beyond any measures which may already be in place, the next step in the process is for the “Rapporteur” to develop a proposal for a strategy to limit those risks.

The Risk Assessment Report is also presented to the Organisation for Economic Co-operation and Development as a contribution to the Chapter 19, Agenda 21 goals for evaluating chemicals, agreed at the United Nations Conference on Environment and Development, held in Rio de Janeiro in 1992. This Risk Assessment improves our knowledge about the risks to human health and the environment from exposure to chemicals. We hope you will agree that the results of this in-depth study and intensive co-operation will make a worthwhile contribution to the Community objective of reducing the overall risks from exposure to chemicals.



**Barry Mc Sweeney**  
Director-General  
Joint Research Centre



**J. Currie**  
Director-General  
Environment, Nuclear Safety and Civil Protection

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<sup>1</sup> O.J. No L 084, 05/04/199 p.0001 – 0075

<sup>2</sup> O.J. No L 161, 29/06/1994 p. 0003 – 0011

<sup>3</sup> Technical Guidance Document, Part I – V, ISBN 92-827-801 [1234]





## 0 OVERALL RESULTS OF THE RISK ASSESSMENT

CAS Number: 84852-15-3  
EINECS Number: 284-325-5  
IUPAC Name: 4-Nonylphenol (branched)

CAS Number: 25154-52-3  
EINECS Number: 246-672-0  
IUPAC Name: Nonylphenol

### Environment

(x) **i)** There is a need for further information and/or testing.

This conclusion applies to the aquatic (sediment) compartment for all life cycle stages (except production of tri-(4-nonylphenyl) phosphite (TNPP) and the use of veterinary medicine products containing nonylphenol ethoxylates). The PNEC for sediment was derived from that for aquatic organisms. It could therefore be revised by performing toxicity tests on sediment organisms. However, the requirement for further testing should await the outcome of the risk reduction strategy for the aquatic (surface water) compartment, since the sediment PECs will be directly affected by any measures to reduce concentrations in water.

(x) **ii)** There is at present no need for further information and/or testing and no need for risk reduction measures beyond those, which are being applied already.

This conclusion applies to the aquatic (surface water and sediment) compartment for production of TNPP and the use of veterinary medicine products containing nonylphenol ethoxylates, and to the atmospheric compartment and micro-organisms in wastewater treatment plant for all life cycle stages. It also applies to the terrestrial compartment for the following life cycle stages (as well as to regional soil concentrations derived from all sources):

- Production of nonylphenol;
- Production of nonylphenol/formaldehyde resins;
- Production of epoxy resins;
- Production of TNPP;
- Production of other plastic stabilisers;
- Production of phenolic oximes;
- Use of nonylphenol ethoxylates in agriculture (pesticide formulations); and
- Domestic and industrial use of paint containing nonylphenol ethoxylates.

This conclusion also applies to the following life cycle stages for secondary poisoning (as well as to regional concentrations derived from all sources):

- Production of nonylphenol;
- Production of nonylphenol/formaldehyde resins;
- Production of epoxy resins;
- Production of TNPP;
- Production of other plastic stabilisers;
- Production of phenolic oximes;
- Use of nonylphenol ethoxylates in agriculture (pesticide formulations);

- Use of nonylphenol ethoxylates in agriculture (veterinary medicines);
  - Use of paint containing nonylphenol ethoxylates;
  - Use of nonylphenol ethoxylates in the photographic industry; and
  - Use of nonylphenol ethoxylates in the polymer industry.
- (x)    **iii)**    There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

This conclusion applies to the aquatic (surface water) compartment for the following life cycle stages (as well as to regional concentrations derived from all sources):

- Production of nonylphenol;
- Production of phenol/formaldehyde resins;
- Production of epoxy resins;
- Production of other plastic stabilisers;
- Production of phenolic oximes;
- Production of nonylphenol ethoxylates;
- Formulation of nonylphenol ethoxylates; and
- Nonylphenol ethoxylate use in all applications (i.e. agriculture\*; captive use by the chemical industry; civil engineering; electrical engineering; industrial and institutional cleaning; leather processing; metal extraction and processing; mineral fuel and oil industry; paint production and use; photographic industry; polymer industry; pulp, paper and board industry; textile industry).

This conclusion also applies to the following life cycle stages for the terrestrial compartment:

- Production of nonylphenol ethoxylates;
- Formulation of nonylphenol ethoxylates;
- Use of nonylphenol ethoxylates in agriculture (veterinary medicines);
- Captive use of nonylphenol ethoxylates by the chemical industry;
- Use of nonylphenol ethoxylates in civil engineering;
- Use of nonylphenol ethoxylates in electrical engineering;
- Use of nonylphenol ethoxylates in industrial and institutional cleaning;
- Use of nonylphenol ethoxylates in leather processing;
- Use of nonylphenol ethoxylates in metal extraction and processing;
- Use of nonylphenol ethoxylates in the mineral fuel and oil industry;
- Production of paint containing nonylphenol ethoxylates;
- Use of nonylphenol ethoxylates in the photographic industry;
- Use of nonylphenol ethoxylates in the polymer industry;
- Use of nonylphenol ethoxylates in the pulp, paper and board industry; and
- Use of nonylphenol ethoxylates in the textile industry.

---

\* This does not apply to use in veterinary medicines.

It also applies to the following life cycle stages for secondary poisoning:

- Production of nonylphenol ethoxylates;
- Formulation of nonylphenol ethoxylates;
- Captive use of nonylphenol ethoxylates within the chemical industry;
- Use of nonylphenol ethoxylates in civil engineering;
- Use of nonylphenol ethoxylates in the electrical engineering industry;
- Use of nonylphenol ethoxylates in industrial and institutional cleaning;
- Use of nonylphenol ethoxylates in leather processing;
- Use of nonylphenol ethoxylates in metal extraction and processing;
- Use of nonylphenol ethoxylates in the mineral fuel and oil industry;
- Production of paint containing nonylphenol ethoxylates;
- Use of nonylphenol ethoxylates in the pulp, paper and board industry; and
- Use of nonylphenol ethoxylates in the textile industry.

#### Human health

- ( ) **i)** There is need for further information and/or testing.
- (x) **ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.
- ( ) **iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (ii)** is reached because the minimum data requirements according to Article 9(2) of Regulation 793/93 have been met and no further data are required.

#### *Workers*

- ( ) **i)** There is need for further information and/or testing.
- (x) **ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.
- (x) **iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (iii)** is reached for workers during nonylphenol manufacture, use as an intermediate and during speciality paint spray applications because for repeated dose toxicity and reproductive effects, the margins between actual exposure and N(L)OEALs are low. The corrosivity of the substance in relation to the skin and eye is unlikely to be expressed when good occupational hygiene practices are in operation. However, because of the variation in hygiene practice for the spraying of paints, there are concerns for corrosivity, and **conclusion (iii)** is reached for this scenario. These results give rise to concerns for risks to human health.

**Conclusion (ii)** is reached for remaining scenarios.

### *Consumers*

- ( ) **i)** There is need for further information and/or testing.
- (x) **ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.
- ( ) **iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (ii)** is reached because there are sufficiently large margins between actual or modelled exposures and LD<sub>50</sub> values and N(L)OAELs, so that it can be concluded that there is no cause for concern for human health.

### *Man indirectly exposed via the environment*

- (x) **i)** There is need for further information and/or testing.
- (x) **ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.
- ( ) **iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (i)** is reached for exposure in the vicinity of a nonylphenol plant because further information is required to refine the risk characterisation. Very low margins of safety (MOS) are found for repeated dose toxicity and reproductive effects. These margins of safety are based on comparison of the N(L)OAELs with modelled exposure data. Further information on emissions into the local environment from plants involved in production and use of nonylphenol is required to refine the risk characterisation. However, the requirement for further information should await the outcome of the risk reduction strategy for the aquatic (surface water) compartment, since the exposure will be directly affected by any measures to reduce concentrations in water.

The margins of safety for regional exposure do not give rise to concern for these endpoints and result in a **conclusion (ii)**. **Conclusion (ii)** is also reached for acute toxicity and corrosivity since these are endpoints of low concern for both local and regional scenarios.

### *Combined exposure*

- (x) **i)** There is need for further information and/or testing.
- (x) **ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.
- ( ) **iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (i)** is reached because although the MOS values based upon repeated dose toxicity and reproductive effects indicate a cause for concern, the risk characterisation can be refined once risk reduction measures have been considered for workers and further information on local environmental exposure has been obtained (but see comment under “Man indirectly exposed via the environment” above).

**Conclusion (ii)** is reached for acute toxicity and corrosivity, which are of low concern for this scenario.

Risks from physicochemical properties

- ( ) **i)** There is need for further information and/or testing.
- (x) **ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.
- ( ) **iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (ii)** is reached because there are no significant risks to humans from physicochemical properties.



# CONTENTS

<b>1 GENERAL SUBSTANCE INFORMATION</b> .....	7
<b>1.1 IDENTIFICATION OF THE SUBSTANCE</b> .....	7
<b>1.2 PURITY/IMPURITIES, ADDITIVES</b> .....	8
1.2.1 Purity.....	8
1.2.2 Additives.....	8
<b>1.3 PHYSICO-CHEMICAL PROPERTIES</b> .....	8
1.3.1 Physical state (at ntp).....	8
1.3.2 Melting point.....	8
1.3.3 Boiling point.....	8
1.3.4 Relative density.....	9
1.3.5 Vapour pressure.....	9
1.3.6 Water solubility.....	10
1.3.7 n-Octanol-water partition coefficient.....	11
1.3.8 Flash point.....	11
1.3.9 Autoflammability.....	11
1.3.10 Explosivity.....	11
1.3.11 Oxidising properties.....	11
1.3.12 Viscosity.....	11
1.3.13 Other physical-chemical properties.....	12
1.3.14 Summary of physico-chemical properties.....	12
<b>1.4 CLASSIFICATION</b> .....	13
1.4.1 Current classification.....	13
<b>2 GENERAL INFORMATION ON EXPOSURE</b> .....	15
<b>2.1 PRODUCTION</b> .....	15
2.1.1 Production processes.....	15
2.1.2 Production capacity.....	15
<b>2.2 USES</b> .....	16
2.2.1 Introduction.....	16
2.2.1.1 Nonylphenol ethoxylates.....	16
2.2.1.2 Polymer industry.....	17
2.2.1.3 Manufacture of phenolic oximes.....	18
2.2.2 Use of nonylphenol ethoxylates.....	18
2.2.2.1 Captive use.....	21
2.2.2.2 Electrical engineering industry.....	21
2.2.2.3 Industrial and institutional cleaning.....	21
2.2.2.4 Textile auxiliaries.....	21
2.2.2.5 Leather auxiliaries.....	21
2.2.2.6 Agriculture.....	21
2.2.2.7 Emulsion polymers.....	22
2.2.2.8 Speciality Paints.....	22
2.2.2.9 Pulp and paper.....	22
2.2.2.10 Metal industry.....	22
2.2.2.11 Miscellaneous uses.....	22
<b>2.3 TRENDS</b> .....	23
<b>2.4 LEGISLATIVE CONTROLS</b> .....	23
<b>3 ENVIRONMENT RISK ASSESSMENT</b> .....	25
<b>3.1 ENVIRONMENTAL EXPOSURE</b> .....	25
3.1.1 General discussion.....	25
3.1.1.1 Environmental releases.....	25
3.1.1.1.1 Releases of nonylphenol.....	25
3.1.1.1.2 Releases of nonylphenol ethoxylates.....	35

3.1.1.1.3	Summary of regional and continental releases of nonylphenol to the environment .....	51
3.1.1.2	Degradation in the environment .....	54
3.1.1.2.1	Atmospheric degradation .....	54
3.1.1.2.2	Aquatic degradation .....	54
3.1.1.2.3	Degradation in soil .....	57
3.1.1.2.4	Discussion of degradation data .....	59
3.1.1.2.5	Summary of environmental degradation .....	61
3.1.1.3	Distribution .....	61
3.1.1.3.1	Adsorption .....	61
3.1.1.3.2	Precipitation .....	63
3.1.1.3.3	Volatilisation .....	64
3.1.1.3.4	Distribution in wastewater treatment plants .....	64
3.1.1.3.5	Accumulation and metabolism .....	64
3.1.2	Aquatic compartment (incl. sediment) .....	67
3.1.2.1	Predicted environmental concentrations in water .....	67
3.1.2.1.1	Calculation of $PEC_{local}$ .....	67
3.1.2.1.2	Calculation of $PEC_{regional(water)}$ and $PEC_{continental(water)}$ .....	77
3.1.2.1.3	Calculation of Predicted Environmental Concentration for Sewage Treatment Plants ( $PEC_{stp}$ ) .....	77
3.1.2.1.4	Calculation of $PEC_{sediment}$ .....	77
3.1.2.1.5	Summary of calculated PECs for surface water .....	78
3.1.2.2	Measured levels in water .....	79
3.1.2.2.1	Surface waters .....	79
3.1.2.2.2	Seawater .....	81
3.1.2.2.3	Groundwater .....	81
3.1.2.2.4	Effluent from industrial processes .....	82
3.1.2.2.5	Wastewater treatment plant .....	82
3.1.2.2.6	Sediment .....	85
3.1.2.2.7	Comparison of PECs with measured data .....	86
3.1.3	Terrestrial compartment .....	87
3.1.3.1	Calculated PEC for soil .....	87
3.1.3.2	Measured levels .....	93
3.1.4	Atmospheric compartment .....	94
3.1.5	Non compartment specific effects relevant for the food chain (Secondary poisoning) .....	95
<b>3.2</b>	<b>EFFECTS ASSESSMENT: HAZARD IDENTIFICATION AND DOSE (CONCENTRATION) - RESPONSE (EFFECT ASSESSMENT)</b> .....	<b>97</b>
3.2.1	Aquatic compartment (including sediment) .....	97
3.2.1.1	Toxicity test results .....	97
3.2.1.1.1	Criteria for validation .....	97
3.2.1.1.2	Fish .....	97
3.2.1.1.3	Aquatic invertebrates .....	98
3.2.1.1.4	Aquatic algae and plants .....	107
3.2.1.1.5	Micro-organisms .....	107
3.2.1.1.6	Amphibians .....	108
3.2.1.1.7	Endocrine disruption .....	108
3.2.1.1.8	Field Studies .....	112
3.2.1.2	Calculation of Predicted No Effect Concentration (PNEC) .....	117
3.2.1.2.1	Surface water .....	117
3.2.1.2.2	Sewage treatment plants .....	118
3.2.1.2.3	Sediment .....	118
3.2.2	Terrestrial compartment .....	118
3.2.2.1	Terrestrial effect data .....	118
3.2.2.2	Calculation of $PNEC_{soil}$ .....	119
3.2.3	Atmosphere .....	119
3.2.4	Non compartment specific effects relevant to the food chain (secondary poisoning) .....	120



<b>3.3 RISK CHARACTERISATION</b> .....	120
3.3.1 Aquatic compartment (including sediment).....	120
3.3.2 Terrestrial compartment.....	125
3.3.3 Atmosphere.....	128
3.3.4 Non compartment specific effects relevant for the food chain (Secondary poisoning) .....	129
<b>4 HUMAN HEALTH</b> .....	132
<b>4.1 HUMAN HEALTH (TOXICITY)</b> .....	132
4.1.1 Exposure assessment .....	132
4.1.1.1 Occupational exposure.....	132
4.1.1.1.1 General introduction .....	132
4.1.1.1.2 Occupational exposure to nonylphenol during its manufacture and use as a chemical intermediate .....	133
4.1.1.1.3 Occupational exposure to residual nonylphenol during the use of its derivatives.....	135
4.1.1.1.4 Manufacture of nonylphenol containing speciality paints .....	135
4.1.1.1.5 Use of speciality paints containing nonylphenol .....	136
4.1.1.1.6 General discussion .....	138
4.1.1.2 Consumer exposure .....	140
4.1.1.2.1 Introduction .....	140
4.1.1.2.2 Potential exposure from nonylphenol ethoxylates .....	141
4.1.1.2.3 Exposures from migration of residual nonylphenol from food contact materials.....	143
4.1.1.2.4 Potential exposure from phenolic resin coatings .....	148
4.1.1.2.5 Hardeners for 2-component adhesives .....	149
4.1.1.2.6 Summary.....	149
4.1.1.3 Indirect exposure via the environment.....	149
4.1.1.4 Combined exposure .....	150
4.1.2 Effects assessment: Hazard identification and dose (concentration)-response (effect) assessment .....	154
4.1.2.1 Toxicokinetics, metabolism and distribution.....	154
4.1.2.1.1 Studies in animals .....	154
4.1.2.1.2 Studies in humans .....	157
4.1.2.1.3 Summary of toxicokinetics, metabolism and distribution.....	158
4.1.2.2 Acute toxicity .....	159
4.1.2.2.1 Inhalation.....	159
4.1.2.2.2 Oral .....	159
4.1.2.2.3 Dermal .....	159
4.1.2.2.4 Summary of acute toxicity.....	159
4.1.2.3 Irritation.....	159
4.1.2.3.1 Skin.....	159
4.1.2.3.2 Eye.....	160
4.1.2.3.3 Respiratory tract.....	160
4.1.2.3.4 Summary of irritation.....	161
4.1.2.4 Corrosivity .....	161
4.1.2.5 Sensitisation.....	161
4.1.2.5.1 Skin.....	161
4.1.2.5.2 Respiratory tract.....	162
4.1.2.5.3 Summary of sensitisation.....	162
4.1.2.6 Repeated dose toxicity.....	162
4.1.2.6.1 Animal data.....	162
4.1.2.6.2 Human data.....	167
4.1.2.6.3 Summary of repeated dose toxicity.....	167
4.1.2.7 Mutagenicity.....	167
4.1.2.7.1 Studies in vitro.....	168
4.1.2.7.2 Studies in vivo .....	168
4.1.2.7.3 Summary of mutagenicity.....	169
4.1.2.8 Carcinogenicity.....	169

4.1.2.9	Toxicity to reproduction .....	169
4.1.2.9.1	Studies investigating oestrogenic activity.....	169
4.1.2.9.2	Effects on fertility .....	171
4.1.2.9.3	Developmental toxicity.....	173
4.1.2.9.4	Summary of toxicity to reproduction.....	176
4.1.3	Risk characterisation.....	177
4.1.3.1	General aspects .....	177
4.1.3.2	Workers .....	180
4.1.3.2.1	Introduction .....	180
4.1.3.2.2	Comparison of exposure and effects.....	180
4.1.3.2.3	Summary of risk characterisation for workers.....	184
4.1.3.3	Consumers .....	184
4.1.3.3.1	Introduction .....	184
4.1.3.3.2	Comparison of exposure and effects.....	185
4.1.3.3.3	Summary of risk characterisation for consumers.....	186
4.1.3.4	Indirect exposure via the environment.....	186
4.1.3.4.1	Introduction .....	186
4.1.3.4.2	Comparison of exposure and effects.....	187
4.1.3.4.3	Summary of risk characterisation for exposure via the environment.....	187
4.1.3.5	Combined exposure .....	188
<b>4.2</b>	<b>HUMAN HEALTH (PHYSICOCHEMICAL PROPERTIES)</b> .....	<b>188</b>
<b>5</b>	<b>RESULTS</b> .....	<b>189</b>
<b>5.1</b>	<b>INTRODUCTION</b> .....	<b>189</b>
<b>5.2</b>	<b>ENVIRONMENT</b> .....	<b>189</b>
<b>5.3</b>	<b>HUMAN HEALTH</b> .....	<b>191</b>
<b>5.4</b>	<b>RISKS FROM PHYSICOCHEMICAL PROPERTIES</b> .....	<b>194</b>
<b>6</b>	<b>REFERENCES</b> .....	<b>195</b>
	<b>GLOSSARY</b> .....	<b>205</b>
<b>Appendix 1</b>	Formation of nonylphenol during the biodegradation of nonylphenol ethoxylates .....	208
<b>Appendix 2</b>	EUSES Modelling .....	225
<b>Appendix 3</b>	Comparison of EU nonylphenol Risk Assessment Report and US EPA RM-1 document For para nonylphenol (USEPA, 1996).....	226

## TABLES

Table 1.1	Vapour Pressure data of 4-nonylphenol .....	9
Table 1.2	Physical and chemical properties of nonylphenol .....	13
Table 2.1	Production volume, exports and imports (1997) .....	15
Table 2.2	Use of Nonylphenol within the EU (1994,1997) .....	16
Table 2.3	Industrial use categories for nonylphenol ethoxylates in the EU (1994) (CEFIC, 1996).....	19
Table 2.4	Functional use categories for nonylphenol ethoxylates in the EU (1994) (CEFIC, 1996).....	20
Table 2.5	Production and use of nonylphenol ethoxylates within the EU (1997).....	20
Table 3.1	Summary of emissions from nonylphenol production sites.....	27
Table 3.2	Summary of releases from nonylphenol ethoxylate production plants.....	31
Table 3.3	Summary of regional emissions.....	51
Table 3.4	Summary of continental emissions .....	52
Table 3.5	Soil characteristics and calculated K values .....	61
Table 3.6	Nonylphenol and nonylphenol ethoxylate concentrations due to riverwater infiltration.....	63
Table 3.7	Fraction of emission directed to air, surface water, sludge and degraded as calculated by EUSES.....	64

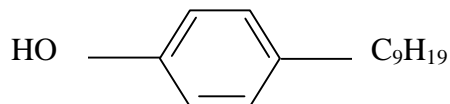
Table 3.8	Summary of calculated concentrations for water and sediment .....	78
Table 3.9	PEC for Secondary Poisoning .....	96
Table 3.10	Toxicity of nonylphenol to fish .....	99
Table 3.11	Toxicity of nonylphenol to aquatic invertebrates .....	102
Table 3.12	Toxicity of nonylphenol to aquatic algae and plants .....	106
Table 3.13	Summary of measured concentrations in various phases found in the field study .....	113
Table 3.14	Effects observed on zooplankton and macroinvertebrate populations .....	115
Table 3.15	Summary of aquatic toxicity .....	117
Table 3.16	Toxicity to terrestrial plants .....	118
Table 3.17	Toxicity to terrestrial invertebrates .....	119
Table 3.18	Comparison of calculated concentrations for water and sediment and PNECs for water, sediment and micro-organisms .....	122
Table 3.19	PEC/PNEC ratios for the terrestrial compartment .....	127
Table 3.20	PEC/PNEC ratio for fish and earthworms .....	129
Table 4.1	Occupational exposure to nonylphenol during its use as a chemical intermediate .....	134
Table 4.2	Summary of occupational exposure data taken forward to risk characterisation .....	140
Table 4.3	Consumer exposure to hair dyes .....	142
Table 4.4	Residual levels of nonylphenol in TNPP .....	144
Table 4.5	Use of trisnonylphenylphosphite in food-packaging materials .....	144
Table 4.6	Potential Nonylphenol exposure from LLDPE <sup>a</sup> .....	145
Table 4.7	Potential Nonylphenol exposure from HIPS .....	146
Table 4.8	Overall exposures .....	146
Table 4.9	Levels of NPE-4 in food packaging materials .....	147
Table 4.10	Assumptions for calculation of potential migration .....	147
Table 4.11	Assumptions (paper and paperboard) .....	148
Table 4.12	Indirect exposure of man via the environment .....	151
Table 4.13	Number of animals with histopathological abnormalities in the kidney (n=10) .....	165
Table 4.14	Summary of the risk characterisation for workers during nonylphenol manufacture and use as an intermediate ...	182
Table 4.15	Summary of the risk characterisation for workers during the manufacture of speciality paint .....	184
Table 4.16	Summary of the risk characterisation for workers during speciality paint spray applications .....	184
Table 4.17	Risk characterisation for consumers for acute toxicity .....	185
Table 4.18	Risk characterisation for consumers for corrosivity (skin/eye) .....	185
Table 4.19	Risk characterisation for consumers for corrosivity (respiratory tract) .....	185
Table 4.20	Risk characterisation for consumers for repeated dose toxicity .....	186
Table 4.21	Risk characterisation for consumers for reproductive effects .....	186
Table 4.22	Summary of risk characterisation for humans exposed via the environment .....	187
Table 4.23	Risk characterisation for combined exposure .....	187
Table 5.1	Summary of risk characterisation for the environment .....	190
Table A	Results from standard biodegradation tests (Gerike, 1987) .....	209
Table B	Removal of NPnEO in waste water treatment in the United States. ....	216
Table C	Results of incubation of OPnEO with activated sludge. ....	217
Table D	Results of incubation of OPnEO with primary sewage .....	218
Table E	Results of incubation of OPnEC with primary sewage .....	218
Table F	Results of incubation of OPnEO under anaerobic conditions .....	219
Table G	Results of incubation of OPnEC under anaerobic conditions. ....	219
Table H	Summary of behaviour of nonylphenol ethoxylates during waste water treatment .....	222



# 1 GENERAL SUBSTANCE INFORMATION

## 1.1 IDENTIFICATION OF THE SUBSTANCE

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

The term "nonylphenol" can apply to a large number of isomeric compounds of general formula  $C_6H_4(OH)C_9H_{19}$ . Nonylphenols may vary in two ways: the substitution position of the nonyl group on the phenol molecule; and the degree of branching of the nonyl group. Since the nonyl moiety is formed by polymerising propylene, the degree of branching may be considerable and varied. Many of the individual branched isomers have their own CAS numbers.

This assessment covers two substances identified on the second ESR priority list: nonylphenol (EINECS Number: 246-672-0, CAS Number: 25154-52-3) and phenol, 4-nonyl, branched (EINECS Number: 284-325-5, CAS Number: 84852-15-3).

It is understood that nonylphenol (CAS Number: 25154-52-3) as originally defined by CAS (Chemical Abstract Service) covered all nonylphenols. However, subsequent revisions redefined it to cover only straight chain nonylphenol, other isomers having different CAS numbers. Given the method of manufacture of nonylphenols, very little if any straight chain nonylphenol is produced. That which is produced is only likely to be present at very low levels in commercial mixtures. The commercially produced nonylphenols are predominantly 4-nonylphenol with a varied and undefined degree of branching in the alkyl group. This assessment covers commercially produced material (predominantly 4-nonylphenol, branched). This material will also contain smaller amounts of other isomers and impurities, and falls under the CAS Number 84852-15-3.

In carrying out this assessment data from any of the isomers are assumed to be representative for nonylphenol unless otherwise specified, and nonylphenol (NP) is used as the generic name referring to these substances.

## 1.2 PURITY/IMPURITIES, ADDITIVES

### 1.2.1 Purity

The purity of commercial nonylphenol is reported as 90% w/w with the following impurities:

2-Nonylphenol	5% w/w
2,4-Dinonylphenol	5% w/w

### 1.2.2 Additives

There are no reported additives.

## 1.3 PHYSICO-CHEMICAL PROPERTIES

The varied degree of branching in the nonyl group may be a factor in the variability of the physical-chemical properties reported.

**Table 1.2** summarises the chemical and physical properties of nonylphenol.

### 1.3.1 Physical state (at ntp)

Commercially produced nonylphenol is a clear to pale yellow viscous liquid with a slight phenolic odour.

### 1.3.2 Melting point

A pour point (i.e. the lowest temperature at which movement of the substance is observed, which is an appropriate measurement for oily substances of this type) of circa -8°C (Hüls, 1994) has been measured according to DIN ISO 3016. Values of -10°C (Industrial Chemicals, 1975), <20°C (Kirk-Othmer, 1991), -8°C (Hüls, 1994) and 10°C (ICI, 1995) have also been reported.

The IUCLID data set also quotes a value of 2°C (Dutch Institute for the Working Environment, 1991). This latter value appears to refer to the straight chained (i.e. n-nonyl) derivative (CAS Number 25154-52-3), but it is uncertain whether this refers to a sample of nonylphenols covered by the original (all nonylphenols) or revised (straight chain) CAS definition.

In view of the complex nature of the substance the value of -8°C is preferred as it is derived using a standard method.

### 1.3.3 Boiling point

Studies conducted to GLP (Roy F. Weston Inc., 1990a) suggest that some thermal decomposition occurs before the boiling point (>300°C) is reached and hence this material may not have a specific boiling range.

The boiling range has been quoted as 290-302°C (Hüls, 1994); 287-306°C, with decomposition (Industrial Chemicals, 1975); 293-297°C (Merck Index, 1989); and 295°C (ICI, 1995). Other values include 295°C (Dutch Institute for the Working Environment, 1991) and 310°C (Kirk-Othmer, 1993).

The actual boiling/decomposition range will depend on the purity and origin of the material and the values quoted here can be considered representative of the commercially available material.

### 1.3.4 Relative density

The relative density has been quoted at 0.949-0.952 (Hüls, 1994) at 20°C when measured to ASTM 3505. Other reported values are 0.945 (ICI, 1995) and 0.950 (Merck Index, 1989).

A value of 0.95 at 20°C can be considered an appropriate value for this parameter.

### 1.3.5 Vapour pressure

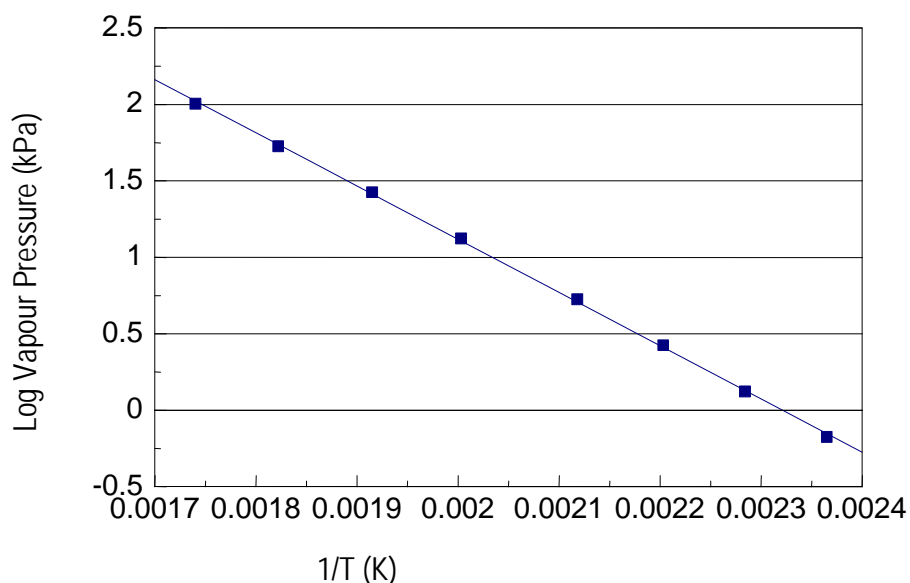
A range of vapour pressure data (at elevated temperatures) have been supplied by Hüls (Hüls, 1996a) and these are displayed in **Table 1.1** and **Figure 1.1**.

A value of 3.1 kPa at 180°C (ICI, 1995) compares with the value of 2.66 kPa at 180.8°C from Hüls.

Table 1.1 Vapour Pressure data of 4-nonylphenol

Temperature °C	Vapour Pressure, kPa
149.70	0.67
164.70	1.33
180.80	2.66
199.10	5.32
226.00	13.30
249.10	26.70
275.80	53.30
301.90	101.30

Figure 1.1 Vapour pressure variation with temperature



It can be seen that a plot of  $1/T$  (K) versus  $\log_{10}$  (Vapour Pressure, kPa) is a straight line showing that the data are reliable and consistent. Extrapolation of the data indicates a vapour pressure of approximately 0.3 Pa at 25°C. This value will be used for modelling purposes.

### 1.3.6 Water solubility

4-Nonylphenol is described as practically insoluble in water (Merck Index, 1989) and sparingly soluble (Industrial Chemicals, 1975).

The IUCLID data set gives values of 11 mg/l at 20°C (Hüls, 1994) using OECD Guideline 105. A value of 3 mg/l is quoted without supporting evidence in a Hüls data sheet (Hüls, 1995c) under the CAS Number 25154-52-3. This may reflect confusion over CAS numbers.

A value of 6.237 mg/l at 25°C and pH 7 has been reported (Roy F. Weston Inc., 1990c), whilst for artificial seawater the value is 3.63 mg/l (Roy F. Weston Inc., 1991) using US EPA guidelines (1990). Ahel (1987) reports a further value for water solubility of 5.43 mg/l at 20°C.

One material safety data sheet (ICI, 1995) quotes a water solubility of 230 mg/l at 20°C. This value is at variance with the other data sources, and is now thought to have been measured on impure samples (ICI Personal communication, 1996).

Although no data have been found to show the solubility variation of a particular brand of nonylphenol with pH, the solubility is likely to be influenced by this factor. At environmental pHs, it is thought that nonylphenol would be present mainly in the undissociated form (pKa of 10; see Section 1.3.13). A water solubility of 6 mg/l at 20°C will be used for environmental modelling purposes.



### 1.3.7 n-Octanol-water partition coefficient

The n-octanol-water partition coefficient ( $\log K_{ow}$ ) has been reported as 3.28 at 20°C, by the shake flask method, to OECD guideline 107 (Hüls 1989a). A value of >3.8 to >4.77 at 25°C has been reported in other studies conducted to GLP at varying pH (Roy F. Weston Inc., 1990b). The values in this report are stated as “greater than” because the level of the test substance in water was below the detection limit of 32.5 µg/l. A value of 4.2 to 4.7 is also reported although the test conditions were not stated (ICI, 1995). In a study by Ahel and Giger (1993), nonylphenol was measured in both the octanol and water phases, and a partition coefficient of 4.48 reported.

A  $\log K_{ow}$  of 5.76 has been reported in the literature (Itokawa et al., 1989). The original reference has been closely examined and it was found that this value relates to the straight chained 4-(n)-nonyl phenol derivative and not to the 4-nonyl phenol (branched) compound.

A  $\log K_{ow}$  of 4.48 will be used for environmental modelling purposes.

### 1.3.8 Flash point

Values of 149°C (open cup), and 155°C (closed cup) have been assigned by Hüls when tested to ASTM guideline D 93 and DIN ISO 3016 (Hüls, 1994).

The ICI data sheet gives a value of 148°C (closed cup) (ICI, 1995) whilst Industrial Chemicals (1975) quotes a value of 141°C (open cup).

Given the complex nature of the isomers and differences in the test methods used, some variation in the values quoted should be expected.

The flash point will be taken as 141-155°C with the lower value being used for any risk assessment.

### 1.3.9 Autoflammability

The Hüls data sheet quotes a value of "about 370°C" for autoflammability conducted to DIN 51794. ICI do not quote a value for this parameter in their data sheet and no other sources of this parameter have been located.

### 1.3.10 Explosivity

There is no explosion limit under standard conditions (Hüls, 1994). Nonylphenol is not expected to have explosive properties on the basis of its chemical structure.

### 1.3.11 Oxidising properties

Nonylphenol is not an oxidising agent on the basis of its chemical structure.

### 1.3.12 Viscosity

The viscosity (for CAS Number: 25154-52-3) has been quoted as about 2,500 mPa s at 20°C (Hüls, 1994).

### 1.3.13 Other physical-chemical properties

The Henry's law constant may be calculated from the vapour pressure, molecular weight and water solubility of the substance using the following equation:

$$HENRY = \frac{VP \cdot MOLW}{SOL} \quad (21)$$

Explanation of symbols:

VP	vapour pressure	[Pa]	data set
MOLW	molecular weight	[g.mol <sup>-1</sup> ]	data set
SOL	solubility	[mg.l <sup>-1</sup> ]	data set
HENRY	Henry's law constant	[Pa.m <sup>3</sup> .mol <sup>-1</sup> ]	

Using a vapour pressure of 0.3 Pa, a molecular weight of 220.34 g/mol and a water solubility of 6 mg/l gives a Henry's law constant for nonylphenol of 11.02 Pa.m<sup>3</sup>.mol<sup>-1</sup>.

A pKa value of 4.53 is reported in the IUCLID for nonylphenol. The pKa value for phenol is reported as 9.9 and an alkyl substituted phenol would be expected to be slightly less acidic and have a higher pKa value than phenol. This suggests that the value reported in the IUCLID is wrong. A more realistic pKa value is likely to be ~10, though it could be higher than this. At this pKa value nonylphenol would be undissociated at environmental pHs.

### 1.3.14 Summary of physico-chemical properties

The physico-chemical data for 4-nonylphenol are acceptable in that for each parameter the value has been determined by an acceptable method. In most cases the supporting data, which are less well reported, are generally consistent with this.

The two main sources of data are Hüls and ICI, although some information has been obtained from studies conducted in the USA by the Chemical Manufacturers Association (CMA). These data were obtained in material from Schenectady Chemicals of New York.

For those parameters where companies have reported values there appears to be a difference between submitted values for melting point. For boiling point the ICI value (295°C) is within the range reported by Hüls (290-302°C), although the relative density of the ICI product (0.945) is lower than the Hüls product (0.949-0.952). The vapour pressure is also slightly different, the ICI product having a vapour pressure of 3.1 kPa at 180°C, Hüls 2.66 kPa at 180.8°C.

Finally the n-octanol-water partition coefficients are slightly different: ICI quoted the log Kow at 4.2-4.7, Hüls at 3.28 (the CMA data suggest >3.8 to >4.77).

Some of these differences may relate to experimental methods but there is some evidence that the products made by the two companies have slightly different physico-chemical properties, possibly due to different degrees of branching in the nonyl chain. This may also explain the differences between physico-chemical data for nonylphenol from USA reports.

Table 1.2 Physical and chemical properties of nonylphenol

Property	Value	Comments
Physical state at ntp	Clear to pale-yellow viscous liquid	Slight phenolic odour
Molecular weight	220.34 g/mol	
Melting point	circa -8°C	Approximate only due to nature of the material - may vary according to production process used.
Boiling point	290-300°C	Nonylphenol undergoes thermal decomposition before it reaches its boiling point.
Relative density	0.95 at 20°C	ASTM 3505
Vapour Pressure	circa 0.3 Pa at 25°C (some evidence actual value may be lower)	Extrapolated value - see text
Partition coefficient	log Kow 4.48	See text
Water solubility	6 mg/l at 20°C	See text for discussion of other values - may be pH dependent
Flash point	141-155°C (lowest value used for risk assessment)	149-155°C when tested to ASTM D-93 by Hüls
Autoflammability	circa 370°C	Hüls to DIN 51794
Oxidising properties	not applicable	
Viscosity	2,500 mPa s at 20°C	Hüls

## 1.4 CLASSIFICATION

### 1.4.1 Current classification

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

## 2 GENERAL INFORMATION ON EXPOSURE

### 2.1 PRODUCTION

#### 2.1.1 Production processes

There are three main processes used to manufacture nonylphenol; these are detailed below. The process varies between producers.

1. Phenol and mixed nonenes are reacted in the presence of a catalyst in a batch process. The catalyst used is montmorillonite clay/fulcat and phosphoric acid.
2. Phenol and mixed nonenes are reacted in the presence of a sulfonated ion exchange resin in a batch process. The catalyst/precoat system can be reused for between 40-500 batches.
3. Phenol and mixed nonenes are reacted in the presence of a fixed bed ion exchange resin in a continuous process. The catalyst has a life of about three months.

The nonylphenol producers reported that in 1994 total EU production was 77,505 tonnes. Of this amount 62,730 tonnes of nonylphenol were produced by continuous production methods (81% of the production volume) and 14,775 tonnes by batch production methods in dedicated equipment (19% of the production volume) (CEFIC, 1996). Industry has reported that in 1997 the total EU production of nonylphenol was 73,500 tonnes. During the period 1994-1997 one major producer of nonylphenol stopped manufacture and another smaller producer was identified. The overall effect of this is a decrease in the amount of nonylphenol reported as being produced over the period 1994-1997. The actual reduction is probably slightly larger than reported due to the fact that one production company was not included in the 1994 survey.

#### 2.1.2 Production capacity

Data in this Section are based upon a survey of nonylphenol and nonylphenol ethoxylate producers and users (CEFIC, 1996).

Four companies within the EU currently (as of 1997) produce nonylphenol. A fifth company is reported to have stopped production of nonylphenol in 1996. **Table 2.1** details production volumes, exports and imports of nonylphenol. The lifecycle of nonylphenol is shown in **Figure 2.1**.

Table 2.1 Production volume, exports and imports (1997)

	Amount (tonnes/year)
Production volume in EU	73,500
Exports from EU	3,500
Imports into EU	8,500
Tonnage (Use in EU) (Production volume + Imports of nonylphenol – Exports of nonylphenol)	78,500

## 2.2 USES

### 2.2.1 Introduction

**Table 2.2** details the uses of nonylphenol within the EU and these are illustrated in Figure 2.1. From the table it can be seen that the overall tonnage of nonylphenol used within the EU appears to have remained fairly constant over the period 1994-1997. This is despite one major producer stopping manufacture of nonylphenol. The amount of nonylphenol used for nonylphenol ethoxylate production also appears to have risen slightly in this period.

Table 2.2 Use of Nonylphenol within the EU (1994,1997)

	Volume		Percentage of tonnage (Use)	
	1994	1997	1994	1997
Production of nonylphenol ethoxylates	42,350	47,000	54	60
Production of resins, plastics, stabilisers etc.	33,750	29,000	43	37
Production of phenolic oximes	2,400	2,500	3	3
Total	78,500	78,500	100	100

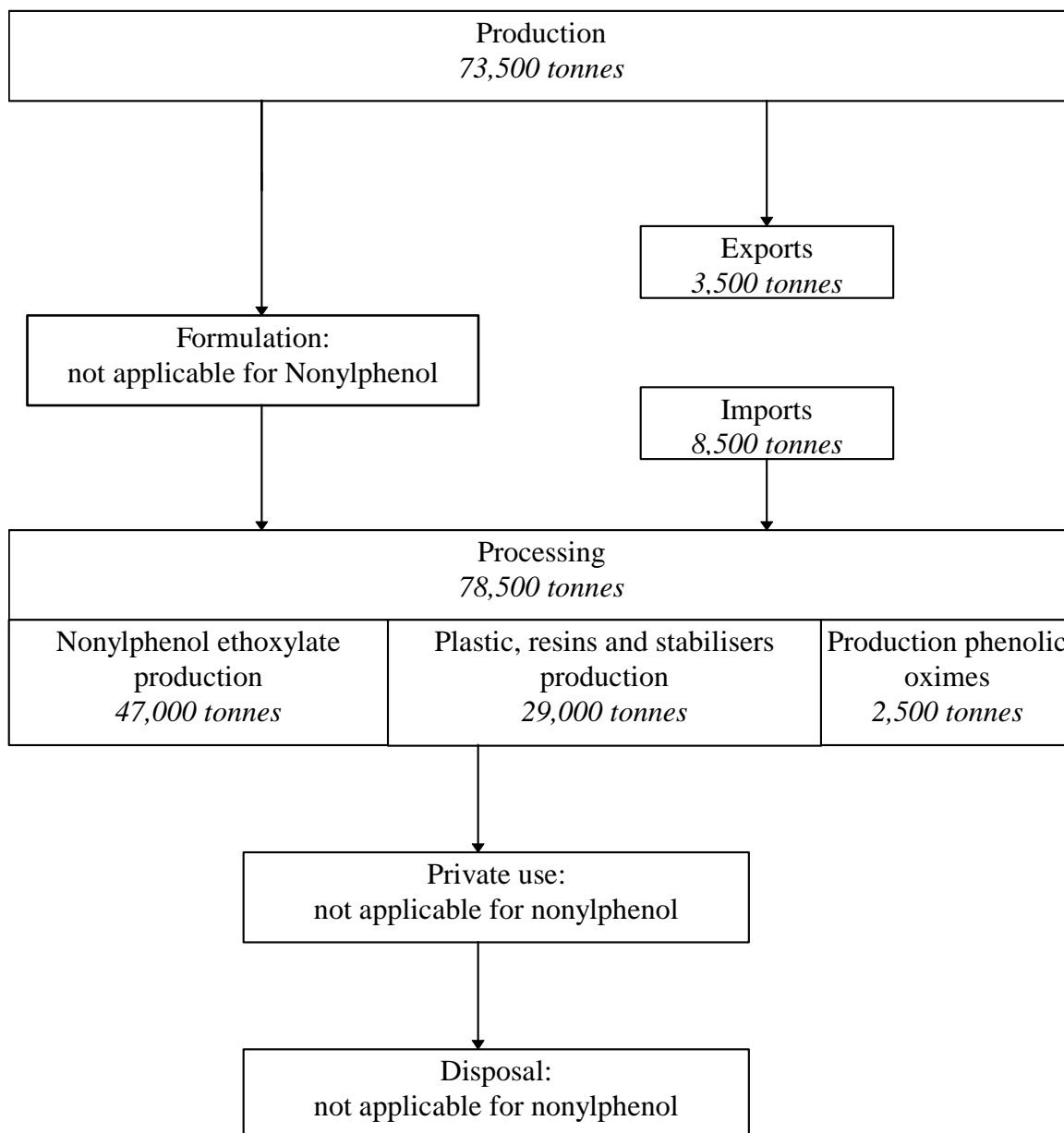
#### 2.2.1.1 Nonylphenol ethoxylates

Nonylphenol ethoxylates (NPEOs) are produced by the ethoxylation of nonylphenol. The nonylphenol is heated with an alkali catalyst (potassium hydroxide). Water is produced at this stage and the mixture is dehydrated at about 120°C. Ethylene oxide is then added under vacuum. It reacts preferentially with free nonylphenol until all of the phenol is reacted, and subsequently the ethoxylate chain becomes extended. The reaction is exothermic and can become explosive above an optimal addition rate. The length of the ethoxylate chain is varied by controlling the ratio of nonylphenol to ethylene oxide or by the reaction time. The nonylphenol ethoxylates are neutralised to pH 6-8 using acetic acid. Any residual water will initiate the formation of polyethylene glycol, which is present in most nonylphenol ethoxylates as a non-active impurity.

There are two main methods for producing nonylphenol ethoxylates in the EU. One method uses a loop reactor, where nonylphenol circulates around the loop whilst the ethylene oxide is introduced gradually under controlled temperatures and pressure. Batches of nonylphenol ethoxylate are produced in quantities of 6-40 tonnes and are then usually pumped directly into road tankers for delivery or storage. There is very little free nonylphenol in the resulting ethoxylates because nonylphenol is more reactive than the ethoxylates and is usually fully consumed in the reaction. The other method used is the “stirred tank” process. No further details of this method have been received.

Nonylphenol ethoxylate producers reported that production of nonylphenol ethoxylates was 109,808 tonnes in 1994 and 118,000 tonnes in 1997 in the EU. This was all by batch production methods using multi-purpose equipment (CEFIC, 1996).

Figure 2.1 Nonylphenol lifecycle (all figures refer to the quantity of nonylphenol) (1997)



### 2.2.1.2 Polymer industry

The main use of nonylphenol in the plastics industry is as a monomer in the production of phenol/formaldehyde resins. Other uses include as an intermediate in the production of tri-(4-nonylphenyl) phosphite (TNPP) and as a catalyst in the curing of epoxy resins. To the knowledge of the nonylphenol producers nonylphenol is not used as a free additive in resins, plastics or stabilisers. There is a potential for consumer exposure due to the consumer use of epoxy resins.

In 1997 the total amount of nonylphenol used in the polymer industry was reported by industry as 29,000 tonnes. This was split between the various applications as follows: phenolic resin production 22,500 tonnes; TNPP production 4,000 tonnes; catalyst in epoxy resin production 1,500 tonnes; and use in other plastic stabilisers 1,000 tonnes.

### 2.2.1.3 **Manufacture of phenolic oximes**

Nonylphenol is used by one company within the EU to manufacture phenolic oximes, which are used as a reagent for the extraction and purification of copper from ore. The total quantity of nonylphenol used in this application is 2,500 tonnes/year. This is all used at one site within the EU. All the phenolic oximes produced are exported to customers outside of the EU. Phenolic oximes are not thought to be used in the EU for this application.

### 2.2.2 **Use of nonylphenol ethoxylates**

Appendix 1 considers the breakdown of nonylphenol ethoxylates in the environment and concludes that, under some conditions, nonylphenol is one of the breakdown products. As nonylphenol ethoxylates are one of the principal uses of nonylphenol, their use and potential breakdown needs to be fully considered to adequately assess the risk of nonylphenol to the environment. Therefore the uses of nonylphenol ethoxylates are covered in some detail in this assessment.

CEFIC (1996) undertook a survey of nonylphenol ethoxylate producers and trade group members to gain a better understanding of the uses of nonylphenol ethoxylates. The results summarised in **Tables 2.3** and **2.4** give details of the amounts of nonylphenol ethoxylates used in different industries as specified by the various industrial use categories and functional use categories. It has become apparent from comments received by industry and in trying to refine the risk assessment report that this approach does not accurately represent the actual use pattern of nonylphenol ethoxylates within the EU. Therefore industry has provided a breakdown of nonylphenol ethoxylate use within the EU based upon 1997 production volumes; these data are presented in **Table 2.5**.



**Table 2.3** Industrial use categories for nonylphenol ethoxylates in the EU (1994) (CEFIC, 1996)

Industry Category number	Industrial use	Main category	Nonylphenol ethoxylate (tonnes/year)	% <sup>a</sup>	Nonylphenol (tonnes/year) <sup>b</sup>
1	Agricultural industry	4	4,919	7.57	1,774
2	Chemical industry: Basic chemicals		93	0.14	28
3	Chemicals industry: Chemicals used in synthesis	(1)/2	4,588	7.01	1,641
4	Electrical/electronic engineering industry	3/2	93	0.14	28
5	Personal domestic		3,670	5.65	1,566
6	Public domain		19,286	29.67	7,194
7	Leather processing industry	2/3	6,274	9.62	2,462
8	Metal extraction, refining and processing industry	2/3	93	0.14	28
9	Mineral fuel and oil industry	3/4	93	0.14	28
10	Photographic industry	2/3	93	0.14	28
11	Polymers industry	2	4,679	7.2	1,899
12	Pulp, paper and board industry	2/3	802	1.23	276
13	Textile processing industry	2/3	7,734	11.9	1,576
14	Paints, lacquers and varnishes industry	2/3/4	3,997	6.15	28
15	Engineering industry, civil and mechanical		93	0.14	3,065
0	Other		8,500	13.07	28
	Total (include imports)		65,007		24,560
	Exports		35,400		

See Appendix I of the Technical Guidance Document for definitions

a - % refers to the percentage of total ethoxylates used.

b - Nonylphenol refers to estimated amount of nonylphenol used to produce the ethoxylate.

**Table 2.4** Functional use categories for nonylphenol ethoxylates in the EU (1994) (CEFIC, 1996)

Use category number	Functional use	Percentage
9	Cleaning/washing agents	44.7
13	Construction materials and additives	1.4
15	Cosmetics	1.5
16	Dust binding agents	1.4
23	Flotation agents	1.7
25	Foaming agents	2.8
33	Intermediates	0.2
38	Plant protection products, agricultural	0.1
50	Surface active agents	46.1
0	Others	0.1

See Appendix I of the Technical Guidance Document for definitions

**Table 2.5** Production and use of nonylphenol ethoxylates within the EU (1997)

	Volume (tonnes)	
NPEO production	118,000	
NPEO imports	5,600	
NPEO exports	46,000	
Total EU Use	77,600	
Use		As percentage of EU Use
Captive use	7,000	9
Industrial and institutional cleaning	23,000	30
Textile auxiliaries	8,000	10
Leather auxiliaries	6,000	8
Agriculture	5,000	6
Emulsion polymerisation	9,000	12
Paints	4,000	5
Pulp and Paper	1,000	1
Metal industry	2,000	3
Other niche markets	7,000	9
Total	72,000	93
Difference Use and EU Use	5,600	

The volume used does not appear to take account of the import volume of 5,600 tonnes. Industry thinks that this volume is probably divided among the other applications.

NPEO = Nonylphenol ethoxylates

Other niche markets covered by this survey are the use of nonylphenol ethoxylates in the photographic industry, electronic industry, mineral fuel and oil industry and civil engineering industry. It also covers nonylphenol ethoxylate users who purchase small quantities of material per year from the nonylphenol producers for use in a variety of end applications.

### **2.2.2.1 Captive use**

Nonylphenol ethoxylates are used in the chemical industry in the synthesis of nonylphenol ether sulphates and nonylphenol ether phosphates. Both of these compounds are used as emulsifiers in the chemical industry.

### **2.2.2.2 Electrical engineering industry**

In the electrical engineering industry nonylphenol ethoxylates are reported as being used in fluxes in the manufacture of printed circuit boards, in dyes to identify cracks in printed circuit boards and as a component of chemical baths used in the etching of circuit boards. Nonylphenol ethoxylates may also be present in cleaning products used to clean electrical components. However, cleaning products for some electrical equipment such as printed circuit boards are required to have less than 10 parts per million (ppm) of certain metal ions. The catalysts used in the production of nonylphenol ethoxylates mean that metal ion concentrations are often far in excess of this, therefore a special grade nonylphenol ethoxylate would be needed to meet the requirements. The concentration of nonylphenol ethoxylates in cleaning products for the metal industry is reported as approximately 5% w/w.

### **2.2.2.3 Industrial and institutional cleaning**

Nonylphenol ethoxylates are used in laundries, for floor and surface cleaning in buildings, as vehicle cleaners, anti-static cleaners and metal cleaning. Nonylphenol ethoxylates typically account for <5% by weight of the final formulation. Domestic (i.e. public) consumption of nonylphenol based cleaning products should be virtually zero within the EU due to voluntary bans and agreements with industry. Industry has provided information that heavy-duty hand cleansers no longer contain nonylphenols and so this particular use is not considered further in this risk assessment.

### **2.2.2.4 Textile auxiliaries**

Nonylphenol ethoxylates are used in several processes of textile manufacture including scouring, fibre lubrication and dye levelling. The main use is in wool scouring where natural oils are removed from the wool. Nonylphenol ethoxylates are used because of their detergent and fibre lubricating (conditioning) properties and because they are not adsorbed into the wool (unlike anionic surfactants).

### **2.2.2.5 Leather auxiliaries**

Nonylphenol ethoxylates are thought to be used in the wet degreasing of hides in the leather industry.

### **2.2.2.6 Agriculture**

Nonylphenol ethoxylates act as a wetting agent in agrochemical (pesticide) formulations to increase the efficiency of spraying and reduce the amount of active ingredient that needs to be applied. They may also be incorporated as dispersants and emulsifiers or added to the spray tank at the time of application.

Nonylphenol ethoxylates are also used in veterinary medicinal products as surfactants in teat dips and as an aid in the control of mastitis. The dips are usually applied to individual teats using a teat cup after milking, although pre-milking dipping is becoming more common.

#### **2.2.2.7 Emulsion polymers**

Nonylphenol ethoxylates are added to acrylic esters used for specialist coatings, adhesives and fibre bonding. They act as dispersants and aid the stability of the formulation. Nonylphenol ethoxylates are also thought to be present in the polymerisation reactions used to make polymer solutions that are used for wastewater treatment.

#### **2.2.2.8 Speciality Paints**

Nonylphenol ethoxylates are used in the preparation of paint resin (polyvinyl acetates - PVA) and also as a paint mixture stabiliser. Typical formulations contain 0.6-3% nonylphenol ethoxylates.

#### **2.2.2.9 Pulp and paper**

Nonylphenol ethoxylates are thought to be used in the pulp and paper industry in the wetting of pulp fibres.

#### **2.2.2.10 Metal industry**

Nonylphenol ethoxylates are used in metal cleaning processes (iron and steel manufacture), steel phosphating, electronics cleaning (for metal contacts) and cleaning of metal products prior to storage. Nonylphenol ethoxylates are also used in the formulation and usage of cutting and drilling oils. Cutting and drilling oils are mainly emulsions of white spirit, water and hydrophobic surfactants.

#### **2.2.2.11 Miscellaneous uses**

A variety of other uses exist for nonylphenol ethoxylates. These are usually in niche markets for specific applications. Further details are given below.

Nonylphenol ethoxylate phosphate esters are used as additives in lubricating oil, particularly for military use in gearboxes. The nonylphenol ethoxylate esters prevent aggregation of metal fragments in engine boxes and reduce the impact of water contamination.

Nonylphenol ethoxylates of ethoxylate chain length 9 and 11 are used as spermicides (Merck Index, 1989).

Nonylphenol ethoxylates are thought to be used as a surfactant in some cosmetic formulations.

Nonylphenol ethoxylates are used as wetting agents in the developing of photographic film.

Nonylphenol ethoxylates are used in the civil and mechanical engineering industry. Possible uses include in the manufacture of wall construction materials, road surface materials, and also in cleaning of metals etc. Nonylphenol ethoxylates may also be present in some plastic materials used in construction, particularly if an emulsion polymerisation route has produced them.

However, no further information is available on this possible use and no specific risk characterisation has been conducted.

Possible products containing nonylphenol ethoxylate that are used in the public domain include non-agricultural pesticides, vehicle and office cleaning agents and office products such as correction fluids and inks.

### **2.3 TRENDS**

A comparison of production and use figures provided by industry for 1994 and 1997 enables a limited analysis of trends in recent years to be performed. The overall production volume of nonylphenol within the EU has fallen by about 5-10% during this period. The total amount of nonylphenol used in the production of nonylphenol ethoxylates has risen slightly in this period. The use in the plastics and polymer industry appears to have dropped slightly. This drop may be due to a better understanding of the uses of nonylphenol in 1997 compared to 1994.

For nonylphenol ethoxylates the total amount produced and used within the EU appears to have risen slightly. The biggest use of nonylphenol ethoxylates is still in industrial and institutional cleaning products with the amount used appearing to remain unchanged over the period. Considering the voluntary agreements between member states and industry to phase out nonylphenol ethoxylates in all detergent applications by the year 2000, the tonnage in this application would be expected to drop in the future. In other applications the use appears to have stayed fairly constant over the period.

### **2.4 LEGISLATIVE CONTROLS**

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.

Information has been gathered by Sweden on the implementation of PARCOM Recommendation 92/8 by a number of contracting parties. From the information obtained it appears that virtually all domestic uses of nonylphenol ethoxylates as cleaning agents have been phased out. In most countries this has been achieved by either voluntary action or as a negotiated agreement. In Switzerland the use of octylphenol ethoxylates and nonylphenol ethoxylates in washing agents and washing auxiliary substances was banned in September 1987.

The phase out of nonylphenol ethoxylates as cleaning agents for industrial uses varies between different countries. In Switzerland their use has been banned. In the Netherlands their use is reported as terminated. In Belgium use has 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 is a result of both administrative actions and voluntary actions from industry.

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 diisobutylphenol 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. Germany found that the target of a complete phase out in the area of washing and cleaning agents by 1992 was not achieved. Among the reasons given for this failure were a number of low to medium size companies involved which probably were not members of the associations having subscribed to the voluntary agreement; foreign manufacturers and importers continuing to sell products containing alkylphenols in Germany; voluntary commitments were found not to cover all areas of application; and the competitive position of alkylphenols compared to alternative products.

In Finland PARCOM Recommendation 92/8 had not yet been implemented in 1997. However the amount of nonylphenol ethoxylates used in household cleaning agents has decreased sharply during the last few years but the use has not been completely phased out.

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 the UK there is no specific legislation aimed at nonylphenol or nonylphenol ethoxylates. However, they are covered indirectly by legislation such as integrated pollution control (IPC). Under IPC, releases are required to meet environmental quality standards (EQSs). An operational EQS has been developed for nonylphenol of 1 µg/l.

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.

## **3 ENVIRONMENT RISK ASSESSMENT**

### **3.1 ENVIRONMENTAL EXPOSURE**

#### **3.1.1 General discussion**

##### **3.1.1.1 Environmental releases**

In considering releases of nonylphenol to the environment the life cycles of the major products of nonylphenol have to be considered. The sections below consider the release of nonylphenol due to its production and use and from its major products.

Reference is made to the default emissions calculated using the Technical Guidance Document (TGD) and implemented in the EUSES model. Information has been supplied by the nonylphenol producers on the amounts of nonylphenol and nonylphenol ethoxylates used in a number of Use Categories and Industry Categories (**Tables 2.3** and **2.4**) in 1994. These data were updated by industry to reflect the position in 1997 (**Table 2.5**). These tonnages have been used with the default emission scenarios given in Chapter 3 Appendix 1 of the TGD along with additional information supplied by industry to give default releases for the different life cycle stages of nonylphenol and nonylphenol ethoxylates.

##### **3.1.1.1.1 Releases of nonylphenol**

###### **3.1.1.1.1.1 Releases during production**

Nonylphenol is produced at four sites within the EU. Information has been received on emissions from all of these sites and this is summarised below. Information has also been reported by a fifth company which ceased production of nonylphenol in 1996, but this is not included in the data set.

###### *Site A*

Measured levels are reported for site A and these will be used in the PEC calculations and risk characterisation section. During production of nonylphenol the amount of nonylphenol released to air is 52 g/year and to water (before treatment) is 475 kg/year. Nonylphenol is also used as an intermediate on this site, in which case the TGD recommends that emissions from production and processing should be summed together. Approximately 224 kg/year of nonylphenol ethoxylate are released to air from processing, which the company considers to be equivalent to 90 kg of nonylphenol per annum. For water, emissions from the intermediate plant (before treatment) are 224 tonnes/year nonylphenol ethoxylate, which the company considers to be equivalent to 90 tonnes/year nonylphenol. This gives a total release of nonylphenol from the site of 90 kg/year to air and 90 tonnes/year to water (before treatment). On a daily basis, the emissions from the production site are 0.00016 kg/day to air and 1.4 kg/day to water (before treatment). This is based upon 330 days operation per year. For the processing site nonylphenol is processed for 2,400 hours/year and this gives a daily emission of 0.45 kg/day to air and 450 kg/day to water (before treatment) based upon 12 hours processing a day. This gives a maximum daily emission for the site of 0.45 kg/day to air and 451 kg/day to water (before treatment). The release to water is the amount released from the production and processing operations and takes no account of on-site treatment.

At site A all the alkyl phenols are passed to a small separation unit of the alkyl phenol plant. In the separation unit the oil layer is continuously skimmed off by a rotating skimmer and sent to a special storage tank and the oily layer is burnt in the central boiler house. The water phase is sent to the main wastewater treatment plants. At site A, there are two wastewater treatment plants which are both working under aerobic conditions. All the dried sludges from plants are burnt. Based upon measurements of nonylphenol in the outflows from the wastewater treatment plants serving the site the total emissions of nonylphenol and nonylphenol derivatives to receiving waters are as follows: nonylphenol 11.8 kg/year, NPEC (nonylphenol ether carboxylate) 12.9 kg/year, NPEO1 (nonylphenol + 1 mole ethylene oxide/mole) 6 kg/year and NPEO2 (nonylphenol + 2 mole ethylene oxide/mole) 7 kg/year. The measured levels of nonylphenol and its derivatives in the outflow of the wastewater treatment plants are <0.2-0.6 µg/l for nonylphenol, 0.3-0.7 µg/l for NPEC, 0.2-0.33 µg/l for NPEO1 and 0.3-0.57 µg/l for NPEO2. The measured levels of nonylphenol and its derivatives in the river after passing site A are <0.2 µg/l for nonylphenol, 0.5 µg/l for NPEC, 0.25-0.3 µg/l for NPEO1 and 0.4 µg/l for NPEO2. These levels are based upon measurements taken in February, June and October 1997.

For modelling purposes (calculating regional and continental concentrations in EUSES) the yearly emission of nonylphenol from the site based upon the measured data will be used (11.8 kg/year nonylphenol).

#### *Site B*

For site B, information on the concentration and behaviour of nonylphenol in the on-site waste treatment plant and effluent from the production site is reported. Nonylphenol was not detectable at a detection limit of 4 µg/l in the effluent from the nonylphenol production plant. The analysis was performed on an effluent sample that had been concentrated 118 times prior to analysis. The concentration of nonylphenol in the unconcentrated sample will therefore be <0.033 µg/l. However as a worst case a concentration of <4 µg/l will be used. A similar analysis on sludges from the nonylphenol production plant found nonylphenol concentrations of <4 µg/l after concentration. The flow rate of the effluent from the nonylphenol production plant is 800 m<sup>3</sup>/h. The effluent is a part of the main site effluent which has a flow rate of 5,000 m<sup>3</sup>/h. This gives a dilution factor for the nonylphenol plant effluent in the site effluent of 6.25. The concentration of nonylphenol in the site effluent is therefore of <0.64 µg/l. The flow rate of the receiving waters is 147,600 m<sup>3</sup>/h, this gives a dilution rate for the site effluent of 30.5. The resultant concentration of nonylphenol in receiving waters is therefore <0.0208 µg/l based upon a concentration of nonylphenol in the effluent from the nonylphenol production plant of <4 µg/l. The total amount of nonylphenol released to receiving waters is calculated as <23.04 kg/year. Atmospheric emissions from the nonylphenol plant are collected and incinerated. The sludge from the on-site wastewater treatment plant is applied to agricultural land in accordance with regional regulations. The regulations do not specify a limit for nonylphenol in the sludge.

#### *Site C*

For site C, the emissions of nonylphenol to air, water and soil are reported as zero. Nonylphenol is not used as an intermediate on the site. Wastewater from the site is collected and incinerated.

#### *Site D*

At site D, all vapour emissions from the plant are collected and incinerated. An estimated 3.5 tonnes/year nonylphenol are released to wastewater. Based upon 285 days production/year



this gives a daily release of 12.3 kg/day to wastewater. The aqueous streams from the nonylphenol plant, together with the streams from the other production plants, are collected and sent to the central wastewater treatment unit. At the central wastewater treatment plant the aqueous wastes undergo neutralisation, settlement of the solid material, equalisation, biological treatment with oxygen, settlement of sludges, final filtration, mixing with well water used as a cooling medium and with the purge water from the towers cooling circuit and finally discharge to the authorised discharge point. The concentration of nonylphenol in the effluent from the on-site treatment plant is reported as <1 µg/l (detection limit of method currently in use). The effluent undergoes dilution by a factor of 5.2 before discharge to receiving waters. This gives a nonylphenol concentration of <0.19 µg/l. This will be further diluted in the receiving waters. The company is in the process of changing its analytical method to one with a detection limit of 0.1 µg/l for nonylphenol. Sludges from the on-site treatment plant are disposed of at authorised disposal sites.

Table 3.1 Summary of emissions from nonylphenol production sites

Site	Releases to Air	Releases to water	Notes
A	52 g/year (0.00016 kg/day) from NP production. 90 kg/year NP (0.45 kg/day) from NPEO production.	475 kg/year (1.4 kg/day) from NP production before WWTP. 90 tonnes/year (450 kg/day) from NPEO production before WWTP. 11.8 kg/year (0.04 kg/day) after WWTP based upon measured level of NP in outflow from plant	NP production for 330 days/annum. NPEO production 2,400 hours/annum (200 days assuming 12hrs/day). Dried sludges from the plant are incinerated.
B	None	<23.04 kg/year (0.06 kg/day) after WWTP	Based upon company estimations. Sludges from WWTP applied to agricultural land.
C	None	None	Waste gases and wastewaters are incinerated
D	None	12.3 kg/day to WWTP 2.15 kg/day after WWTP	Waste gases incinerated. Default release estimation for removal in WWTP used to give release after WWTP. Sludges disposed of to authorised disposal sites.
Total	Regional 0.45 kg/day Continental 0	Regional 2.15 kg/day Continental 0.10 kg/day	

### *Regional and continental emissions*

In calculating the contribution of production plants to regional and continental concentrations the following emissions will be used. For the regional scenario, as there are less than 10 production sites, the releases from site A will be used for releases to air (0.45 kg/day) as this is the site with the largest releases to air. The releases from site D will be used for releases to water as this is the site with the largest release to water (2.15 kg/day after wwt). For the continental scenario, the total emissions to air and water are taken as the sum of the emissions from sites A, B, C and D minus the regional releases. This gives continental releases of 0 to air and 0.10 kg/day to surface water.

#### **3.1.1.1.2 Releases during formulation**

In the Technical Guidance Document, formulation is defined as the stage where the chemical is combined in a process to obtain a product or preparation. For nonylphenol this stage of the life cycle is not relevant as no such step is thought to occur between production and processing.

### 3.1.1.1.3 Releases during processing

In the Technical Guidance Document, processing refers to the life cycle stage where the chemical is applied or used.

#### Production of nonylphenol ethoxylates

Nonylphenol is used as an intermediate in the production of nonylphenol ethoxylates. In 1997 in the EU approximately 47,000 tonnes of nonylphenol were used in the production of nonylphenol ethoxylates and approximately 118,000 tonnes of nonylphenol ethoxylates were produced. There are thought to be 7 companies involved in the manufacture of nonylphenol ethoxylates. Site-specific information on releases and use has been received and is discussed in more detail below.

In discussing releases from nonylphenol ethoxylate production two types of emissions need to be considered. The first is direct release of nonylphenol from the ethoxylate production process. The second is the release of the nonylphenol ethoxylate produced, which may subsequently degrade in the environment to nonylphenol.

#### *Company A*

This is a producer of nonylphenol and nonylphenol ethoxylates. Releases are discussed in Section 3.1.1.1.1 and deal with the combined release from both nonylphenol production and nonylphenol ethoxylate production.

#### *Company B*

This company operates one nonylphenol ethoxylate production site within the EU. Releases of nonylphenol or nonylphenol ethoxylates to water from the plant are reported as 46 tonnes/annum and are discharged directly to receiving waters without effluent treatment. Measurements have been made of nonylphenol in the receiving waters downstream of the site discharge point. In top water the concentration of nonylphenol was between 1.7-3.02 µg/l, in middle waters the concentration was between 1.3-1.6 µg/l and in bottom waters between 0.54-1.2 µg/l. The measurements were made on two separate sampling dates during 1997. Releases to soil are reported as 75 t/a, the type and nature of this release is not specified in the information supplied by the company. No releases to air are reported.

#### *Company C*

Company C operates 3 nonylphenol ethoxylate production plants within the EU. Effluent from two of the sites is treated on-site at a biological treatment plant then off site at a municipal treatment plant. Releases of nonylphenol ethoxylates from the two sites are reported as 12 tonnes/annum and 26 tonnes/annum. The number of days processing at each site varies (54 days one site and 72 days at the other). A worst-case emission scenario would involve emissions from both sites at the same time, this gives a release of 583.33 kg/day nonylphenol ethoxylate. There are no direct releases of nonylphenol from the plant. Sludge from the on site biological wastewater treatment plant is incinerated.

At the company's other site the total release of nonylphenol and nonylphenol ethoxylates to water is reported as 850 kg/annum; this is treated off site at an industrial treatment works.

*Company D*

Company D operates 2 nonylphenol ethoxylate production plants within the EU. Effluent from the works is treated on-site by mechanical and biological treatment of wastewater. At the first site 360 kg (1.2 kg/day) nonylphenol ethoxylates are released to the on-site treatment plant. At the second site 10 kg/year (0.33 kg/day) nonylphenol ethoxylate is released to the on-site treatment plant. At the second site the total flow of wastewater through the wastewater treatment plant is 180,000 m<sup>3</sup>/year (600 m<sup>3</sup>/day). This gives a concentration of 550 µg/l nonylphenol ethoxylate in wastewater treatment plant influent. Production at the first site is due to move to a new site within the EU during 1998.

*Company E*

Company E produces nonylphenol ethoxylates at one site within the EU. Releases to water are reported as zero, as residues from the process are incorporated into the next run. Other wastes from the plant are collected and incinerated.

*Company F*

The wash waters from the nonylphenol ethoxylate plant are concentrated and then incinerated. Releases to water are therefore zero.

*Company G*

Releases to water are reported as 300 kg/annum nonylphenol. Polluted waters are incinerated on-site. Releases to air are reported as very small.

*Default release estimation*

The default release fraction estimations for nonylphenol and nonylphenol ethoxylates from use as a chemical intermediate in the production of nonylphenol ethoxylates are:

Air: Nonylphenol 0.00001 Nonylphenol ethoxylates 0  
 Water Nonylphenol 0.007 Nonylphenol ethoxylates 0.003

The nonylphenol default release estimations are taken from Chapter 3 Appendix 1 of the TGD. For nonylphenol releases Table A3.3 is used assuming main category 3 and for nonylphenol ethoxylate releases Table A1.2 is used assuming main category Ic.

The total amount of nonylphenol used in 1997 for nonylphenol ethoxylate production was 47,000 tonnes and this was converted into 118,000 tonnes nonylphenol ethoxylates. This gives a rough conversion of 2.5 times the amount of nonylphenol used to nonylphenol ethoxylates. This conversion factor will be used to determine the amount of nonylphenol used or nonylphenol ethoxylates produced when information on only one tonnage is available.

From the site-specific data the amount of nonylphenol reported as being used is 32,400 tonnes; this compares to a reported tonnage in 1997 of 47,000, a difference of 14,600 tonnes. This remaining tonnage is assumed to be used at the company which did not report nonylphenol or nonylphenol ethoxylate production data.

These default release estimations have been used with the site-specific information to produce release estimations for nonylphenol processing plants. These are summarised in **Table 3.2**.

In calculating the regional and continental concentrations, 10% of the total emission will be used for the regional model. The total emission minus the regional emission will be used for the continental model.

*Confidential information has also been supplied and used. Further details may be obtained from the rapporteur.*

**Table 3.2** Summary of releases from nonylphenol ethoxylate production plants

	Release to air	Release to water	Other information
Company A	90 kg/a NP 0.45 kg/day NP	0.04 kg/day NP 0.07 kg/day NPEO1 + NPEO2	NP production and processing site. Releases to water after WWTP.
Company B	<i>146 kg/a (0.49 kg/day) NP</i>	46 t/a NP+NPEO <i>(153 kg/day)</i>	Releases direct to receiving waters
Company C Sites 1+2	<i>2.2 kg/a (0.1 kg/day) NP</i>	38 t/a (583.33 kg/day) NPEO	54 and 72 days production a year. Daily estimate based upon a worst-case assumption of both sites releasing at the same time to on-site treatment plant. Releases to on-site treatment plant then municipal treatment plant.
Company C Site 3	<i>28 kg/a (0.56 kg/day) NP</i>	850 kg/a (17 kg/day) NP + NPEO	50 days production a year. Release to industrial treatment plant.
Company D Site 1	<i>35 kg/a (0.12 kg/day) NP</i>	360 kg/a <i>(1.2 kg/day)</i> NPEO	Releases to on-site treatment plant then municipal treatment plant.
Company D Site 2	<i>0.2 kg/a (0.007 kg/day) NP</i>	10 kg/a (0.33 kg/day) NPEO	30 days production a year Release to on-site treatment plant
Company E	<i>1.17 kg/a (0.03 kg/day) NP</i>	0	40 days production a year. Wastewaters incinerated
Company F	<i>160 kg/a (0.8 kg/day) NP</i>	0	200 days production a year. NPEO washwaters concentrated then incinerated.
Company G	0	0	50 weeks production a year. Polluted wastewater incinerated on-site
Total	Total 463 kg/a (2.56 kg/d) NP	153 kg/day NP (Surface water) 0.07 kg/day NPEO (Surface water) 17 kg/day NP (WWTP) 584.86 kg/day NPEO (WWTP)	

Figures in italics are generated by default values or estimated on the basis of available data.  
Where a releases value is given as NP+NPEO the whole release is taken as NP (worst case)

### Releases of nonylphenol from the manufacture of phenolic oximes

Nonylphenol is used by one company within the EU to manufacture phenolic oximes, which are used as a reagent for the extraction and purification of copper from ore. All the phenolic oximes produced are exported to customers outside of the EU. Phenolic oximes are not thought to be used in the EU for this application, and so only releases from production will be considered in the risk assessment.

The wastewater stream is treated on-site in an activated sludge treatment plant. After treatment in the plant the nonylphenol concentration in the wastewater is reported as 0.318 mg/l, which is equivalent to 94 kg/year. This waste stream is emitted into a tidal water system. The company estimates the dilution of the effluent in the receiving waters at 80,000. Nonylphenol is not detectable in the flue gas from the air scrubbing systems. Process residues which have phenol formaldehyde resin characteristics are re-used as boiler fuels. The quantity of such resins recycled each year is calculated at 491 tonnes. Measurement of boiler gas indicates non-detectable levels of nonylphenol. The sludge produced from the on-site wastewater treatment plant is disposed of to landfill.

In calculating the regional and continental PECs the emission to water of 94 kg/year will be used. The local PEC calculations will be based upon the measured levels after wastewater treatment. Emissions to air and soil are zero.

*Confidential information has also been supplied and used. Further details may be obtained from the rapporteur.*

### Production of resins, plastics and stabilisers

The main use of nonylphenol in the plastics industry is as a monomer in the production of nonylphenol/formaldehyde resins. Other reported uses of nonylphenol are as an intermediate in the production of tri-(4-nonylphenyl) phosphite (TNPP), as a catalyst in the curing of epoxy resins and use in plastics stabilisers. The total amount of nonylphenol used within the industry was approximately 29,000 tonnes in 1997.

#### *Nonylphenol/formaldehyde resins*

Nonylphenol is used in nonylphenol/formaldehyde resins, either alone or mixed with other phenols. Although no information on the production of nonylphenol/formaldehyde resins was provided some general information is given in Kirk-Othmer (1996). In the absence of any further information it will be assumed that nonylphenol/formaldehyde resins are manufactured in a similar way to phenol/formaldehyde resins.

In general phenolic resins are manufactured by reaction of a phenol with formaldehyde in the presence of an acid or basic catalyst. They are generally thermosetting in nature. Alkylphenols are used as monomers/comonomers in phenol/formaldehyde resins to reduce the reactivity, hardness, cross-linking density and colour formation and to increase the solubility in non-polar solvents, flexibility and compatibility with natural oils. The formaldehyde used in the manufacture of phenolic resins is generally a 36-50% aqueous solution and is reacted with the phenolic compound in the presence of a strong acid catalyst (e.g. sulphuric acid, oxalic acid) or alkali (e.g. sodium hydroxide, calcium hydroxide, barium hydroxide). At neutral pHs, divalent metal catalysts can be used. Most phenolic resins are produced in a batch process. Depending on the final form of

the resin, the size of the reactor can be around 2-9.5 m<sup>3</sup> for neat or concentrated resins, 19 m<sup>3</sup> for resins that contain a large quantity of water, and 19-38 m<sup>3</sup> for melt-stable products.

Nonylphenol/formaldehyde resins are used as adhesives and tackifiers in the rubber industry (including tyres), paper coating resins and as intermediates for coating formulations, rosin modified resins for printing inks, electrical varnishes and as a modifier in several other applications. Nonylphenol/formaldehyde resins may also be ethoxylated for use in oil recovery. These products greatly reduce the amount of crude oil remaining in oil refinery effluent.

In carbonless copy paper typically a novalak resin is used at about 12% by weight of the formulation. In a typical novalak process, molten phenolic compound is added to the reactor along with an acid catalyst. Formaldehyde solution is then added slowly at a temperature of 90°C to give a formaldehyde to phenol ratio of 0.75:1 to 0.85:1. The reaction is complete after 6-8 hours and volatiles and water are removed by vacuum stripping up to 140-170°C. Steam distillation may also be used to further purify the product. Neutralisation of the acid catalyst with lime may also be needed. Curing agents may also be added to increase the cross-linking density of the final resin.

Nonylphenol/formaldehyde resins have also been reported to be used in contact adhesive applications and, to a lesser extent, in coatings (Kirk Othmer, 1996). Contact adhesives are blends of rubber, phenolic resin and additives either in a solvent or in an aqueous form. The phenolic resins promote adhesion and act as tackifiers. They are usually present at a concentration of 20-40%. In coatings applications, the alkyl group on nonylphenol increases the compatibility with oleoresinous varnishes and alkyds. Common applications include baked-on and electrical insulation varnishes and as modifiers for baking alkyds, rosin and ester gum systems.

No information about residual levels of nonylphenol in the resins is currently available, and therefore only releases from the polymerisation process have been estimated.

There are reported to be around 50 producers of phenol/formaldehyde resins within the EU. Of these producers about 20 are thought to routinely use nonylphenol. It is estimated that nonylphenol is probably used in the production of phenol/formaldehyde resins at 25 sites within the EU. The total amount of nonylphenol used in this application was approximately 22,500 tonnes in 1997.

The default release estimation for nonylphenol/formaldehyde resin production is calculated using Table A3.10 Chapter 3 Appendix 1 of the TGD. The default release fraction estimates are 0.00001 for air and 0.00001 to water. The regional release is taken as 10% of the continental release. The total number of sites using nonylphenol in the production of nonylphenol/formaldehyde resins is estimated to be 25 in the EU and the total tonnage used is estimated to be 22,500 tonnes/annum. Dividing the total tonnage by 25 gives average use at a local site of 900 tonnes/annum. The spread on size of phenol/formaldehyde resin plants is not available therefore as well as the average plant size a worst case of 5 times the average plant size will be used in the local calculation. The default number of processing days is taken; as 300 days/year; though where smaller tonnages are processed a more accurate estimation of 100 days/year will be used.

Air    Local 0.09 kg/day (average) 0.15 kg/day (worst case)  
Regional 0.06 kg/day; Continental 0.56 kg/day

Water Local 0.09 kg/day (average) 0.15 kg/day (worst case)  
Regional 0.06 kg/day; Continental 0.56 kg/day

A phenol/formaldehyde producer in the EU has given the following information. The average amount of nonylphenol used per year is 650 tonnes and production occurs for 70 days/year. The release fraction of nonylphenol to effluent is 0.000008; this effluent is collected and taken off-site for waste treatment. If the release factor is applied to the typical amount processed per year and the average number of days processing per year, the daily discharge to wastewater is 0.07 kg/day. This value appears to be in reasonable agreement with the calculated daily emission for an average size plant. The default values are used for the assessment.

The disposal practice of wastewaters from phenol/formaldehyde production plants is unknown, though it is generally thought that producers do not dispose of wastewaters directly to sewer.

#### *Tri-(4-nonylphenyl) phosphite (TNPP)*

TNPP is used as a secondary antioxidant in polymer formulations. It is widely used in the stabilisation of natural and synthetic rubbers, vinyl polymers, polyolefins and styrenics. TNPP is used as an additive in plastics used for food packaging. TNPP may contain up to 3% free nonylphenol. The amount of TNPP in plastics is not known, although a level of 6% is allowed by the German BGA (Bundesgesundheitsamt). TNPP acts as a stabiliser and in the process the molecule is gradually oxidised and nonylphenol is released. Releases are only considered during manufacture of TNPP from nonylphenol due to lack of information on release during use. Releases to the environment during use though are thought to be negligible. This is based upon the gradual formation of nonylphenol from TNPP during product use. The nonylphenol formed will undergo degradation and/or adsorption.

The principal use of TNPP is in food packaging. This is a relatively short-term application and the amounts of nonylphenol formed are likely to be small. It is also likely that any free nonylphenol formed would be preferentially adsorbed by the food. The Society of the Plastics Industry (SPI) in the United States has performed an analysis to estimate the potential dietary exposure of nonylphenol from the use of TNPP in food contact materials. Using worst-case scenarios, the maximum potential dietary exposure to nonylphenol was estimated to be approximately 35.6 parts per billion. Food packaging has a short lifetime and is typically disposed of to landfill or by incineration. In landfills the potential for leaching from the product and then the landfill site is likely to be very small due to the adsorption properties of nonylphenol.

The total amount of nonylphenol used in this application is 4,000 tonnes/annum. Information from TNPP producers suggests that releases to the environment are zero during production of TNPP. All the waste created during production is reported by industry as being incinerated.

#### *Epoxy resins*

In some epoxy resins nonylphenol is used as an accelerator or curing agent in the hardening component (alkanolamine). Nonylphenol reacts with the alkanolamine to form an amine salt. In the hardening process the nonylphenol amine salt is irreversibly encapsulated in the final resins. Curing agents are typically added to polymer resins at concentrations of 0.5-3% of the total resin. Curing agents cause cross-linking in the resins and so can be considered co-monomers (i.e. nonylphenol is reacted into the polymer structure) in the polymerisation process. The total amount of nonylphenol used in this application is estimated by industry to be 1,500 tonnes in 1997.

In the production process nonylphenol is directly blended with the amine to form the corresponding amine salt. It is then filled into tubes for use. In use, the consumer has to blend the



binder with the nonylphenol-containing amine. After mixing, the blend hardens and all the nonylphenol is encapsulated in the water insoluble matrix. As the nonylphenol is effectively bound up in the epoxy resins once formed, releases from production alone will be considered. The source of releases of nonylphenol from this process are likely to be similar to those from the production of nonylphenol/formaldehyde resins, although here nonylphenol makes up a much smaller part of the total resin than is the case with nonylphenol/formaldehyde resins. The Use Category Document on plastic additives has been used to generate default release estimations. The use category document gives release figures of 0.01% to water for liquid curing agents during raw material handling, 0.01% to air during compounding and zero release during disposal and product service. The use category document gives a typical epoxy resin production-site as producing 80 tonnes epoxy resin per year. Of this amount 10% is the curing agent this gives the amount of nonylphenol used as 8 tonnes/year. This gives a daily release to air and water of 0.0026 kg/day. For the regional and continental scenarios these release factors will be applied to the total amount of nonylphenol used in this application. This gives the following releases:

Air Local 0.0026 kg/day; Regional 0.04 kg/d; Continental 0.36 kg/day  
 Water Local 0.0026 kg/day; Regional 0.04 kg/d; Continental 0.36 kg/day

#### *Use in other plastic stabilisers*

Industry reports that in 1997 approximately 1,000 tonnes nonylphenol was used in plastic stabilisers. No further information is available; therefore it is assumed that figures relate to nonylphenol used in production of plastic stabilisers rather than use as a plastic stabiliser itself. Default release estimations using Table A3.10 in Chapter 3 Appendix 1 of the TGD will be used. Releases will only be considered for the production step. In using the default release estimations, Use Category 43 (Process regulators) and Type III will be assumed. This gives release fractions to air of zero and to water of 0.0005. The number of days processing per year is taken as 300 days and the amount used at local site as 100 tonnes/year. The regional release is taken as 10% of the continental release.

Water Local 0.16 kg/day; Regional 0.14 kg/day; Continental 1.23 kg/day

#### **3.1.1.1.4 Releases during private use**

Releases during private use are not thought to be applicable for nonylphenol.

#### **3.1.1.1.5 Releases during disposal**

Direct disposal of nonylphenol to the environment is unlikely to occur. It is more likely that nonylphenol will reach the environment as part of a product.

#### **3.1.1.1.2 Releases of nonylphenol ethoxylates**

Nonylphenol may be released to the environment due to breakdown of nonylphenol ethoxylates. This section considers the various lifecycle stages of nonylphenol ethoxylates and considers the potential releases of nonylphenol ethoxylate from each stage (See Appendix 1). Section 2 gives more details on the uses and tonnages of nonylphenol ethoxylates used.

### **3.1.1.1.2.1 Releases during production**

The release of nonylphenol and nonylphenol ethoxylates during the production of nonylphenol ethoxylates is covered in Section 3.1.1.1.1.3.

### **3.1.1.1.2.2 Releases during formulation**

The total amount of nonylphenol ethoxylates used in the EU is estimated by industry to be 72,000 tonnes/year. It is assumed that this total tonnage is formulated prior to use within the EU. In general it is assumed that the formulation of nonylphenol ethoxylates occurs at different sites from the production and processing sites, though some companies producing nonylphenol ethoxylates use certain amounts on-site for the production of textile and leather auxiliaries and agrochemical products. In these cases the releases are included in the company estimates used to calculate the releases during nonylphenol ethoxylate production. According to industry, these releases are negligible compared to releases during production. Some companies dilute nonylphenol ethoxylate solutions on-site with water (10-30% dilution) to improve product handling, though this step is not considered a formulation step by industry.

Information on the formulation of fuel and lubricant oils using nonylphenol ethoxylates is contained in the appropriate section below.

Formulators of nonylphenol ethoxylate containing products within the UK have supplied some information:

#### *Company 1*

Company 1 is involved with the formulation of metal cutting fluids containing nonylphenol ethoxylates. The company uses approximately 2 tonnes nonylphenol ethoxylates a month during the formulation step. The level of nonylphenol ethoxylates in the final product is approximately 5% by weight. The company reports releases to the environment as zero during the formulation step.

#### *Company 2*

Company 2 is involved in the formulation of pesticides for domestic use. The material is fully processed and packaged for end use on-site. The total quantity of nonylphenol ethoxylates used is 1,200 kg/year and the average number of days use is 30 days a year. Formulation takes place in an aqueous system at ambient temperature and is fully recycled into the system. No material is released into the water course. Nonylphenol ethoxylates account for 0.1% by weight of the final formulated product.

#### *Company 3*

Company 3 is involved in the formulation of nonylphenol ethoxylate for the textile industry. Approximately 12 tonnes/year nonylphenol ethoxylates are used and the average number of days use is 250 days/year. The ethoxylate is supplied in 200 litre drums; it is then formulated and returned to 200 litre drums. Washings from the mixing vessel are discharged to an on-site treatment plant and then to sewer. The aqueous wastes are treated on-site by chemical coagulation and filtration. Approximately 0.13 tonnes/year nonylphenol ethoxylates are released to the on-site treatment plant.

*Company 4*

Company 4 is involved in the formulation of agricultural products. Approximately 1 tonne/year of nonylphenol ethoxylates are used and the average number of days use is 30 days per year. During formulation activities, releases to the environment are reported as zero. The estimated level of nonylphenol ethoxylates in the final product is 2%.

*Company 5*

Company 5 is involved in the formulation of industrial water treatment chemicals and paper industry process aids. Approximately 240 tonnes/year nonylphenol ethoxylates are used and the average number of days use is 312 days/year. During formulation approximately 0.5 tonnes/year nonylphenol ethoxylates are discharged to water (equivalent to 1.6 kg/day). Wastewater is treated on-site by oxygenation and flocculation of trade effluent and for pH control, it is then discharged to sewer and treated by the local water company. The final products can contain up to 20% nonylphenol ethoxylates.

*Company 6*

Company 6 is involved in the formulation of veterinary medicines and agricultural cleaning products. Approximately 3 tonnes/year of nonylphenol ethoxylates are used and the average number of days use is 20 days/year. Releases to water during formulation of products are approximately 1% w/w of the annual quantity used. These releases are assumed to be direct to receiving waters as there is no on-site treatment. The amount of nonylphenol ethoxylate in the final product is between 5-15% w/w.

The default release estimations of nonylphenol ethoxylate due to formulation are calculated using the emission factors in Table A2.1 Chapter 3 Appendix 1 of the TGD. The default emission factors are 0.0025 to air and 0.003 to wastewater. Regional emissions are taken as 10% of the continental emission. Local emissions are taken as occurring for 300 days a year with 80% of the regional tonnage used at the local site (Table B2.3 Chapter 3 Appendix 1 TGD). This gives the following emissions for nonylphenol ethoxylates.

Air:	Local 48 kg/day;	Regional 49.3 kg/day;	Continental 444 kg/day
Water:	Local 57.6 kg/day;	Regional 59.2 kg/day;	Continental 533 kg/day

The amount used at a local site in the default release estimation is 5,760 tonnes/year. In the site specific data the amount used is a lot less, between 1 tonne/year to 240 tonnes/year in the limited sample reported. This suggests that the default release estimations significantly overestimate the amount used at a local site. In practice, the site-specific data for the UK suggests that formulators are usually involved in formulating products for a specific industry sector and/or product type and that the amounts used at a specific site are relatively small when compared to the overall amount of nonylphenol ethoxylate formulated. Based upon this information a more realistic value for the amount used by a large scale formulator is taken as 1,000 tonnes nonylphenol ethoxylate/year (4 times the tonnage from the largest site specific data), a medium scale formulator as 250 tonnes nonylphenol ethoxylate/year (the largest site specific data) and a small scale formulator as 10 tonnes nonylphenol ethoxylate/year.

The fraction of release to water in the default release estimations is 0.003. This is in line with the release fractions calculated from the site-specific data. The default release estimation would

therefore appear to be a reasonable estimation of losses during formulation when no other data are available.

The default number of days for formulation is 300 days/year. From the site-specific data the number of days processing varies from 20 to approximately 300 a year. The lower number of days occurs at sites using a relatively small amount of nonylphenol ethoxylate (1-3 tonnes/year). For the formulators using larger tonnages of nonylphenol ethoxylates, the number of processing days is in line with the default number of days. Based upon these data it is suggested that for small-scale formulators the number of days formulation is taken as 30 and for medium and large scale processors 300 is used.

Based upon these revised data the emissions to water for large, medium and small scale formulators are calculated as follows:

Large-scale formulator:	Formulating 1,000 tonnes over 300 days/year
Release to water:	3 tonnes/year, 10 kg/day
Medium scale formulator:	Formulating 250 tonnes over 300 days/year
Release to water:	0.75 tonnes/year, 2.5 kg/day
Small-scale formulator:	Formulating 10 tonnes over 30 days/year
Release to water:	0.03 tonnes/year, 1 kg/day

These revised data will be used in the calculation of the PEC for the local scenario.

Additional information obtained from further work on the use of nonylphenol ethoxylates suggests that disposal routes will also vary between different formulators. The two most common disposal routes encountered are wastewater treatment on-site or at a local wastewater treatment plant (this is usually to meet a general water quality requirement not to specifically remove nonylphenol or nonylphenol ethoxylate) and incineration of waste streams.

### **3.1.1.1.2.3 Releases of nonylphenol ethoxylates during processing**

For nonylphenol ethoxylates the processing step is the stage at which the products are used. A wide variety of different use and industrial categories are reported, these are considered below.

#### Agricultural industry

Nonylphenol ethoxylates are used in the agricultural industry as ingredients of formulated pesticide products and as formulation additives. They are also used in some veterinary medicinal products. Nonylphenol is not thought to be used directly in the agricultural industry.

#### *Pesticides*

The method of use and exposure is the same as for pesticide active ingredients. Therefore, the methods used for assessing aquatic exposure of pesticides are also appropriate for assessing the aquatic exposure of nonylphenol ethoxylates used in the agricultural industry.

The amounts of nonylphenol ethoxylates applied to crops are typically equivalent to 50-200 g/ha, with the higher rates being used as wetters and the low rates as emulsifiers. These application rates are used in Sections 3.1.2.1.1 and 3.1.3.1 to estimate the concentration in water and soil as results of this use.

### *Veterinary medicines*

The following information has been obtained from the UK Veterinary Medicines Directorate (VMD) with regard to the use of nonylphenol ethoxylates in veterinary medicinal products. The Veterinary Medicines Directorate are responsible for regulating the use of chemicals used as veterinary medicines within the UK.

The principal use of nonylphenol ethoxylates in veterinary medicinal products is as surfactants in teat dips, which are used in the control of mastitis. The other major use is as a surfactant in sheep dip formulations. Other possible products that may contain nonylphenol ethoxylates in farms are non-veterinary medicine disinfectants such as udder washes and in general cleaning products.

There are two basic types of teat dips that may contain nonylphenol ethoxylates; iodophores and chlorohexanes. Iodophores may be supplied as either a concentrate or a ready to use formulation; in either case the amount of nonylphenol ethoxylate in the formulation as used is approximately 5%. Chlorohexanes are supplied as ready to use formulations and contain <1% nonylphenol ethoxylate. In use the product is used neat with 8-10 ml used per cow with dipping occurring twice daily. 40-50% of the teat dip is likely to be lost during application and ends up in parlour washings. The remaining teat dip is likely to remain on the cow's teat until the next milking period where it will be washed off before milking and is therefore likely to end up in parlour washings as well. For a 100-cow herd about 25 litres of teat dip is likely to be used every 2-3 weeks.

Based upon this data the following generic calculation has been performed for teat dips that contain nonylphenol ethoxylates.

There is 5% nonylphenol ethoxylate in 25 litres of teat formulation, which is used on an average dairy cow herd every 2 weeks. The total amount of nonylphenol ethoxylate used is 1.25 kg NPEO/2 weeks which is equivalent to 0.09 kg NPEO/day. The typical field size to which sludge is applied is 10 hectares (100,000 m<sup>2</sup>). Assuming that 2 weeks parlour washings are collected before application the release rate of nonylphenol ethoxylate is 12.5 mg/m<sup>2</sup> soil per application.

Not all parlour washings are disposed of via manure to land. Some farms have separate systems for dealing with dirty water in which the dirty water is irrigated directly to land on a daily basis.

If 8 ml of product containing 5% nonylphenol ethoxylate is used per cow per milking session, the average amount of nonylphenol ethoxylate used per cow per milking is 400 mg. Assuming that there are two milkings a day and that 18 litres of water is used per day per cow, the average concentration of nonylphenol ethoxylate in dirty water is 44 mg/l. Dirty water is applied to land at the rate of 50,000 litres/hectare per year. This gives a release of nonylphenol ethoxylate to soil of 2.2 kg/hectare/year or 0.6 mg/m<sup>2</sup>/day (assuming constant irrigation over 365 days/year).

Sheep dips do not end up in parlour washings, instead used sheep dip is spread directly onto land at a rate of 5,000 litres per hectare. Alternatively it may be diluted in slurry in a ratio of 3:1 and the resulting mixture spread onto land at 20,000 litres/hectare. The typical concentration of nonylphenol ethoxylate in sheep dip formulations is 800 mg/l. A typical sheep dip volume is about 1,000 litres. The average amount of nonylphenol ethoxylate releases to soil due to application of sheep dips will be 400 mg/m<sup>2</sup> (4 kg/hectare) per application of sheep dip.

It should be noted that other products that contain nonylphenol ethoxylates such as udder washes and general cleaning products might also be present in the parlour washings.

In the UK a major supplier of veterinary medicines has phased out the use of nonylphenol ethoxylates in veterinary medicines since the end of 1997, though it is understood that other companies within the EU are still using nonylphenol ethoxylates within veterinary medicines.

In calculating releases of nonylphenol ethoxylates to surface water from agricultural use the following assumptions will be made:

For the local scenario surface water concentrations will be considered for pesticide application only. The data and PEC calculation provided by industry will be used for this purpose. For the regional and continental scenarios default releases from the TGD will be used.

In calculating local concentrations in soil releases to soil due to pesticide application, application of parlour washings containing teat dip and application of spent sheep dip will all be considered.

The total amount of nonylphenol ethoxylates used in the EU in the agricultural industry is estimated as 5,000 tonnes/year in 1997. Table A3.1 of Chapter 3 Appendix 1 of the TGD gives the following emission factors for use of pesticides and surfactants in the agricultural industry: Air 0.05; Surface water 0.1; Soil 0.85. Applying these factors to the continental tonnage of nonylphenol ethoxylates used gives the following releases:

Air:	Regional 68.4 kg/day; Continental 617 kg/day
Surface water:	Regional 137 kg/day; Continental 1,233 kg/day
Agricultural soil:	Regional 1,164 kg/day; Continental 10,480 kg/day.

#### Captive use by the chemical industry

Use of nonylphenol ethoxylates by the chemical industry for the synthesis of other chemicals may also be referred to as captive use. Nonylphenol ethoxylates are used in the chemical industry in the synthesis of nonylphenol ether sulphates and nonylphenol ether phosphates. Both of these compounds are used as emulsifiers in the chemical industry.

Ten companies within the EU produce nonylphenol ether sulphates. Nonylphenol ether sulphates are normally used as an emulsifier for styrene and other monomers like styrene butadiene, ethylene vinyl esters or vinyl chloride. The product is added to a solution of the monomer in water with stirring to cause emulsification. The batch is then spray dried to obtain fine polymer particles. The condensed water does not contain the emulsifier. The emulsifier is encapsulated in the plastic polymer. Nonylphenol ether sulphates may also be used as emulsifiers in agrochemicals and as an additive to special types of concrete.

Eight companies within the EU produce nonylphenol ethoxylate phosphates. Nonylphenol ethoxylate phosphates are normally used as emulsifiers in agrochemicals or the emulsion polymerisation process. They may also be used in industrial and institutional cleaning products as they have low foaming properties and are highly stable against alkalis.

No information about releases has been supplied and therefore default releases based upon the emission scenario documents for use in synthesis in the chemical industry will be used. In 1997 the amount of nonylphenol used in captive uses by the chemical industry was 7,000 tonnes. The default release estimations of nonylphenol ethoxylate due to use in synthesis in the chemical industry are calculated using the emission factors from the emission scenario document in the TGD. The default emission factors are 0 to air and 0.007 to wastewater. Regional emissions are

taken as 10% of the continental emission. Local emissions are taken as occurring for 300 days a year with 25% (175 tonnes) of the regional tonnage used at the local site (Table B3.2 Chapter 3 Appendix 1 of the TGD). This gives the following emissions for nonylphenol ethoxylates:

Water: Local 4.08 kg/d; Regional 13.4 kg/d; Continental 120 kg/d

#### Electrical engineering industry

In the electrical engineering industry nonylphenol ethoxylates are reported as being used in fluxes in the manufacture of printed circuit boards, in dyes to identify cracks in printed circuit boards and as a component of chemical baths used in the etching of circuit boards. Nonylphenol ethoxylates may also be present in cleaning products used to clean electrical components. However, cleaning products for some electrical equipment such as printed circuit boards are required to have less than 10 parts per million (ppm) of certain metal ions. The catalysts used in the production of nonylphenol ethoxylates mean that metal ion concentrations are often far in excess of this, so a special grade nonylphenol ethoxylate would be needed to meet the requirements. The concentration of nonylphenol ethoxylates in cleaning products for the metal industry is reported as approximately 5% w/w.

The total amount of nonylphenol ethoxylates used in the electrical engineering industry was reported as 93 tonnes/year in 1994. Up to date figures for 1997 have not been received. Based upon the low tonnage, it appears reasonable to assume that industrial and institutional cleaning covers cleaning of metal components. The tonnage considered here is taken as referring to specific uses within the electrical engineering industry such as a part of a flux and as a component of dyes to identify cracks in printed circuit boards. The default release estimations of nonylphenol ethoxylate due to use in the electrical engineering industry are calculated using the emission factors in Table A3.4 Chapter 3 Appendix 1 of the TGD. The default emission factors are 0.0005 to air and 0.005 to wastewater. Regional emissions are taken as 10% of the continental emission. Local emissions are taken as occurring for 15 days a year with 80% (7.4 tonnes) of the regional tonnage used at the local site (Table B3.2 Chapter 3 Appendix 1 of the TGD). This gives the following emissions for nonylphenol ethoxylates:

Air: Local 0.25 kg/d; Regional 0.01 kg/d; Continental 0.11 kg/d  
Water: Local 2.46 kg/d; Regional 0.13 kg/d; Continental 1.15 kg/d

#### Public domain

Nonylphenol ethoxylates are used in the public domain in industrial and institutional cleaning products. This section also covers releases from the use of nonylphenol ethoxylate based detergents in other industry categories, for example cleaning agents in the electrical and electronic industry.

The total amount of nonylphenol ethoxylates used in industrial and institutional cleaning products was reported as 23,000 tonnes for 1997. The default release estimations of nonylphenol ethoxylate due to use in the public domain are calculated using the emission factors in Table A3.5 Chapter 3 Appendix 1 of the TGD. The default emission factors are 0.0025 to air and 0.9 to wastewater. Regional emissions are taken as 10% of the continental emission. Local emissions are taken as occurring for 200 days a year with 0.2% (4.6 tonnes) of the regional tonnage used at the local site (Table B3.3 Chapter 3 Appendix 1 of the TGD). This gives the following emissions for nonylphenol ethoxylates:

Air: Local 0.06 kg/d; Regional 15.7 kg/d; Continental 141.8 kg/d  
Water: Local 20.7 kg/d; Regional 5,671 kg/d; Continental 51,041 kg/d

### Leather processing industry

Nonylphenol ethoxylates are thought to be used as auxiliaries in the wet degreasing of hides in the leather processing industry. The total amount of nonylphenol ethoxylate used in leather industry auxiliaries is reported as 6,000 tonnes for 1997. Information supplied by industry puts the volume of nonylphenol ethoxylates in leather auxiliaries used within the EU at 3,137 tonnes/year, with the rest being sold outside the EU. The total number of leather processing sites within the EU is estimated as 1,000 by industry, and the number of days emission for the local scenario is estimated at 200 per year. No further information about releases from the leather industry has been supplied, so the default release values from Table A3.6 Chapter 3 Appendix 1 of the TGD will be used.

The default emissions to the environment are 0.001 to air and 0.9 to wastewater. Regional emissions are taken as 10% of the continental emission. For the local site an average site based on the total number of sites within the EU and total tonnage used is calculated as using 3 tonnes nonylphenol ethoxylate per year. The sizes of leather processing sites are thought to vary, so a worst-case scenario will be used which assumes that a local site uses 5 times the average site volume, i.e. 15 tonnes/year. Using these factors the releases to the environment from the leather processing industry are as follows:

Air: Local 0.015 kg/d (average) 0.075 kg/d (worst case)  
Regional 0.9 kg/d; Continental 7.7 kg/d

Water: Local 13.5 kg/d (average) 67.5 kg/d (worst case)  
Regional 774 kg/d; Continental 6,962 kg/d

### Metal extraction, refining and processing industry

Nonylphenol ethoxylates are used in the metal extraction, refining and processing industry in the formulation and usage of cutting and drilling oils. Cutting and drilling oils are mainly emulsions of white spirit, water and hydrophobic surfactants. In Western Europe there are approximately 50 large companies using these oils. Before the spent cutting and drilling oils are released to the wastewater, they are split into two phases in a separating plant by the addition of salts. The oily phase, which contains more than 90% of the surfactants, is burnt. The water phase is released to the wastewater. All the large companies use this procedure.

As well as the use of cutting and drilling oils by the big companies, nonylphenol ethoxylates are also thought to be a constituent of general metal working fluids. The use of metal working fluids is thought to be widespread in small to medium scale companies. It has been estimated that in the UK there may be approximately 3,000 companies using metal cutting fluids. Nonylphenol ethoxylates may also be added to some neat oils where these are required to be water-washable, for example in quenching oils.

Nonylphenol ethoxylates are reported as being used in alkaline cleaners and other metal finishing products. Approximately 50% of alkaline cleaners are thought to contain nonylphenol ethoxylates. The use of these cleaners and other nonylphenol ethoxylate-based detergents for cleaning in the metal working industry is considered under industrial and institutional cleaning.



The total amount of nonylphenol ethoxylates used within the metal extraction, refining and processing industry were estimated to be 2,000 tonnes in 1997. Based upon the data for large-scale processors using metal cutting fluids it is estimated that the amount used in the local scenario is 20% of the regional amount and the number of emission days is 100 per year. No other information on releases to the environment has been supplied, so the default release estimations from Table A3.7 Chapter 3 Appendix 1 of the TGD will be used. The default emission factors are 0.0002 to air and 0.316 to wastewater. The emission to wastewater will be reduced by 90% to take into account the current waste disposal practices at large scale processors. No information on the amount used by smaller companies has been obtained, it is reasonable to assume that the amounts used are significantly less than by the big companies. The releases below will therefore be taken as a realistic worst-case example of releases from the metal industry. The default release estimations for nonylphenol ethoxylates are:

Air: Local 0.08 kg/d; Regional 0.11 kg/d; Continental 0.99 kg/d

Water: Local 114 kg/d; Regional 156 kg/d; Continental 1,402 kg/d

### Mineral fuel and oil industry

Information on the use of nonylphenol and nonylphenol ethoxylates in the mineral fuel and oil industry has been supplied by members of the ATC (Additives Technical Committee, an affiliated organisation of CEFIC).

In fuels, detergents are used to clean engines internally as a means of meeting vehicle emission targets to enable performance targets for vehicles to be met. The active ingredients are included in additive packages produced by additive manufacturers. The amount of active ingredient present is likely to be relatively small. Nonylphenol ethoxylate phosphate esters (which are typically 90% by weight nonylphenol ethoxylate) are used as additives in some lubricating oils, particularly for military use. Nonylphenol ethoxylates may also be present in sulphonate and phenate based lubricants.

Nonylphenol may be used in the fuel and oil industry as a raw material in the manufacture of fuel additive components. Nonylphenol and nonylphenol ethoxylates are both used in the blending of fuel additive packages for use in either fuel oil or lubricants. The additive manufacture and blending operations are thought to be the main sources of environmental releases of both nonylphenol and nonylphenol ethoxylates due to use in the fuel and oil industry.

Once produced the additive packages are sold onto customers who use them in the blending of lubricants or fuels. The blended product is then sold onto the general public for use. The fate of the additive package then depends upon whether the additive package is used in a lubricant or a fuel oil. For lubricants, losses are expected to be as follows; on road during use, consumed (burnt) during use and disposal by oil drain. At this stage the level of the component in the lubricant is very low. There are not expected to be any major environmental losses at this stage. Fuels oils are consumed during use (burnt) and there are expected to be no other potential sources of release.

The total amount of nonylphenol ethoxylates used in the mineral fuel and oil industry was reported as 93 tonnes/year in 1994. More up to date figures are not available.

The ATC have carried out a survey of their members to try and quantify releases of nonylphenol and nonylphenol ethoxylates from additive manufacture and blending. From the data supplied in

the survey the following conclusions may be drawn with respect to fuel additive component manufacture and blending:

- Not all sites use nonylphenol or nonylphenol ethoxylates.
- Some sites are only involved in the blending of additive packages and not in the manufacture of the additive components.
- Manufacture of the additive component is equivalent to use in the chemical industry as an intermediate in the manufacture of chemical derivatives.
- The type of waste disposal operation carried out at each site varies. The most common forms of waste disposal reported are: incineration of waste material; on-site treatment of wastewaters (oil separation, biological treatment); treatment at industrial WWTP.
- Losses of nonylphenol from manufacture and blending operations are between 0.5-2.5 kg/day (Not all of these losses are to wastewater, some are incinerated).
- Losses of nonylphenol ethoxylates from blending operations are between 0.01-20 kg/day (Not all of these losses are to wastewater, some are incinerated).

Releases of nonylphenol and nonylphenol ethoxylates to the environment during use are assumed to be zero.

For the continental and regional modelling the following releases of nonylphenol and nonylphenol ethoxylate to water will be used for additive manufacture and blending. These values are based upon data presented in the ATC survey.

Water: Regional 1 kg/day nonylphenol; Continental 10 kg/day nonylphenol

#### Photographic industry

Nonylphenol ethoxylates are reported as being used as wetting agents in the developing of photographic film. Information from the photographic industry suggests that nonylphenol ethoxylates are used in products intended for home use by the amateur photographer, photo developers who develop film for amateur photographers and in some professional products. The concentration of nonylphenol ethoxylates in these products is between 3-5% w/w. The products are sold as concentrates and the user prepares the formula by adding water.

Information obtained from the photographic industry suggests that the use of these products varies from company to company with some companies not using any nonylphenol based products. At large scale plants wastewater treatment is not aimed at specifically removing or reducing the nonylphenol content of the waters. However the treatments that the wastewaters undergo are likely to reduce the amount of nonylphenol reaching receiving waters.

Regulations in some EU countries require that commercial photo developers do not discharge products such as wetting agents to the sewer. The largest users of photo-chemicals pre-treat their chemicals and then discharge to sewers, whereas the small and medium scale users generally have their wastes hauled off site and incinerated by a third party. However, small amounts of chemical resulting from carryover of solution to wash tanks do get discharged directly to sewer. In addition products used by home hobbyists are generally discharged directly to sewer.

The total amount of nonylphenol ethoxylates used in the photographic industry was reported as 93 tonnes/year in 1994; up to date information has not been obtained. The default release estimations of nonylphenol ethoxylate due to use in the photographic industry are calculated

using the emission factors in Table A3.9 Chapter 3 Appendix 1 TGD. The default emission factors are 0.000035 to air and 0.8 to wastewater. Regional emissions are taken as 10% of the continental emission. Local emissions are taken as occurring for 300 days a year with 5% (0.465 tonnes/year) of the regional tonnage used at the local site (Table B3.8 Chapter 3 Appendix 1 of the TGD). This gives approximately 200 sites within the EU, this figure would appear to be realistic for large-scale commercial developers but unrealistic for small-scale photographic developers. In the UK, there are thought to be around 1,000-2,000 small-scale users and 6 large commercial users. Releases from small-scale users may therefore be up to 150-300 times smaller than from large-scale users. A conservative estimate of 150 times smaller (3.1 kg nonylphenol ethoxylates used per annum) will be used to calculate local releases from small-scale users. This gives the following emissions for nonylphenol ethoxylates.

Air: Local  $3 \cdot 10^{-7}$  kg/day (small user) 0.00005 kg/day (large user)  
Regional 0.0009 kg/day; Continental 0.008 kg/day

Water: Local 0.008 kg/day (small user) 1.24 kg/day (large user)  
Regional 20 kg/day; Continental 183 kg/day

### Emulsion polymers

Nonylphenol ethoxylates are used as processing aids in the formulation of a number of emulsion polymers including polyvinyl acetates and acrylic acids.

The European Polymer Dispersion and Latex Association (EPDLA) which is a CEFIC Sector Group representing the European manufacturers of polymer dispersions and latices have supplied the following information.

Many polymer dispersions contain alkyl phenol ethoxylates as surfactants used in the manufacturing process. The end applications for polymer dispersions include in paints, paper, inks, adhesives, and carpet backings. At manufacturing sites, the amount used varies between 3-2,000 tonnes/year. This is based upon a survey of seven manufacturing sites. Production typically occurs for 300 days a year or more. Releases to air are reported as zero. Releases to water during manufacture are reported as being very low and a conservative estimate of the amount released is 0.1 kg/tonne produced. The level of nonylphenol ethoxylates in the final product is between 0 to 5%. From the survey of manufacturers wastewater is reported as typically being treated on-site or is totally enclosed (no liquid effluent stream).

Releases during polymer dispersion manufacture will be considered in this section. Releases from the use of these dispersions will be considered in the sections on the paint industry and pulp and paper industry.

In 1997 the total amount of nonylphenol ethoxylates used in the production of emulsion polymers was approximately 9,000 tonnes. Emulsion polymers are estimated to be produced at 70 sites within the EU; of these 50 are thought to use nonylphenol ethoxylate based processing aids.

The release factors estimated by the EPDLA will be used to calculate release from the manufacture of polymer dispersions. A worst-case usage at a local site of 3,000 tonnes/year will be considered for the local scenario. The regional releases will be taken as 10% of the continental releases. This gives the following emissions of nonylphenol ethoxylates due to use in the manufacture of polymer dispersions.

Water: Local 1 kg/d; Regional 0.25 kg/d; Continental 2.22 kg/d

### Pulp, paper and board industry

A variety of uses for nonylphenol ethoxylates within the pulp and paper industry have been identified. Nonylphenol ethoxylates are used in defoamers in the wet end of paper manufacture, where they help to ensure even dispersion of the defoaming agents. They are also used in retention aids, where again their function is to help disperse the actual retention agents. In these uses they are present in the product at ~1%. Nonylphenol ethoxylates may be used in felt cleaners and conditioners during the cleaning of woollen and synthetic drying machines. These products may contain up to 10% of the ethoxylates. Other possible uses are as cleaning agents, tissue softeners and in the de-lignification of wood.

The total amount of nonylphenol ethoxylates used within the pulp, paper and board industry within the EU is estimated as 1,000 tonnes for 1997. Industry reports that 20% of this amount is exported. The total number of users within the EU is estimated by industry as 1,300. The total number of days operation per year is estimated by industry as 100; however a survey of the paper industry in Germany suggested a figure of over 300 days per year.

No specific information on the releases of nonylphenol ethoxylates from this industry is available. Therefore the emission scenario for this industry from the Technical Guidance has been used to estimate releases.

#### *Anti-foaming agent use*

Taking board production as an example, the level of use of anti-foaming agents is 0.03% (related to the amount of board produced). As nonylphenol ethoxylates are present at 1% in the anti-foaming agent, this corresponds to 0.0003%, or 3 g ethoxylate/tonne paper. Board production rates are given as 100-1,000 tonnes/day; taking the larger figure gives 3 kg/day nonylphenol ethoxylate use. There is no retention of these agents on the paper, and so the release is 3 kg/day. However there is considerable recycling of process water and consequent reduction in the amount of chemical used. The degree of closure for board is given as 95%, so the actual releases are 0.15 kg/day. Water usage for board production is given as 10 m<sup>3</sup>/tonne of paper, which is 10<sup>4</sup> m<sup>3</sup>/day for this site.

Similar calculations for the other paper types give the following values (with the volume of water in which they are released): newsprint 15 g/day (3 · 10<sup>4</sup> m<sup>3</sup>/day); printing and writing paper 1.35 kg/day (5.5x10<sup>4</sup> m<sup>3</sup>/day); tissue 270 g/day (1.14 · 10<sup>4</sup> m<sup>3</sup>/day).

#### *Retention aid use*

Again taking board production as an example, retention aids are used at 0.1-0.5% by weight of paper. Taking the high end of this range, and 1% as the nonylphenol ethoxylate content in the retention aid, gives the use of nonylphenol ethoxylates as 0.05 kg/tonne paper. Taking the same values for production as above, this leads to 50 kg ethoxylate use per day. The release of retention aids is given as 10-30% in the emission scenario; however, this is taken to apply to the actual retention aid substances themselves, and the nonylphenol ethoxylates are assumed to be completely released. Thus the daily release is 2.5 kg, in the same volume of water, 10<sup>4</sup> m<sup>3</sup>.

Retention aids are only used with board and newsprint; a similar calculation of newsprint gives a release of 12.5 kg/day, in a volume of  $3 \cdot 10^4 \text{ m}^3$ .

As a worst case it will be assumed that both the retention aid and anti-foaming agent used contain nonylphenol ethoxylates, so the release is the sum of the two estimates above. Thus the worst-case release is for newsprint production, at 12.7 kg/day (in a volume of  $3 \cdot 10^4 \text{ m}^3$ ).

As complete release to water is assumed, there are no releases to air or to soil. For the regional release, 10% of the continental emissions are assumed. The continental release is the amount used in this area, 800 tonnes.

The emissions are therefore:

Water: Local 12.5 kg/day; Regional 219 kg/d; Continental 1,973 kg/d

#### Textile processing industry

Nonylphenol ethoxylates are used primarily in wool scouring, but are also used as fibre lubricants and dye levellers.

The total amount of nonylphenol ethoxylate used within the textile processing industry within the EU is reported as 8,000 tonnes for 1997. Industry estimates that approximately 40% of this amount is exported outside of the EU. Industry also estimates that there are approximately 1,000-2,000 textile processing sites within the EU.

For the regional and continental scenarios the default release estimations of nonylphenol ethoxylate due to use in the textile industry are calculated using the emission factors in Table A3.14 Chapter 3 Appendix 1 of the TGD. The default emission factors are 0.05 to air and 0.85 to wastewater. Regional emissions are taken as 10% of the continental emission. For the local scenario the use category document on surfactants gives information on the amount of nonylphenol ethoxylate release during textile processing, the release to wastewater is 280 kg/day. This gives the following emissions for nonylphenol ethoxylates:

Air: Regional 110 kg/day; Continental 986 kg/day

Water: Local 280 kg/day; Regional 1,863 kg/day; Continental 16,767 kg/day

#### Paints, lacquers and varnishes industry

Nonylphenol ethoxylates are used in the preparation of paint resins and are also present in paints as a stabiliser/emulsifier.

The European Polymer Dispersion and Latex Association (EPDLA) which is a CEFIC Sector Group representing the European manufactures of polymer dispersions and latices have supplied the following information.

Based upon a survey of nine paint manufacturing sites within the EU the following information has been obtained. The amount used per site is between 30-200 tonnes/year. Production typically occurs for 250 days/year. Releases to air and soil are zero. A conservative release factor for nonylphenol ethoxylates to water is 5 kg per tonne used. The amount of nonylphenol ethoxylate added to the end product is up to 5%. Of the production plants surveyed most discharge

wastewater to a municipal wastewater treatment plant. Approximately 50% also have their own treatment unit. The above releases include both the nonylphenol ethoxylates present in dispersions and those added during the paint manufacture.

The above information will be used to calculate releases during paint manufacture. The local site will be assumed to use 200 tonnes/year nonylphenol ethoxylates in the manufacturing process. The total amount of nonylphenol ethoxylates used in the manufacture of paints within the EU is reported as 4,000 tonnes in 1997, and the regional releases are taken as 10% of the continental releases. This gives the following releases of nonylphenol ethoxylates due to paint manufacture:

Water Local 4 kg/d; Regional 5.5 kg/day; Continental 49.3 kg/day

Nonylphenol ethoxylates are mainly used in decorative emulsions but small volumes are also used in other applications such as water-based 'refinish' paints for vehicle re-coating. In decorative emulsions nonylphenol ethoxylates are used in the manufacture of the emulsion and directly as emulsifiers and dispersants in water-based paints. Nonylphenol ethoxylates are most widely used as dispersants in coloured emulsions. The residual nonylphenol content in the emulsion polymer is considered negligible. The total amount of nonylphenol ethoxylate used in a 1 kg tin of emulsion paint is around 0.5-2% w/w (5-20 g). In 1993 in the UK, it was estimated that two thirds of emulsion paints contained nonylphenol ethoxylates in the concentration range 0.6-3%. The decorative paint market was estimated to be 350 million litres per year in the UK of which 70% was water-based (CES, 1993).

Nonylphenol ethoxylates are used in industrial coatings. The paint industry estimates that these coatings are applied at 5,000 sites within the EU. The default release factor for the paint industry from the TGD of 0.005 to wastewater is considered to be reasonably accurate for paint use. The number of days use per year is estimated at 240 per year.

Other possible uses of nonylphenol ethoxylates in the coatings industry include in the formulation of inks for laser jet printers and in the formulation of 'blanket wash' chemicals for use with lithographic printers.

The total amount of nonylphenol ethoxylates used in the paint, lacquers and varnishes industry was reported to be 4,000 tonnes in 1997. Of this amount approximately 20% was used in industrial paints and 80% in decorative emulsions and other applications.

No information about releases of paints during use has been received so the default release estimations of nonylphenol ethoxylate due to use in the paint, lacquers and varnishes industry are calculated using the emission factors in Table A3.15 Chapter 3 Appendix 1 of the TGD. The default emission factors are 0 to air and 0.005 to wastewater. The paint industry thinks these estimates are probably quite realistic for industrial paints. They will be used here to apply to all types of use. Regional emissions are taken as 10% of the continental emission. Local emissions are taken as occurring for 240 days a year with 0.5 tonnes used at an industrial site per year. This is based upon an average quantity used per industrial site (160 kg/year) scaled to take account of different size plants.

Use of domestic emulsions is harder to quantify. Based upon figures for the UK the amount of nonylphenol ethoxylates in paints used in a local area is calculated to be 582 kg/year by scaling total UK use of domestic emulsion paints to 10,000 people. Use by individual households is likely to be intermittent but overall use should be spread over 365 days a year.

Releases from other uses such as printing inks are assumed to be negligible when compared to these two release sources. (Table B3.13 Chapter 3 Appendix 1 of the TGD).

For the regional and continental scenario, the total amount of nonylphenol ethoxylates used in the emulsion part of the paint needs to be considered. The total amount of nonylphenol ethoxylate used to manufacture emulsion polymers is 9,000 tonnes/year. This is also considered in the total regional and continental releases. As the local releases are based upon nonylphenol ethoxylate levels in the paint, they are assumed to include emission from the polymer emulsion. This gives the following emissions for nonylphenol ethoxylates:

Water: Local 0.008 kg/day (domestic emulsion) 0.01 kg/day (industrial)  
Regional 17.8 kg/day; Continental 160 kg/day

#### Civil and mechanical engineering industry

Nonylphenol ethoxylates may be used in the civil and mechanical engineering industry in the manufacture of wall construction materials, road surface materials, and also to clean metals, etc. Nonylphenol ethoxylates may also be present in some plastic materials used in construction, particularly if an emulsion polymerisation route has produced them.

Nonylphenol ethoxylates or a nonylphenol ethoxylate derivative may also be used in cement as an air-entraining admixture. In this application the use of nonylphenol ethoxylates is assumed to be minor compared to the major air-entraining admixtures used. This suggests that the number of sites where nonylphenol ethoxylates admixtures are used is small. Nonylphenol ethoxylates may also be used in bitumen emulsions in road building.

In 1994, the total amount of nonylphenol ethoxylates used in the civil engineering industry was estimated to be 93 tonnes/year. No further information on the uses or releases of nonylphenol ethoxylates from this industry has been obtained. For the use of plastics within the civil engineering industry, releases from production of plastics and use of nonylphenol-based additives is considered elsewhere in this report. As the tonnage used is relatively small the most likely use would appear to be as an admixture in cements and possibly as an additive to bitumen emulsions. The default release estimations of nonylphenol ethoxylate due to use in the civil engineering industry are calculated using the emission factors in Table A3.16 Chapter 3 Appendix 1 of the TGD. The default emission factors are 0.001 to air and 0.1 to wastewater. Regional emissions are assumed to be 10% of the continental emission. Local emissions are assumed to occur for 30 days a year with 80% of the regional tonnage (7.5 tonnes) used at the local site (Table B3.14 Chapter 3 Appendix 1 of the TGD). This gives the following emissions for nonylphenol ethoxylates:

Air: Local 0.25 kg/day; Regional 0.026 kg/day; Continental 0.23 kg/day  
Water: Local 24.8 kg/day; Regional 2.55 kg/day; Continental 22.9 kg/day

#### Other uses

In a survey of nonylphenol ethoxylate use conducted by industry in 1997 the total amount of nonylphenol ethoxylates used in other niche markets was estimated at 7,000 tonnes/year. The uses are thought to include use in the civil and mechanical engineering industry, use in photographic chemicals, as an additive in the mineral fuel and oil industry and in the electrical and electronic industry. These are considered elsewhere in the report. In the 1994 survey

conducted by industry, these uses accounted for a total of 372 tonnes. Assuming that use has remained the same this leaves approximately 6,600 tonnes used in other niche markets. Industry has referred to other niche markets where it supplies customers with small quantities on a regular basis and does not know the specific end use of the product although they are likely to be covered in the above industry categories.

For the purposes of this risk assessment local releases will be considered to have been calculated in the above release estimations. For the regional and continental scenario, 6,600 tonnes are considered to be used in industrial and institutional cleaning which is the largest single use of nonylphenol ethoxylates within the EU. In addition to this tonnage, the imported nonylphenol ethoxylates (5,600 tonnes) will be considered to be used in the same application giving a total tonnage of 12,200 tonnes. The default release assumption for industrial and institutional cleaning are 0.0025 to air and 0.9 to wastewater. Regional emissions are taken as 10% of the continental emission. This gives the following for regional and continental releases from other unknown uses:

Air    Regional 8.4 kg/day; Continental 75.2 kg/day  
Water Regional 3,008 kg/day; Continental 27,074 kg/day

#### **3.1.1.1.2.4            Releases from private use**

Possible products containing nonylphenol ethoxylate that are used in the public domain include non-agricultural pesticides, vehicle and office cleaning agents, office products such as correction fluids and inks, fuel oils, paints and coatings, photographic chemicals intended for home developing and building materials. Within the EU, industry has a voluntary agreement to phase out the use of nonylphenol ethoxylates in domestic detergents.

Quantifying these releases to the environment is difficult, as little information is available. In the latest survey by industry the tonnage of nonylphenol ethoxylate used is split into different categories by use. Private use is not considered as a separate category. Releases from use of these products are therefore considered to be included in the processing section above and are not considered further here.

#### **3.1.1.1.2.5            Releases during disposal**

Most of the environmental release of nonylphenol ethoxylates tends to be associated with the processing (use) stage and so disposal is not considered in this study. For some applications, such as paints and emulsion polymers, the nonylphenol ethoxylate will form part of the finished surface/plastic/rubber and so is likely to be disposed of to landfill or incinerated in that form. For many other uses, nonylphenol ethoxylates are used in aqueous solutions and so are expected to enter into wastewater upon disposal of the solution during use, and these releases have been included in the processing sections above.



### 3.1.1.1.3 Summary of regional and continental releases of nonylphenol to the environment

Table 3.3 Summary of regional emissions

Life Cycle Stage	Regional Emission (kg/day) NP (Surface Water)	Regional Emission (kg/day) NPEO (Wastewater)	As % of NP Burden	As % of NPEO Burden
Nonylphenol				
NP Production	2.15		0.7	
NPEO Production (NP release)	15.3 <i>0.595</i> (1.7 Wastewater)		4.8 0.19	
Phenol/formaldehyde resins	<i>0.002</i> (0.06 Wastewater)		0.0006	
TNPP production	0		0	
Epoxy resins	<i>0.01</i> (0.04 Wastewater)		0.003	
Production of other plastic stabilisers	<i>0.05</i> (0.14 Wastewater)		0.016	
Phenolic oximes	0.26		0.08	
Sub Total	18.4		5.8	
Nonylphenol ethoxylates				
NPEO Production (NPEO release)	<i>1.47</i>	58.5	0.46	0.49
Formulation	<i>1.48</i>	59.2	0.46	0.49
Agricultural use	<i>3.43</i>	137	1.1	1.1
Captive use by chemical industry	<i>0.34</i>	13.4	0.1	0.11
Electrical engineering industry	<i>0.003</i>	0.13	0.0009	0.001
Industrial and institutional cleaning	<i>142</i>	5,671	44.5	47.2
Leather processing	<i>19.4</i>	774	6.1	6.5
Metal extraction	<i>3.9</i>	156	1.2	1.3
Mineral fuel and oil (Manufacture and blending)	<i>0.025</i>	1	0.008	0.008
Photographic industry	<i>0.5</i>	20	0.16	0.17
Polymer industry	<i>0.006</i>	0.25	0.002	0.002
Pulp, paper and board industry	<i>5.48</i>	219	1.7	1.8
Textile processing	<i>46.6</i>	1,863	14.6	15.5
Paints, lacquers and varnishes	<i>0.14</i> (Manufacture) <i>0.45</i> (Use)	5.5 (Manufacture) 17.8 (Use)	0.04 0.14	0.05 0.15
Civil engineering	<i>0.06</i>	2.55	0.02	0.02
Other applications	<i>75.2</i> (Includes import tonnage)	3,008 (Includes import tonnage)	23.6	25.1
Sub Total	300.5	12,006	94.2	100
Total	319		100	

Table 3.4 Summary of continental emissions

Life Cycle Stage	Continental Emission (kg/day) NP (Surface Water)	Continental Emission (kg/day) NPEO (Wastewater)	As % of NP Burden	As % of NPEO Burden
Nonylphenol				
NP Production	0.1		0.003	
NPEO Production (NP release)	137.7 <i>0.38</i> (15.3 Wastewater)		4.62 0.01	
Phenol/formaldehyde resins	<i>0.20</i> (0.56 Wastewater)		0.007	
TNPP production	0		0	
Epoxy resins	<i>0.12</i> (0.36 Wastewater)		0.004	
Production of other plastic stabilisers	<i>0.43</i> (1.23 Wastewater)		0.01	
Phenolic oximes	0		0	
Sub Total	139		4.7	
NPEO				
NPEO Production (NPEO release)	<i>152</i>	526	5.10	0.49
Formulation	<i>13.3</i>	533	0.45	0.49
Agricultural use	<i>30.8</i>	1,233	1.03	1.14
Captive use by chemical industry	<i>3</i>	120	0.10	0.11
Electrical engineering industry	<i>0.03</i>	1.15	0.001	0.001
Industrial and institutional cleaning	<i>1,276</i>	51,041	42.8	47.2
Leather processing	<i>174</i>	6,962	5.84	6.44
Metal extraction	<i>35</i>	1,402	1.17	1.30
Mineral fuel and oil (Manufacture and blending)	<i>0.25</i>	10	0.008	0.009
Photographic industry	<i>4.58</i>	183	0.15	0.17
Polymer industry	<i>0.06</i>	2.22	0.002	0.002
Pulp, paper and board industry	<i>49.3</i>	1,973	1.65	1.83
Textile processing	<i>419</i>	16,767	14.1	15.5
Paints, lacquers and varnishes	<i>1.23</i> <i>4</i>	49.3 (Manufacture) <i>160</i> (Use)	0.04 <i>0.13</i>	0.05 <i>0.15</i>
Civil engineering	<i>0.57</i>	22.9	0.02	0.02
Other applications	<i>677</i>	27,074	22.7	25.1
Sub Total	2,840	108,060	95.3	100.2
Total	2,979		100	

Notes to accompany Tables 3.3 and 3.4:

Figures in italics have been calculated using the following methods.

For nonylphenol lifecycle stages where a release is given to wastewater treatment plant the surface water release is calculated by multiplying the release by the  $F_{stip}$  (Fraction of emission directed to surface waters after wastewater treatment); for nonylphenol this is 0.35 (See Section 3.1.1.3.4 for further details). For some lifecycle stages two emissions are given; this is where data about direct emissions to surface and to wastewater treatment plants are known.

For nonylphenol ethoxylates the emission of the nonylphenol ethoxylate to the wastewater treatment plant is multiplied by 2.5% to give the resultant emission of nonylphenol to surface waters (See Appendix 1 for further details).

In addition to the emissions summarised in **Tables 3.3** and **3.4** there are emissions to air and emissions to sewage sludge due to treatment in wastewater treatment plants.

Direct emissions of nonylphenol to air are calculated as 0.774 kg/day for the regional model and 2.9 kg/day for the continental model. In addition to the direct emissions of nonylphenol to air there may also be indirect emissions of nonylphenol to air due to treatment of wastes containing nonylphenol in a wastewater treatment plant. In EUSES the fraction of emission to wastewater treatment plants directed to air during treatment is calculated as 0.06. This value is used by EUSES in calculating atmospheric concentrations in the regional and continental models.

There may also be emission of nonylphenol to air due to the breakdown of nonylphenol ethoxylates in wastewater treatment plants, though no information on the amounts released is available. In Appendix 1 the behaviour of nonylphenol ethoxylates in wastewater treatment plants is considered. From the data presented releases of nonylphenol to air should be negligible.

The total emission of nonylphenol ethoxylates to air is calculated as 253 kg/day in the regional model and 2,273 kg/day in the continental model. There is no information on how this will break down in the atmosphere to nonylphenol. A worst-case assumption would be the instantaneous breakdown of nonylphenol ethoxylate in the atmosphere to nonylphenol. Assuming that this is the case and with an average chain length of 7 for the nonylphenol ethoxylate the emission of nonylphenol due to breakdown of nonylphenol ethoxylate would be 105 kg/d in the regional model and 943 kg/day in the continental model.

Total emissions to air of nonylphenol for input into EUSES for the regional and continental models are therefore taken as the sum of direct emissions of nonylphenol and indirect emissions due to breakdown of nonylphenol ethoxylates. This gives emissions of 106 kg/day for the regional model and 946 kg/day for the continental model. In addition EUSES calculates indirect emissions from wastewater treatment plants.

During wastewater treatment nonylphenol may be adsorbed onto sewage sludge. In EUSES the fraction of emission to wastewater treatment plants adsorbed to sludge during treatment is calculated as 0.34. This value is used by EUSES in calculating sludge concentrations in the regional and continental models. For nonylphenol ethoxylate wastewaters the fraction of emission to wastewater treatment plants adsorbed to sludge as nonylphenol during treatment is calculated as 0.195 (Appendix 1). Using this figure with the total nonylphenol ethoxylate emissions to wastewater detailed in **Tables 3.3** and **3.4** gives the total amount of nonylphenol adsorbed to sludge as 2,330 kg/day and 20,980 kg/day in the regional and continental models respectively.

### 3.1.1.2 Degradation in the environment

#### 3.1.1.2.1 Atmospheric degradation

Nonylphenol released to the atmosphere is likely to be degraded by reaction with hydroxyl radicals. The rate constant has been estimated using the AOP program (Syracuse, 1991) to be  $5.4 \cdot 10^{-11} \text{ cm}^3 \cdot \text{molec}^{-1} \cdot \text{s}^{-1}$ . The pseudo first-order rate constant for degradation in air can be calculated from this rate constant using the following equation:

$$\begin{aligned} k_{\text{deg}_{\text{air}}} &= k_{\text{OH}} \cdot \text{OHCONC}_{\text{air}} \cdot 24 \cdot 3,600 \\ &= 2.3 \text{ d}^{-1} \end{aligned}$$

$k_{\text{deg}_{\text{air}}}$  Pseudo first order rate constant for degradation in air [ $\text{d}^{-1}$ ]

$k_{\text{OH}}$  Specific degradation rate constant with OH-radicals  
[ $5.4 \cdot 10^{-11} \text{ cm}^3 \cdot \text{molec}^{-1} \cdot \text{s}^{-1}$ ]

$\text{OHCONC}_{\text{air}}$  Concentration of OH radicals in the atmosphere [ $5 \cdot 10^5 \text{ molec} \cdot \text{cm}^{-3}$ ]

From this rate constant the half-life for the reaction of hydroxyl radicals with nonylphenol in the atmosphere is calculated as 0.3 days. The fraction of chemical absorbed to aerosol particles is also low. Therefore the potential for transport of nonylphenol in the atmospheric environment is low.

The reaction rate is such that nonylphenol is unlikely to be transported far from its emission source. It is unlikely to move from the troposphere to the stratosphere and contribute to ozone depletion. Nonylphenol is not thought to contribute to low-level ozone formation.

#### 3.1.1.2.2 Aquatic degradation

##### Abiotic

Hydrolysis and photolysis are thought to be negligible removal processes for nonylphenol in the aquatic environment. This is based upon the stability of nonylphenol during storage and several biodegradation studies where no degradation was observed in the control experiments. The authors concluded in these studies that abiotic degradation was likely to be negligible (Corti et al., 1995; Trocmé et al., 1988).

##### Biodegradation

Ready biodegradation test results are available for nonylphenol. A limited number of biodegradation studies from non-standard tests are also reported. Information on the degradation of nonylphenol ethoxylates is contained in Appendix 1.

The biodegradability of nonylphenol has been determined in the modified Sturm test (EEC Directive 79/831 ENV/283/80) (Hüls, 1996b). In the study nonylphenol at a concentration of 22.8 mg/l was added to a liquid mineral medium which was inoculated and aerated at a temperature of 21-23°C for 32 days. The inoculum used in the test was activated sludge from a municipal sewage plant and had a bacterial count of  $18 \cdot 10^5$  CFU/ml (colony forming units/ml). The experiments were carried out both with and without an emulsifier (at a concentration of 20 mg C/l) present in the nonylphenol test solution. Control experiments were conducted using the emulsifier only and a control substance (sodium benzoate). Degradation was monitored by measuring the actual  $\text{CO}_2$

evolution compared with the theoretical amount that would be evolved if the substance was completely oxidised. The control substance (sodium benzoate) achieved a degradation level of 102% within 20 days, reaching the threshold for ready biodegradability within 14 days. This indicated that the inoculum used had sufficient biological activity. Nonylphenol, with and without emulsifier, achieved a degradation level of 0% within a period of 32 days. When tested on its own the emulsifier achieved a degradation level of 0% within the 32-day period.

In a second study the biodegradability of nonylphenol was again studied in the modified Sturm test (EEC Directive 79/831 ENV/283/80) (Hüls, 1996c) but adapted activated sludge was used as the inoculum. In this case the activated sludge was adapted prior to use in the test by incubation with nonylphenol at a concentration of 5 mg/l for 13 days and then 50 mg/l for a further 5 weeks. The test conditions were then the same as in the previous test with the exception that the duration of the test was 40 days. Nonylphenol (22.8 mg/l) was tested with and without an emulsifier (at a concentration of 20 mg C/l) and sodium benzoate was used as a control substance. Nonylphenol without emulsifier achieved a degradation level of 0% within the 40-day period. Nonylphenol and the emulsifier achieved a degradation level of 78% within the 40-day period (the control with emulsifier alone showed 0% degradation).

Taken together, the results obtained in the two modified Sturm tests above indicate that nonylphenol is not readily biodegradable but there is evidence that nonylphenol may undergo biodegradation with adapted micro-organisms and so could be considered to be inherently biodegradable. The difference in the degradability of nonylphenol seen in the second test with and without the emulsifier is difficult to explain other than in the absence of the emulsifier the availability of nonylphenol to the micro-organisms may be reduced.

Two other ready biodegradation tests have been carried out with nonylphenol. The results of these have been reported by Williams and Varineau (1996). In both tests the nonylphenol used was a commercial grade which contained a highly branched alkyl chain and the inocula for the two tests were derived from sewage treatment plants receiving predominantly municipal waste. In an OECD 301 B test, nonylphenol was tested at a concentration of 12.2 mg/l (10 mg C/l). The nonylphenol was weighed onto a small plastic sheet which was then added to the dilution water in the reactor. The biodegradation was followed by monitoring the amount of CO<sub>2</sub> generated and ~10% biodegradation was seen after 10 days incubation, rising to 53% by day 28. Few other details of this test are currently available. In an OECD 301F test (manometric respirometry) (Staples et al., 1999), oxygen consumption was used to determine the extent of biodegradation. Nonylphenol was tested at a concentration of 31 mg/l (92.4 mg ThOD/l) at 22°C and no carrier solvents were used in the test (the test substance was added directly to the dilution water). The purity of the nonylphenol used was given as 95.6% p-nonylphenol, with the rest as o-nonylphenol, which is in line with the purity of typical commercial products given in Section 1. The average bacterial population of the inoculum used was 10<sup>6</sup> CFU/ml. The control substance (sodium benzoate) showed >94% degradation within 28 days. For nonylphenol ~19% biodegradation was seen in 10 days, rising to 62% in 28 days.

In both the OECD 301B and 301F tests, nonylphenol shows significant biodegradation but fails to meet the criteria for ready biodegradability (10 day window) and so these results will be taken to give an indication of inherent biodegradability rather than ready biodegradability.

The biodegradation of nonylphenol has been studied using a BOD test for insoluble substances (in accordance with ISO 10708/draft) (Hüls, 1996e). In the test, nonylphenol (concentration 334 mg/l) was incubated with activated sludge from an industrial wastewater treatment plant for 28

days. The extent of biodegradation, based on oxygen uptake compared to theoretical oxygen uptake, was 7% for nonylphenol. The control substance (diethylene glycol) showed 91% degradation over the same time period.

Corti et al. (1995) studied the microbial degradation of nonylphenol in axenic cultures using a yeast related to the species *Candida maltosa* strain LMAR1 isolated from sludge samples collected at a treatment plant of textile industrial wastewaters. A pure isomer, 4-(1-nonyl)phenol, with a linear alkyl chain was synthesised and used as the sole source of carbon and energy in the experiments. The yeast strain LMAR1 was shown to be able to grow when incubated in yeast broth at 28°C with nonylphenol (at a concentration of 100 mg/l) as the sole source of carbon and energy. The number of colony forming units (CFU) increased from  $4.5 \cdot 10^6$  cells/ml to  $5.6 \cdot 10^8$  cell/ml over the 21 days incubation period in the presence of nonylphenol, compared to a small increase from  $1.7 \cdot 10^6$  cells/ml to  $3.8 \cdot 10^6$  cells/ml in unfed controls. Extracts of the cultures were taken at different times and analysed by GLC. The extracts showed a disappearance of the nonylphenol peak signal after 7 days incubation, with at least four new peaks appearing in the trace representing various degradation products. No significant abiotic degradation was observed in the control experiments. The authors concluded that *Candida maltosa* is capable of biodegrading nonylphenol, the growth of the yeast suggesting that nonylphenol is at least partially utilised as a carbon and energy source. 4-Acetyl phenol was suggested as a possible metabolite. However, as this experiment was carried out with a single isomer of nonylphenol with a linear alkyl chain, it is not clear if the branched chain nonylphenol isomers would behave similarly.

The influence of nonylphenol on microbial growth was also evaluated by cultivating the LMAR1 strain on yeast broth supplemented with glucose (10 g/l) in the presence of 50 and 200 mg/l nonylphenol. In these cultures, cell growth was monitored with time by optical density. The cell growth dynamics showed a longer lag phase in cultures containing 50 or 100 mg/l nonylphenol than in cultures containing glucose only. This lag phase suggested a possible toxic effect of nonylphenol on *Candida maltosa* (Corti et al., 1995).

Ekelund et al. (1993) studied the biodegradation of 4-nonylphenol in seawater and sediment. In the experiments  $^{14}\text{C}$  uniformly ring-labelled nonylphenol (synthesised using nonene containing a mixture of branched isomers) was used. The reaction flasks used contained seawater or seawater plus sieved soft bottom sediment. Formalin was added to four flasks containing seawater and half of the flasks containing seawater and sediment were bubbled with nitrogen gas prior to the start of the experiment.  $11 \mu\text{g } ^{14}\text{C}$  ring-labelled nonylphenol was dissolved in acetone and added to small glass plates, the solvent was then evaporated and the glass plates added to the reaction flasks. The flasks were incubated at  $11 \pm 2^\circ\text{C}$  in the dark for 16 weeks. In flasks containing formalin no  $^{14}\text{CO}_2$  was recovered, indicating that any  $^{14}\text{CO}_2$  must come from the nonylphenol in the presence of living organisms. In the absence of sediment, degradation (as measured by  $^{14}\text{CO}_2$  production) was very slow at 0.06% per day up to 28 days then 1% per day after 28 days, suggesting a period of adaptation is required. In the presence of sediment the degradation rate was faster at 1.2% per day. In the low oxygen experiments the reaction rate was slow. The increase in degradation rate in the sediment system was attributed to the higher number of micro-organisms present. The overall recovery of  $^{14}\text{C}$  from these experiments was around 64% (44% in the  $\text{CO}_2$  fraction) in the flasks without sediment and 49% (46% in the  $\text{CO}_2$  fraction) in the flasks with sediment. Thus around 45% of the ring-label was converted to  $\text{CO}_2$  in 8 weeks, giving a mineralisation half-life of slightly longer than 56 days. However, the low overall recovery of  $^{14}\text{C}$ -label in the experiments indicates that the actual extent of biodegradation may be higher (with a resulting shorter half-life) than implied by the  $^{14}\text{CO}_2$  measurements (for example incorporation of the  $^{14}\text{C}$ -label into biomass may have occurred).

Gaffney (1976) studied the biodegradation of a standard mixture of nine chemicals (including nonylphenol) in domestic wastewater and municipal wastewater. The concentration tested was 1 mg/l. Hexane and acetone were used as carrier solvents and allowed to evaporate before the tests were performed. Samples were extracted with hexane and quantified by GC with FID and ECD detectors. No degradation of nonylphenol was observed in tests with domestic wastewater. In tests with municipal wastewater the concentration of nonylphenol decreased by 45% in 135 hours. It should be noted that the municipal wastewaters contained nonylphenol and a variety of other pollutants, and so may have been adapted.

The degradation of nonylphenol in stream and pond water has been studied under simulated field conditions (Sundaram and Szeto, 1981). The water and sediments used were taken from Northland Creek and Hargraft Lake, Ontario, Canada. The degradation experiments were carried out by incubating samples of the water or water plus sediment (100 g pond sediment in 200 ml pond water) with nonylphenol (1 mg/l) in either open or closed flasks at 16°C for up to 44 days, under artificial light (16 hours light and 8 hours dark per day). At various times during the study samples were analysed for the presence of nonylphenol by HPLC analysis. When incubated in either pond water (pH 7.3) or stream water (pH 6.9) in open flasks, nonylphenol was found to disappear from solution rapidly with a half-life of around 2.5 days for both systems. No degradation products were detected in the water during the experiment and it was thought that the removal from solution was due to volatilisation and co-distillation rather than degradation. When nonylphenol was incubated in either pond water or stream water in sealed flasks, the half-life was found to be 16.5 days in stream water and 16.3 days in pond water. Unidentified transformation products (more polar than the parent nonylphenol) were also shown to be formed in the experiment and it was thought by the authors that these could be formed by microbial degradation or photo-oxidation. In incubations in pond water with sediment present, most of the nonylphenol initially adsorbed onto the sediment phase. The sediment phase showed a maximum nonylphenol concentration after around 10 days which subsequently reduced, with only 20% of the added nonylphenol being present after 70 days. This removal was thought to be due to microbial degradation as the concentration in autoclaved samples remained constant over the same time period.

### 3.1.1.2.3 Degradation in soil

Trocme et al. (1988) studied the fate of nonylphenol in a simplified soil system and its effect on microbial activity. The soil system was made up of sewage sludge compost (1/3 dry matter) and sandstone (2/3 dry matter) and had the following characteristics: pH 6.8, total nitrogen 0.5%, organic carbon 11%, carbon:nitrogen ratio 20, total phosphorus 1%, cation exchange capacity 22.1 meq/100g, water holding capacity 51%. Nonylphenol was dissolved in ethanol (0.4 ml/g spiked compost) and mixed with part of the compost, the ethanol was then left to evaporate off. The spiked compost was mixed with the remaining compost to give a 60 g sample. Two concentrations of nonylphenol were applied (100 mg/kg and 1,000 mg/kg) plus a control sample spiked with ethanol. The cells were incubated at 60% field moisture capacity at 25°C in the dark for 40 days. Carbon dioxide was removed periodically by flushing the cells with carbon dioxide free air, the adsorbed carbon dioxide was determined by a conductivity method and volatilisation of nonylphenol measured by phenol traps. Nonylphenol persistence was also studied under aseptic conditions. Samples were sterilised by gamma irradiation, spiked with 100 mg/kg nonylphenol then incubated for 24 hours under the above conditions. The authors found that carbon dioxide evolution was significantly depressed by the 4th day in the 1,000 mg/kg spiked sample, and a decrease was noted in the adenosine triphosphate (ATP) content in the 1,000 mg/kg sample after 5 days. No significant changes in carbon dioxide evolution or ATP content were

observed in the control and 100 mg/kg sample. After 40 days incubation 11% nonylphenol remained in the 100 mg/kg sample and 38% remained in the 1,000 mg/kg sample. In both samples volatilisation was insignificant with 0.22% volatilisation over 40 days in the 1,000 mg/kg sample. In both samples nonylphenol concentrations started decreasing after 5 days incubation; loss was rapid at first then slowed down. Nonylphenol was more persistent under the semi-sterile conditions with 76% nonylphenol recoverable after 24 days. The authors suggested that nonylphenol underwent microbial degradation after a period of induction of the micro-organisms. The chromatographic profile for nonylphenol taken at various times during the test indicated that certain isomers of nonylphenol degraded more easily than others.

Marcomini et al. (1992) studied the fate of nonylphenol in sludge amended soil. Soil samples were collected from the upper 5 cm of planted grassland that had received anaerobically digested sludge at an average application rate of 13.5 tonnes/ha year (dry weight). The sludge was applied to the surface soil as a liquid spread, four to six times per year. Samples were dried at 60°C, pulverised to a particle size of <300 µm and stored in the dark at 4°C. Nonylphenol was analysed by extraction with hexane and quantified by HPLC with a UV-fluorescence detector. The initial concentration of nonylphenol in the soil was 4.7 mg/kg and this had dropped to 0.46 mg/kg dry weight after 322 days. The concentration of nonylphenol in a soil that did not have sludge applied was <0.02 mg/kg (dry weight). The disappearance of nonylphenol was fast in the first two weeks followed by a slow disappearance from days 30-90; from day 150 no significant disappearance was noted and nonylphenol was classed as being persistent. The half-lives for degradation in the soil were estimated as 8 days for the initial degradation, 90 days for the second stage and >360 days after 150 days of application. These half-lives are for primary biodegradation and were calculated assuming pseudo first order kinetics.

The primary biodegradation of nonylphenol in soil has been studied in field trials over a period of 1 year (Küchler et al., 1994). Areas of land (each 6·3 m) were treated with either sewage sludge or sanitary effluent which contained nonylphenol, along with nonylphenol ethoxylates. Initially it was found that the concentration of nonylphenol increased slightly, possibly due to formation from the degradation of nonylphenol ethoxylates present. The concentration of nonylphenol was then found to decrease rapidly in the soil, with no nonylphenol being detected in any sample (samples were collected at depths of 0-10 cm, 10-20 cm and 20-30 cm) after 20 days. Nonylphenol did not leach from the 0-10 cm depth layer into lower layers, indicating that biodegradation is the most likely removal mechanism.

Kirchman et al. (1991) studied the biodegradation of 4-n-nonylphenol in soil (the substance tested presumably has a straight alkyl chain rather than a branched chain as typically found in commercial products). In the test nonylphenol was added to soil at concentrations of 10 or 500 mg/kg and incubated in sealed flasks for 3 months. Degradation was monitored by analysis for the parent compound and also CO<sub>2</sub> evolution. Based on parent compound analysis, less than 10% of the added nonylphenol remained after 10 days incubation, and nonylphenol was not detected (<0.02 mg/kg) after 20 days incubation. At the higher concentration tested, CO<sub>2</sub> evolution was higher than that seen in controls and indicated that around 61% of the nonylphenol carbon was converted to CO<sub>2</sub> after 94 days incubation. However, at the 10 mg/kg concentration the CO<sub>2</sub> evolution was similar to controls and so it is not possible to infer anything about the rate of mineralisation at this concentration. A short-term (7 day) inhibition on nitrification was seen in the system exposed to 500 mg/kg nonylphenol.



Further evidence for biodegradation of nonylphenol in soil was reported in BUA (1988). In this report the results of an unpublished industry study were given that indicated that around 95% degradation/removal of nonylphenol occurred after 48 days incubation at 275 mg/kg in soil.

Other reports of degradation of nonylphenol in soil have been summarised by the Danish EPA (Personal communication, 1997). Kingsbury et al. (1981) (Ref Danish EPA) did not detect nonylphenol in soil samples taken from a field exposed with 0.47 litres nonylphenol/ha by aerial deposition. Schörbel (1985) (Ref Danish EPA) applied 275 mg nonylphenol/kg to an OECD standard soil. After 48 days 95% of the nonylphenol was metabolised with degradation of the aromatic ring. Diercxsens and Taradellas (1987) (Ref Danish EPA) noted nearly complete disappearance of nonylphenol three months after sewage sludge application. Giger et al. (1984) observed a 80-90% reduction in nonylphenol soil concentrations 104 days after manure application. Reduction in the soil concentration was initially rapid.

#### **3.1.1.2.4 Discussion of degradation data**

The data available indicate that nonylphenol undergoes biodegradation in water, sediment and soil systems. The results from standard biodegradation tests are variable but indicate that nonylphenol is probably inherently biodegradable.

A possible explanation for some of the inconsistencies found in the various tests could be due to the toxicity of nonylphenol to micro-organisms at the concentrations used in some of the tests. No toxicity screening tests were carried out as part of the ready biodegradability tests. The results by Corti et al. (1995) would appear to support this assumption in that cultures of yeast grown in the presence of nonylphenol exhibited a longer lag phase than control cultures.

A second factor that seems to be important in the biodegradation of nonylphenol is that micro-organisms need a period of adaptation. Ekelund et al. (1993) studied the degradation of nonylphenol in seawater and found that nonylphenol was degradable. The rate of degradation increased after 28 days suggesting that a period of adaptation of the micro-organisms is required. Gaffney (1976) observed biodegradation of nonylphenol in municipal wastewaters which contained nonylphenol and so may have been adapted. No biodegradation was observed in tests with domestic wastewater which was not adapted.

Another factor is that the nonylphenol supplied is a mixture of compounds with differing degrees of branching/isomers in the nonyl chain. It is known that in general increased branching in alkyl chains causes a reduction in biodegradability and so it may be expected that some of the components of the nonylphenol mixture would degrade faster than others. In the degradation results of Trocmé et al. (1988) some direct evidence for this was found in the chromatographic analysis of nonylphenol at various times during the test (some nonylphenol peaks decreased faster than others). Such an effect may explain why in many of the tests the degradation of nonylphenol appears to follow two or more “phases”, with an initial relatively rapid removal of nonylphenol followed by one or more slower phases of removal, although there are many other possible explanations for such behaviour (e.g. a reduction of viability of micro-organisms with time).

A final consideration applicable to some of the data is that nonylphenol itself contains 9 carbon atoms on the alkyl chain and 6 carbon atoms on the aromatic ring. Thus when CO<sub>2</sub> evolution is used as the endpoint to show mineralisation, theoretically 60% CO<sub>2</sub> evolution could be seen from mineralisation of the alkyl chain only, without any degradation of the aromatic ring. However,

there are several tests (both for nonylphenol and nonylphenol ethoxylates - see Appendix 1) using ring-labelling that clearly show that the aromatic ring undergoes degradation to CO<sub>2</sub>.

Based upon the data nonylphenol is not considered readily biodegradable. However, significant biodegradation was seen in ready biodegradability tests when adapted micro-organisms were used. The widespread use and distribution of nonylphenol and its ethoxylates makes some degree of acclimation more likely. Therefore nonylphenol is considered as being inherently biodegradable and a rate constant of 0.1 h<sup>-1</sup> will be used in the sewage treatment model. In the assessment this rate constant has only been applied to estimation of predicted environmental concentrations (PECs) from production and use of nonylphenol itself, where it is reasonable to assume that the sewage treatment plant is acclimated to the presence of nonylphenol in the discharge. For the modelling of nonylphenol concentrations from the use of nonylphenol ethoxylates the information on the behaviour of nonylphenol ethoxylates in sewage treatment plants given in Appendix 1 is used.

According to the Technical Guidance Document the default first order rate constant for biodegradation of an inherently biodegradable substance in surface water is  $k=4.7 \cdot 10^{-3} \text{ d}^{-1}$ . This is equivalent to a half-life for biodegradation in surface waters of 150 days. This value is consistent with the available measured data.

For soil, the suggested half-life for an inherently biodegradable substance with a  $K_{p_{soil}}$  in the range  $>100 - \leq 1,000 \text{ l/kg}$  is 3,000 days ( $K_{p_{soil}} = 263 \text{ l/kg}$  for nonylphenol). The estimated half-life in soil of 3,000 days appears to be larger than that suggested by the experimental data, but it should be that most of the experiments determined primary biodegradation (which generally has a half-life of the order of 20-30 days or less), and not ultimate mineralisation. The data of Kirchman et al. (1991) indicates that the half-life for mineralisation of 4-n-nonylphenol in soil is around 100 days. However it is possible that branched chain nonylphenol would have a longer half-life than this. For this reason an estimated half-life for soil of 300 days (the Technical Guidance default for inherently biodegradable substances with  $K_{p_{soil}} < 100 \text{ l/kg}$ ) will be used in the assessment. There is some rationale in the experimental data for choosing this value since in the Technical Guidance the  $K_{p_{soil}}$  is used only to modify the estimated half-life in soil to take into account that degradation in soil is only thought to occur in the pore water phase. However, the primary degradation data in soil for nonylphenol indicates that it is available for degradation and so a decrease in the biodegradation rate over that estimated in the Technical Guidance for an inherently degradable substance with  $K_{p_{soil}} < 100$  may not be warranted for nonylphenol.

Based on a half-life of 300 days in soil, the rate constants for degradation of nonylphenol are  $2.3 \cdot 10^{-3} \text{ d}^{-1}$  in soil and  $2.3 \cdot 10^{-4} \text{ d}^{-1}$  in sediment (estimated by the methods in the Technical Guidance Document).

The rate constants and half-lives estimated for nonylphenol in surface water, sediment and soil are thought to be representative of a realistic worst case for mineralisation of nonylphenol. In some situations, particularly where well-adapted micro-organisms are present, the actual half-life for nonylphenol in surface water and soil may be less than these values. In contrast, in other situations the actual half-lives could be longer than estimated here, given that the overall degradation rate of nonylphenol in the environment will depend on the factors mentioned above, such as the possibility of minor amounts of more persistent nonylphenol isomers being present in the product or the absence of suitably adapted micro-organisms.

### 3.1.1.2.5 Summary of environmental degradation

Nonylphenol released to the atmosphere is likely to be degraded by reaction with hydroxyl radicals, with a half-life of around 0.3 days.

Based upon the available biodegradation data, nonylphenol is inherently biodegradable, and so the rate constant for biodegradation in a WWTP is taken as  $0.1 \text{ h}^{-1}$  for modelling of the removal during wastewater treatment at plants producing or processing nonylphenol itself. There is evidence from other tests that substantial biodegradation of nonylphenol will occur in surface water and soil, possibly after a period of adaptation. Half-lives for biodegradation in soil of 300 days and surface water of 150 days have been estimated. It is possible that nonylphenol is toxic to micro-organisms at the high concentrations used in many of the tests, which may explain some of the differences between the various results. The estimated half-lives are thought to be representative of a realistic worst case for mineralisation of nonylphenol. However, given that the biodegradation of nonylphenol depends on several factors, the actual half-life in a given environment could be different (longer or shorter) than the estimated values, depending on the prevailing conditions.

### 3.1.1.3 Distribution

#### 3.1.1.3.1 Adsorption

The soil adsorption isotherm of nonylphenol has been determined using USEPA TSCA environmental fate test guidelines (Roy F. Weston Inc, 1990d). Nonylphenol (CAS Number 84852-15-3) with a purity >95% was used in the study. Three surface soils were used in the study and their characteristics are detailed in **Table 3.5**. Analysis of samples was done by HPLC. In the test the adsorption of nonylphenol onto the soil was determined by equilibrating aqueous solutions containing different concentrations of the test chemical with a known quantity of soil. The distribution of the chemical between the water and solid phases was measured at equilibrium and the resulting sorption constants ( $K_{p_{\text{soil}}}$ ) were then calculated using the Freundlich equation. The time for nonylphenol and the solid phase to come to equilibrium was calculated as 3 days. **Table 3.5** details the calculated sorption coefficients.

**Table 3.5** Soil characteristics and calculated K values

Parameter	Soil 1	Soil 2	Soil 3
Cation exchange capacity (meq/100 g)	28.4	46.2	24.6
Exchangeable bases (meq/100 g)	27.8	45.8	17.2
Exchangeable acids (meq/100 g)	0.6	0.4	7.4
Total organic carbon (%)	0.82	10.2	8.6
pH	7.1	7.3	6.4
$K_{p_{\text{soil}}}$ (l/kg)	4,009	2,301	5,164

The results indicate that nonylphenol is expected to adsorb strongly to soils and sediments in the environment. Recoveries of nonylphenol from control vessels were low, suggesting that either sorption to the test vessels may occur or the nonylphenol is removed by an abiotic mechanism. Recovery of nonylphenol from the test vessels was found to be related to the concentration of test substance in the vessels, with higher recoveries being observed in test vessels containing soil. In using these results the wide range of  $K_{oc}$  values derived, ( $\log K_{oc}$  4.35-5.69), needs to be

taken into account, since this indicates that factors other than organic carbon content may have been important in the adsorption. The interpretation of the results is further complicated by the fact that control experiments showed low recoveries of nonylphenol that may be due to adsorption of nonylphenol to the walls of the vessel and so would lead to an overestimate of the adsorption being calculated.

Ahel et al. (1994) measured the occurrence of nonylphenol ethoxylates and their metabolites of nonylphenol ethoxylates in surface waters and sediments in the Glatt River in Switzerland. The surface water and sediment concentrations of nonylphenol are reported in Section 3.1.2.2. The authors noted seasonal variations in the concentrations of the ethoxylates and metabolites with lower concentrations occurring at higher temperatures. This variation was less pronounced for nonylphenol than the other species, and this was thought to be due to the resistance of nonylphenol to biodegradation. For nonylphenol, elimination was thought to occur by photochemical degradation and adsorption to sediments. The ratio of nonylphenol concentrations in sludge to nonylphenol concentrations in water ranged from 364 to 5,100 indicating preferential association of nonylphenol to sediments. The major input of nonylphenol and nonylphenol ethoxylates to the river was from sewage treatment plants.

Ahel et al. (1996) studied the infiltration of nonylphenolic compounds from river water to groundwater in the Glatt River region of Switzerland. Two sites were chosen, one near a heavily polluted part of the River Glatt and the other at a moderately polluted site on the River Sitter. The main source of pollutants at the Glatt river site was treated wastewaters from publicly owned mechanical and biological sewage treatment plants. The Sitter River site was chosen because it has a relatively fast infiltration rate of groundwater by river water. Samples were extracted by steam extraction, formaldehyde was added as a preservative and quantification was by HPLC. **Table 3.6** shows the concentration of nonylphenol in river water and groundwater at the River Glatt site, and these concentrations are repeated in the measured level section (Section 3.1.2.2). The average concentrations are lower in groundwater than river water suggesting an elimination of nonylphenol. However the maximum concentrations observed in river water and groundwater are of a similar order of magnitude suggesting that breakthrough of nonylphenol into the aquifer may occur. When breakthrough occurs this may be due to either the polluted water exceeding the adsorption capacity of the aquifer or biological transformation procedures occurring leading to the formation of nonylphenol. The aquifer closest to the river is responsible for most of the elimination of nonylphenol; if the dissolved oxygen concentrations drop too low the conditions can become anaerobic favouring the formation of nonylphenol (See Appendix 1 for more details). At the Sitter River site concentrations were generally lower; the concentration of nonylphenol in the river was 1.8 µg/l and in groundwater 0.09 µg/l, giving an elimination of 94.8%. Concentrations in groundwater and river water were found to be less in summer than in winter, and the elimination efficiency in winter was also found to be significantly less. Retardation factors for nonylphenol in sediment and river aquifers have been calculated for nonylphenol from its log  $K_{ow}$  (4.48). The calculated retardation factors are 109-430 for river sediment, 11.7-216 for the aquifer close to river bed (<5 m) and 1-11.7 for aquifer far from river bed (>5 m).

Although the data of Ahel et al. (1994 and 1996) are useful for determining the adsorptive behaviour of nonylphenol in the environment, the actual concentrations measured are unlikely to reflect the current situation since the samples were collected in 1984, before a Swiss ban on the use of nonylphenol ethoxylates (a major source of nonylphenol in the samples) was enforced.

**Table 3.6** Nonylphenol and nonylphenol ethoxylate concentrations due to riverwater infiltration

Sampling Point	Concentration ( $\mu\text{g/l}$ )	
	Arithmetic mean (16 determinations)	Range
Glatt River	2.7	0.7-26
Groundwater 2.5m from river	0.96	<0.1-29
Groundwater 5m from river	0.40	<0.1-4.4
Groundwater 7m from river	0.44	<0.1-3.4
Groundwater 13m from river	0.20	<0.1-33

The following partition coefficients for nonylphenol have been calculated using EUSES based on a log  $K_{ow}$  of 4.48.

$K_{oc}$	5,360 l/kg	Partition coefficient organic carbon-water
$K_{p_{susp}}$	536 l/kg	Partition coefficient solids-water in suspended matter
$K_{p_{sed}}$	268 l/kg	Partition coefficient solids-water in sediment
$K_{p_{soil}}$	107 l/kg	Partition coefficient solids-water in soil
$K_{soil-water}$	161 $\text{m}^3/\text{m}^3$	Soil-water partitioning coefficient
$K_{susp-water}$	135 $\text{m}^3/\text{m}^3$	Suspended matter-water partitioning coefficient
$K_{sed-water}$	135 $\text{m}^3/\text{m}^3$	Sediment-water partitioning coefficient

Although the  $K_{oc}$  value estimated here is slightly lower than that measured in various soils ( $K_{oc}$  22,000-490,000), there is some evidence that the experimental values may be too high due to adsorption of nonylphenol to the test vessel. As a result the estimated value will be used in the risk assessment, although it is possible that the actual adsorption onto soil and sediment may be higher than estimated here, possibly due to factors other than organic carbon content being important in the process.

Given that nonylphenol is a weak acid, the pH may also have an effect on its adsorptive behaviour. However, the  $pK_a$  is thought to be around 10, meaning that in most situations encountered in the environment, nonylphenol will be present in the undissociated and hence more hydrophobic form.

Experimental data and calculated partition coefficients suggest that nonylphenol will be strongly adsorbed to soils, sludges and sediments. Evidence from measured levels indicates that adsorption to soil may be governed by factors other than organic carbon content.

### 3.1.1.3.2 Precipitation

Nonylphenol is relatively short-lived in the atmospheric environment, based upon the reaction with hydroxyl radicals. Nonylphenol is not very volatile (See Section 3.1.1.3.3.) and so it is unlikely to enter the atmosphere in large amounts. Removal of nonylphenol from the atmosphere by precipitation is therefore likely to be negligible with resulting rain water concentrations being low. As the lifetime of nonylphenol in the atmosphere is relatively short it is unlikely to be transported a long distance from its point of emission. Concentrations due to precipitation of nonylphenol from the atmosphere are therefore likely to be greatest near the point of emission.

### 3.1.1.3.3 Volatilisation

The volatilisation of nonylphenol from surface water to air may be estimated by the Henry's Law constant. This is calculated as  $11.02 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$  for nonylphenol in Section 1.3.10. The air-water partitioning coefficient ( $K_{\text{air-water}}$ ) may be derived from the Henry's law constant and is calculated as  $4.65 \cdot 10^{-3} \text{ m}^3/\text{m}^3$ . The  $K_{\text{air-water}}$  and Henry's law constant are low suggesting that volatilisation is unlikely to be a significant removal mechanism for nonylphenol from water systems and that it is unlikely to be transported very far in the atmosphere.

### 3.1.1.3.4 Distribution in wastewater treatment plants

The distribution of nonylphenol in wastewater treatment plants has been calculated for nonylphenol using EUSES. For comparison the calculation has been done assuming both inherently and not readily biodegradable conditions for nonylphenol in the plant. In line with the discussion on degradation of nonylphenol in Section 3.1.1.2.4 the inherent distribution pattern is taken forward in the risk assessment.

Table 3.7 Fraction of emission directed to air, surface water, sludge and degraded as calculated by EUSES

	Inherently biodegradable	Not readily biodegradable
Fraction to air	0.0669	0.0962
Fraction to surface water	0.350	0.527
Fraction to sludge	0.344	0.377
Fraction degraded	0.239	0

It can be seen that the main effect of degradation is on the amount of nonylphenol entering the water phase, with the fraction going to sludge only marginally effected. It should also be noted that this applies to releases of nonylphenol while releases of nonylphenol ethoxylates to wastewater plants are considered in Appendix 1.

### 3.1.1.3.5 Accumulation and metabolism

Ahel et al. (1993) studied the bioaccumulation potential of nonylphenol in freshwater organisms in the Glatt River and one of its tributaries, the Chriesbach, in Switzerland. Samples of microphytic algae were collected in the summer and autumn and frozen ( $-20^{\circ}\text{C}$ ) until analysis. Fish and duck samples were also collected and dissected, and specific organs and tissues were deep frozen until analysis. Dry matter content was determined for each sample. Nonylphenol was extracted from the samples by steam distillation and extraction with cyclohexane, the extraction efficiency being 100%. The extracts were quantified by HPLC. The limit of quantification was  $0.03 \text{ mg/kg}$  dry weight based on  $10 \text{ g}$  of fresh weight. Nonylphenol was detected in the following concentrations in microphytic algae; *Cladophora glomerata*  $38 \text{ mg/kg}$  dry weight, *Fontinalis antipyretica*  $4.2 \text{ mg/kg}$  dry weight and *Potamogeton crispus*  $2.5 \text{ mg/kg}$  dry weight. The average concentration of nonylphenol in the river was  $3.9 \text{ }\mu\text{g/l}$ . The bioconcentration factor (BCF) of nonylphenol in the algae *Cladophora glomerata* was calculated as  $10,000 \text{ l/kg}$  dry weight. Due to possible variations in nonylphenol concentrations this value indicates the possible magnitude of bioconcentration not an exact BCF. The concentration of nonylphenol in *Cladophora glomerata* was found to vary depending upon location and season with higher concentrations being observed in summer than autumn and nearer to the sewage outfall. The calculated BCFs

were 6,600-7,700 l/kg dry weight. Nonylphenol concentrations in fish organs were as follows: *Squalius cephalus*, muscle 0.18 mg/kg dry weight, gut 0.46-1.2 mg/kg dry weight, liver 1.0-1.4 mg/kg dry weight, gills 0.98-1.4 mg/kg dry weight; *Barbus barbus* L., muscle 0.38 mg/kg dry weight, gut 0.05 mg/kg dry weight, liver 0.98 mg/kg dry weight, gills <0.03 mg/kg dry weight, heart 0.30 mg/kg dry weight, roe 0.09 mg/kg dry weight; *Oncorhynchus mykiss*, muscle 0.15 mg/kg dry weight, gut 1.6 mg/kg dry weight. Based upon the average concentration of nonylphenol in water, the BCF in fish was calculated as 13-408 l/kg dry weight on an individual organ basis. The concentration of nonylphenol in organs of a duck (mallard, *Anas boscas*) was: muscle 1.20 mg/kg dry weight, liver 0.10 mg/kg dry weight, guts 0.54 mg/kg dry weight, stomach 0.19-0.24 mg/kg dry weight, heart <0.03 mg/kg dry weight and brain 0.19 mg/kg dry weight. The authors concluded that the lower concentration in fish than in algae indicated that little accumulation through the food chain was occurring.

Ekelund et al. (1990) studied the bioaccumulation of nonylphenol in marine animals. <sup>14</sup>C-labelled p-nonylphenol was synthesised from uniformly labelled phenol and unlabelled nonene for use in the bioaccumulation studies. Three marine species were used in the studies, the common mussel (*Mytilus edulis* L.), common shrimp (*Crangon crangon* L.) and three-spined stickleback (*Gasterosteus aculeatus* L.). The animals were exposed to the <sup>14</sup>C-nonylphenol in flow-through systems. Acetone was used as a solvent for the nonylphenol added to the seawater, at a concentration of 20 mg/l. The flow through each tank was approximately 85 ml/min. Each tank contained 10 litres of water and 110 animals (60 g soft tissue mussels, 45 g shrimps and 85 g sticklebacks respectively). Exposure was for 16 days followed by an elimination period of 32 days. Samples were taken at regular intervals throughout the experiment, and stored at -20°C for analysis. The extraction efficiency of nonylphenol from water was 80 ± 4% and the nonylphenol concentrations in the test ranged from 4.9-6.4 µg/l. Nonylphenol concentrations in the tissues of the species were of 670-680 µg/kg fresh weight for the shrimp, 16,260-25,600 µg/kg fresh weight for the mussel, and 5,730-6,300 µg/kg fresh weight for the fish. The following bioconcentration factors were calculated on a fresh weight basis: shrimp 90-110, mussel 2,740-4,120, fish 1,200-1,300; on a fat basis: shrimp 5,500-7,500, mussel 169,300-216,600, fish 16,700-17,800. The authors found that steady state bioaccumulation had been reached by the end of the exposure period for shrimp and fish, whereas for mussel steady state had not been achieved by 16 days. The above BCFs for mussel are based upon an extrapolation from the available data to a steady state concentration and are based on total radioactivity measurements. The elimination of nonylphenol was observed to be rapid from fish. For mussels a significant proportion of the nonylphenol in mussel tissue remained after the 30-day elimination period. Since the BCFs are based on total <sup>14</sup>C measurements, the presence of metabolites in the organisms may have led to an overestimate of the accumulation of nonylphenol seen, particularly for fish. However for mussels, analysis after 4, 8 and 16 days exposure showed that >80% of the radioactivity present co-chromatographed with nonylphenol (BCF corrected for this would be 2,190-3,300 on a fresh weight basis).

Granmo et al. (1991) studied the bioaccumulation of nonylphenol in field tests using caged mussels (*Mytilus edulis*). The mussels were exposed to nonylphenol near to a wastewater outlet from a chemical plant producing surfactants between August and October 1984. The measured BCFs found were around 340 on a fresh weight basis, with the highest concentrations in mussels being found in those nearest the outfall.

A much lower BCF of 10 has been measured in mussels by McLeese et al. (1980a). In this experiment, mussels were exposed to a pesticide formulation, reportedly containing around 50%

nonylphenol and the uptake (over 4 days) and excretion (over 8 days) was determined. Excretion from the organism was rapid (half-life of 0.3 days).

The bioconcentration of nonylphenol in the fathead minnow (*Pimephales promelas*) has been studied (Ward and Boeri, 1991a). Fathead minnows (0.5-1 g wt) were exposed to nominal concentrations of 5 µg/l and 25 µg/l nonylphenol in an intermittent flow-through system for 20 days. The exposure period was then followed by a 7-day depuration period. The system was analysed for nonylphenol concentrations, dissolved oxygen content, temperature and pH. All the parameters were found to be within acceptable limits for the test conditions and species. Measured levels of nonylphenol were 4.9 µg/l and 22.7 µg/l in the two test systems respectively. Acetone was added to increase the solubility of nonylphenol in the water. Samples were extracted with hexane and quantified by HPLC. The concentration of nonylphenol in tissues increased from background concentrations to steady state concentrations during the first 3-10 days of exposure. Uptake and depuration of nonylphenol appeared to be independent of the concentration of the test substance in water. Exposure of fathead minnows to 4.9 µg/l nonylphenol in water for 20 days resulted in a BCF of 271 l/kg fresh weight with an uptake rate constant of 133 day<sup>-1</sup> and a depuration rate constant of 0.49 day<sup>-1</sup>. Exposure to 22.7 µg/l nonylphenol for 20 days resulted in a BCF of 344 l/kg fresh weight with an uptake rate constant of 193 day<sup>-1</sup> and a depuration rate constant of 0.56 day<sup>-1</sup>. Analysis of viscera and carcasses from fish collected on the last day of the uptake phase indicated that the concentration of nonylphenol in the viscera was 1.6 to 7.1 times the concentration in the carcass.

Lewis and Lech (1996) studied the uptake, disposition, and persistence of nonylphenol from water in rainbow trout (*Oncorhynchus mykiss*). They exposed juvenile rainbow trout weighing 40g to 60g under static conditions to 36 µg/l <sup>14</sup>C-nonylphenol for 14 hours. The <sup>14</sup>C-nonylphenol (uniformly ring labelled) was detected in the following tissues in descending order of concentration: bile, liver, kidney, fat, gill, heart, muscle. The half-life of <sup>14</sup>C-nonylphenol in specific tissues was determined by exposing juvenile rainbow trout weighing 40 to 60g under static conditions to 18 µg/l <sup>14</sup>C-nonylphenol for 8 hours. The half-life was calculated as 19.8 hours in fat, 18.6 hours in muscle and 5.9 hours in liver. The bioconcentration of <sup>14</sup>C-nonylphenol in the rainbow trout carcass was determined by exposing juvenile rainbow trout weighing 40 to 60g under static conditions to 18 µg/l <sup>14</sup>C-nonylphenol for 5-24 hours. The calculated bioconcentration factors were 23.2 for the carcass after 5-hour exposure and 110.1 for the viscera after 24 hour-exposure.

Brooke (1993b) determined bioconcentration factors for fathead minnow (*Pimephales promelas*) and bluegills (*Lepomis macrochirus*) over 28 day-exposure to 5 concentrations of nonylphenol. For fathead minnows exposed to concentrations of 9.3, 19.2, 38.1, 77.5 and 193 µg/l, the mean BCF (on a wet weight basis) was 586±273 after 14 days and 741±206 after 28 days. The BCF was found to be independent of concentration at 28 days but not at 14 days. Reduced growth of the fish was seen at the two highest concentrations tested. For bluegill exposed to concentrations of 5.6, 12.4, 27.6, 59 and 126 µg/l, the mean BCF (on a wet weight basis) was 262±70 after 14 days and 220 after 28 days. The BCF for this species was found to be independent of exposure concentration at the three lowest concentrations, but the BCF at the two higher concentrations was found to be lower, particularly at 14 days, than that obtained at the lower concentrations.

The bioconcentration of nonylphenol in juvenile Atlantic salmon (*Salmo salar*) was studied by McLeese et al. (1981) over 4 day-exposure. The uptake rate constant was measured to be 45-day<sup>-1</sup> and the excretion rate constant was 0.16 day<sup>-1</sup>, giving a wet weight bioconcentration factor of around 280. The excretion half-life was estimated to be around 4 days.



Suoanttila (1996) studied the bioconcentration of nonylphenol and nonylphenol ethoxylates in mussels incubated in lake water 1km downstream from a wastewater treatment plant. The wastewater treatment plant received waste containing a high level of nonylphenol ethoxylate surfactants. The bioconcentration factor of nonylphenol in mussels was calculated as 2,000 on a dry weight basis.

The Danish EPA, in a study of the use of waste products in agriculture (Personal communication, 1997), report BCFs for whole potato and carrot peel (concentration in vegetable/concentration in soil) as follows: whole potato  $BCF_{\text{dry weight}} < 0.05$ ,  $BCF_{\text{fresh weight}} < 0.006$ , carrot peel  $BCF_{\text{dry weight}} < 0.002$ ,  $BCF_{\text{fresh weight}} < 0.0002$ . In calculating these BCFs the detection limit has been used; the actual BCF may be lower than these values.

In a Danish EPA report (Personal communication, 1997) the following information on bioaccumulation in plants is included. Kirchmann and Tengsved (1991) (Ref Danish EPA) observed that the internal concentrations of nonylphenol in spring barley grains (10.1  $\mu\text{g}/\text{kg}$ ) were independent of whether or not the soil was contaminated with nonylphenol up to 12.5 mg nonylphenol per kg. Kampe (1987) did not find an increase in three plant species (clover, wheat and potatoes) upon application of sludge resulting in up to 0.7 mg nonylphenol per kg in the soil. Naturvårdsverket (1992) found that when sludge contaminated with 2.5 g nonylphenol/kg (dry weight) was applied to a field, no increase in the nonylphenol content of grains was observed. The Danish report concluded that no indication of accumulation could be observed in plant species based upon the limited data set available.

It is clear from the available data that nonylphenol bioconcentrates to a significant extent in aquatic species, with BCFs (on a fresh weight basis) of up to 1,300 in fish. However, this value may overestimate the BCF; more reliable values with a mean of 741 have been measured, which are of a similar order of magnitude. Bioconcentration factors of around 2,000-3,000 have been measured in mussels. The BCF calculated from the log Kow of 4.48, using the TGD equation, is 1,280, which agrees well with the measured values. The calculated value of 1,280 will be used in the risk assessment.

### **3.1.2 Aquatic compartment (incl. sediment)**

#### **3.1.2.1 Predicted environmental concentrations in water**

##### **3.1.2.1.1 Calculation of $PEC_{\text{local}}$**

The predicted environment concentrations (PECs) for local water are calculated using the environmental releases detailed in section 3.1.1.1 using the equations set out in Chapter 3 Sections 2.3.7. and 2.3.8.3. of the Technical Guidance Document.

In calculating the local PEC the regional PEC is added to the local concentrations. In this instance the regional PEC is taken as a background concentration. For processes where there are no releases to water the  $PEC_{\text{local}}$  is the same as the  $PEC_{\text{regional}}$ .

It should be noted that for some of the PECs calculated, the concentrations estimated in some parts of the wastewater treatment process (e.g. influent concentrations and sometimes effluent concentrations) are greater than the water solubility of nonylphenol. This could mean that the actual concentrations are over-estimated, but no correction for this has been applied in the calculations.

### 3.1.2.1.1.1 Nonylphenol production

In the EU there are four production plants, one of these plants also uses nonylphenol on-site as an intermediate in the production of nonylphenol ethoxylates. Full details of the emissions from these plants are given in Section 3.1.1.1.1. For all of the sites, site-specific data and measurements of nonylphenol have been reported by industry.

For site A the measured levels of nonylphenol and its derivatives in the outflow of the wastewater treatment plants are  $<0.2-0.6 \mu\text{g/l}$  for nonylphenol,  $0.3-0.7 \mu\text{g/l}$  for NPEC (Nonylphenol ether carboxylate),  $0.2-0.33 \mu\text{g/l}$  for NPEO1 and  $0.3-0.57 \mu\text{g/l}$  for NPEO2. The measured levels of nonylphenol and its derivatives in the river after passing site A are  $<0.2 \mu\text{g/l}$  for nonylphenol,  $0.5 \mu\text{g/l}$  for NPEC,  $0.25-0.3 \mu\text{g/l}$  for NPEO1 and  $0.4 \mu\text{g/l}$  for NPEO2. These are based upon measurements taken in February, June and October 1997. The measured level of nonylphenol in the river after passing the site of  $<0.2 \mu\text{g/l}$  will be used in the risk characterisation section.

For site B the company has calculated the resultant concentration of nonylphenol in receiving waters using measurements of nonylphenol in plant effluent and typical flow rates from the site's wastewater treatment plant and in the receiving waters. The resultant concentration of nonylphenol in receiving waters is calculated as  $<0.0208 \mu\text{g/l}$ . Adding the  $\text{PEC}_{\text{regional}}$  to the concentration in receiving waters gives a  $\text{PEC}_{\text{local}}$  for site B of  $0.60 \mu\text{g/l}$ .

For production site C, wastewaters from the site are reported to be collected and disposed of by incineration. The emissions of wastewater from nonylphenol production are taken as zero. The background concentration ( $\text{PEC}_{\text{regional}}$ ) is therefore taken as the  $\text{PEC}_{\text{local,water}}$ .

For production site D the measured level of nonylphenol in the effluent from the on-site wastewater treatment plant is  $<1 \mu\text{g/l}$  (detection limit). The effluent is diluted by a factor of 5.2 before discharge to receiving waters. This gives a nonylphenol concentration of  $<0.19 \mu\text{g/l}$  which will be further diluted in the receiving water. Applying the standard dilution factor of 10 gives a  $C_{\text{localwater}}$  of  $<0.019 \mu\text{g/l}$ . The  $C_{\text{localwater,ann}}$  is  $<0.15 \mu\text{g/l}$ . Adding on the background regional concentration gives a  $\text{PEC}_{\text{localwater}}$  of  $<0.62 \mu\text{g/l}$ .

### 3.1.2.1.1.2 Processing

#### Nonylphenol ethoxylate production

Site-specific data is available for all the nonylphenol ethoxylate production plants.

Company A is both a nonylphenol producer and processor and therefore emissions from the two operations are considered together above under production.

Releases from production of nonylphenol ethoxylates at Company B are reported as 46 tonnes/annum direct to receiving waters. This is total nonylphenol and nonylphenol ethoxylate. Measurements of the levels of nonylphenol have been made in the receiving waters downstream from the discharge point. In top water the concentration of nonylphenol was between  $1.7-3.02 \mu\text{g/l}$ , in middle waters the concentration was between  $1.3-1.6 \mu\text{g/l}$  and in bottom waters between  $0.54-1.2 \mu\text{g/l}$ . These measured levels will be used in the risk characterisation section.

Company C operates three nonylphenol ethoxylate production plants within the EU. For two of the sites a combined release is reported, the waste from both of these sites being treated on-site at a

biological treatment plant then off site at a municipal treatment plant. As no further information is available the releases from these two plants will be considered together. Default parameters will be used for the wastewater treatment plants. The site reports that it only releases nonylphenol ethoxylates not nonylphenol. Therefore the concentrations in water calculated due to nonylphenol ethoxylate release will be used here to derive a PEC. Company C sites 1 and 2 report a release of 222 kg/day NPEO from one site and 361 kg/day NPEO from the other site. As a worst-case scenario these two emissions will be taken as occurring at the same time. This gives a release of 583 kg/day nonylphenol ethoxylate to the on-site treatment plant. The effluent from the on-site treatment plant is then treated at a municipal treatment plant.

$C_{\text{localinf}}$ to WWTP 1	291.5 mg/l NPEO
$C_{\text{localeff}}$ from WWTP 1	7.29 mg/l NP
$C_{\text{localinf}}$ to WWTP 2	7.29 mg/l NP
$C_{\text{localeff}}$ from WWTP 2	2.55 mg/l NP
$C_{\text{localwater}}$	0.26 mg/l NP
$C_{\text{localwater, ann}}$	0.038 mg/l NP
$PEC_{\text{local}}$	0.30 mg/l
$PEC_{\text{local, ann}}$	0.04 mg/l

At Company C's third site, effluent is treated at an industrial treatment works. No information on the characteristics of the plant is available or of the dilution in the receiving waters.

Daily emission from site	17 kg/day nonylphenol
$C_{\text{localinf}}$ to wwtp	8.5 mg/l
$C_{\text{localeff}}$ from wwtp	2.975 mg/l
$C_{\text{localwater}}$	0.30 mg/l
$C_{\text{localwater, ann}}$	0.04 mg/l
$PEC_{\text{local}}$	0.30 mg/l
$PEC_{\text{local, ann}}$	0.04 mg/l

Company D operates two sites within the EU. At both sites the effluent is treated on-site by mechanical and biological treatment of wastewater. Both plants only report releases of nonylphenol ethoxylates.

Company D site 1 reports a release of 1.2 kg/day nonylphenol ethoxylate to the on-site treatment plant.

$C_{\text{localinf}}$	0.6 mg/l NPEO
$C_{\text{localeff}}$	0.015 mg/l NP
$C_{\text{localwater}}$	1.49 $\mu\text{g/l}$ NP
$C_{\text{localwater, ann}}$	1.22 $\mu\text{g/l}$ NP
$PEC_{\text{local}}$	2.09 $\mu\text{g/l}$
$PEC_{\text{local, ann}}$	1.82 $\mu\text{g/l}$

Company D site 2 reports a release of 0.33 kg/day nonylphenol ethoxylate to the on-site treatment plant.

$C_{\text{localinf}}$	0.55 mg/l NPEO
$C_{\text{localeff}}$	13.8 $\mu\text{g/l}$ NP
$C_{\text{localwater}}$	1.36 $\mu\text{g/l}$ NP

$C_{\text{localwater, ann}}$	0.19 $\mu\text{g/l}$ NP
$\text{PEC}_{\text{local}}$	1.96 $\mu\text{g/l}$
$\text{PEC}_{\text{local, ann}}$	0.78 $\mu\text{g/l}$

Company E reports that releases to water are zero as residues from the process are incorporated into the next run and other wastes are incinerated. The  $\text{PEC}_{\text{local}}$  is taken as equal to the background concentration ( $\text{PEC}_{\text{regional}}$ ).

Company F reports that washwaters are concentrated then incinerated on-site. The  $\text{PEC}_{\text{local}}$  is taken as equal to the background concentration ( $\text{PEC}_{\text{regional}}$ ).

Polluted wastewaters from Company G are incinerated on-site. The local PECs is therefore taken as equal to the background concentration ( $\text{PEC}_{\text{regional}}$ ).

### Release of nonylphenol from the manufacture of phenolic oximes

Phenolic oximes are produced at one site within the EU and the total volume produced is exported for use outside of the EU. The concentration of nonylphenol in the wastewater after treatment at the production plant is 0.318 mg/l. This is discharged to a tidal water system. The dilution factor in receiving waters is estimated by the company as 80,000. The  $C_{\text{localeff}}$  for the plant is taken as 0.318 mg/l, which gives a  $C_{\text{localwater}}$  of 0.004  $\mu\text{g/l}$  and a  $C_{\text{localwater, ann}}$  of 0.002  $\mu\text{g/l}$ . The resultant PECs are  $\text{PEC}_{\text{local}}$  0.60  $\mu\text{g/l}$  and  $\text{PEC}_{\text{local, ann}}$  0.60  $\mu\text{g/l}$ .

### Plastics, resins and stabilisers production

#### *Nonylphenol/formaldehyde resins*

The main use of nonylphenol in the plastic industry is as a monomer in the production of nonylphenol/formaldehyde resins. Releases from nonylphenol/formaldehyde resin manufacturers are calculated using default release estimations and information on the average number of sites within the EU. An average size processor is assessed to use 900 tonnes nonylphenol per year and operate for 100 days a year. A large-scale processor is assessed to use 4,500 tonnes nonylphenol per year and operate for 300 days a year.

Daily emission to wastewater	0.09 kg/day NP	(average)
	0.15 kg/day NP	(large)
$C_{\text{localinf}}$ to wwtp	45 $\mu\text{g/l}$	(average)
	75 $\mu\text{g/l}$	(large)
$C_{\text{localeff}}$ from wwtp	15.75 $\mu\text{g/l}$	(average)
	26.25 $\mu\text{g/l}$	(large)
$C_{\text{localwater}}$	1.6 $\mu\text{g/l}$	(average)
	2.6 $\mu\text{g/l}$	(large)
$C_{\text{localwater, ann}}$	0.43 $\mu\text{g/l}$	(average)
	2.14 $\mu\text{g/l}$	(large)
$\text{PEC}_{\text{local}}$	2.2 $\mu\text{g/l}$	(average)
	3.2 $\mu\text{g/l}$	(large)
$\text{PEC}_{\text{local, ann}}$	1.02 $\mu\text{g/l}$	(average)
	2.73 $\mu\text{g/l}$	(large)

*TNPP production*

Industry reports that all wastewaters from the production of TNPP are incinerated. The  $PEC_{\text{localwater}}$  is taken as equivalent to the background concentration ( $PEC_{\text{regional}}$ ).

*Epoxy resins*

Nonylphenol is used in the production of epoxy resins as an accelerator or curing agent. Using the default release estimations the following PECs are calculated:

Daily emission to wastewater	0.0026 kg/day NP
$C_{\text{localinf}}$	1.3 $\mu\text{g/l}$
$C_{\text{localeff}}$	0.46 $\mu\text{g/l}$
$C_{\text{localwater}}$	0.05 $\mu\text{g/l}$
$C_{\text{localwater, ann}}$	0.04 $\mu\text{g/l}$
$PEC_{\text{localwater}}$	0.65 $\mu\text{g/l}$
$PEC_{\text{localwater,ann}}$	0.64 $\mu\text{g/l}$

*Use in other plastic stabilisers*

Nonylphenol is used in the production of plastic stabilisers. Using the default release estimations the following PECs are calculated:

Daily emission to wastewater	0.16 kg/day NP
$C_{\text{localinf}}$	0.08 mg/l
$C_{\text{localeff}}$	28 $\mu\text{g/l}$
$C_{\text{localwater}}$	2.78 $\mu\text{g/l}$
$C_{\text{localwater, ann}}$	2.28 $\mu\text{g/l}$
$PEC_{\text{localwater}}$	3.38 $\mu\text{g/l}$
$PEC_{\text{localwater,ann}}$	2.88 $\mu\text{g/l}$

**3.1.2.1.1.3 Calculation of  $PEC_{\text{local(water)}}$  from nonylphenol ethoxylate use**

In calculating the  $PEC_{\text{local(water)}}$  of nonylphenol from nonylphenol ethoxylate use it is assumed in the generic calculation that the nonylphenol ethoxylate is degraded in the wastewater treatment plant. Of the nonylphenol ethoxylate entering the wastewater treatment plant approximately 2.5% is assumed to be released as nonylphenol in the effluent (see Appendix 1 for more details). This is for plants using anaerobic sludge digestion. As a worst case it is assumed that a similar figure may apply to all types of plant. In calculating the  $PEC_{\text{local(water)}}$  for nonylphenol from nonylphenol ethoxylates (NPEO) the following equation will be used.

$$C_{\text{localeff}} = C_{\text{localinf}} (\text{NPEO}) \cdot 0.025$$

Nonylphenol ethoxylate formulation

The  $PEC_{\text{local(water)}}$  from nonylphenol ethoxylate formulation is calculated for three different scenarios: a large scale plant which formulates 1,000 tonnes nonylphenol ethoxylates over 300 days a year; a medium scale plant which formulates 250 tonnes nonylphenol ethoxylates over 300 days a year; and a small scale plant which formulates 10 tonnes nonylphenol ethoxylates

over 30 days/year. Using these values plus the default release estimations the following PECs are calculated for formulation:

Daily emission of nonylphenol ethoxylate	10 kg/day	(Large)
	2.5 kg/day	(Medium)
	1 kg/day	(Small)
$C_{\text{localinf}}$ to wwtp	5 mg/l NPEO	(Large)
	1.25 mg/l NPEO	(Medium)
	0.5 mg/l NPEO	(Small)
$C_{\text{localeff}}$ from wwtp	0.125 mg/l NP	(Large)
	0.031 mg/l NP	(Medium)
	0.0125 mg/l NP	(Small)
$C_{\text{localwater}}$	12.4 $\mu\text{g/l}$ NP	(Large)
	3.08 $\mu\text{g/l}$ NP	(Medium)
$C_{\text{localwater,ann}}$	1.24 $\mu\text{g/l}$ NP	(Small)
	10.2 $\mu\text{g/l}$ NP	(Large)
	2.53 $\mu\text{g/l}$ NP	(Medium)
PEC <sub>local</sub>	0.10 $\mu\text{g/l}$ NP	(Small)
	13.0 $\mu\text{g/l}$ NP	(Large)
	3.68 $\mu\text{g/l}$ NP	(Medium)
PEC <sub>local, ann</sub>	1.84 $\mu\text{g/l}$ NP	(Small)
	10.8 $\mu\text{g/l}$ NP	(Large)
	3.12 $\mu\text{g/l}$ NP	(Medium)
	0.69 $\mu\text{g/l}$ NP	(Small)

### Nonylphenol ethoxylate use in agricultural industry

In calculating local exposure of the environment to nonylphenol ethoxylates from pesticide use the following information has been supplied by Zeneca Agrochemicals (Personal communication, 1997).

Pesticide aquatic exposure assessments can be done at various levels of complexity, or tiers. Each new tier results in a more refined risk assessment and gives a more realistic estimate of likely environmental concentrations. Each new tier needs more data on the properties of the chemical involved, and on the precise nature of the situations in which it is used (e.g. soil, crop, climate, season). A first tier of aquatic exposure assessment considers spray drift entry of pesticides, or in this case nonylphenol ethoxylates, into surface waters. Run-off from the soil surface and leaching are not significant sources of water contamination because nonylphenol ethoxylates and nonylphenol are strongly bound to soil (Section 3.1.1.3.1). In calculating local exposure of the environment to nonylphenol ethoxylates in pesticides the When sprayed, some proportion of the material may drift downwind and may deposit on an adjoining surface water. The conventional assumption for risk assessment is an application made from a tractor-mounted boom sprayer, with a surface water one metre downwind onto which drift deposits at a rate equivalent to 4% of the intended application rate in the treated field (Ganzelmeier et al., 1995). The amounts of nonylphenol ethoxylates applied to crops are typically equivalent to 50-200 g/ha, the higher rates being used as wetters, and the lower rates as emulsifiers. In a one-metre deep water body the resulting PEC range for nonylphenol ethoxylates is given by:

$$\begin{aligned} \text{PEC for NPEOs} &= \text{Applied rate} \cdot (\text{Percent drift} / \text{Water depth}) \\ &= 0.2\text{-}0.8 \mu\text{g/l} \end{aligned}$$

The nonylphenol ethoxylate reaching the surface water will be readily broken down by microbial activity. If a worst-case scenario is assumed that nonylphenol ethoxylates break down instantly to nonylphenol, then the PEC range for nonylphenol is given by the following:

$$\text{PEC for NP} = \text{PEC for NPEO} \cdot (\text{Mol wt of NP/Mol wt of NPEO})$$

Taking an average side-chain length of 7 this gives the following PEC:

$$\begin{aligned} \text{PEC for NP} &= \text{PEC for NPEO} \cdot (219/528) \\ &= 0.08\text{-}0.33 \mu\text{g/l} \end{aligned}$$

This estimate of the PEC is very conservative because it assumes the following:

- Presence of surface water 1m downwind of the treated area of the field
- Instantaneous 100% conversion of nonylphenol ethoxylate to nonylphenol
- The concentration is appropriate to that at the edge of a water body; for a water body of any width the average drift entry rate will be less than the 4% assumed here.
- No account is taken of dilution effects in flowing water bodies.

The use of veterinary medicine products is thought not to lead to significant releases to surface waters.

#### Nonylphenol ethoxylate: captive use by the chemical industry

The  $\text{PEC}_{\text{local(water)}}$  is calculated for a generic site (parameters and emissions defined by Emission Scenario Document). For this use a river flow rate of  $60 \text{ m}^3/\text{s}$  is used in accordance with the ESD instead of the standard dilution factor of 10. This gives a dilution rate in the receiving waters of 2,590.

Daily emission of nonylphenol ethoxylate	4.08 kg/day
$C_{\text{localinf}}$ to wwtp	2.04 mg/l NPEO
$C_{\text{localeff}}$ from wwtp	0.051 mg/l NP
$C_{\text{localwater}}$	0.02 $\mu\text{g/l}$ NP
$C_{\text{localwater,ann}}$	0.02 $\mu\text{g/l}$ NP
$\text{PEC}_{\text{local}}$	0.62 $\mu\text{g/l}$
$\text{PEC}_{\text{local, ann}}$	0.62 $\mu\text{g/l}$

#### Nonylphenol ethoxylate use in electrical/electronic engineering industry

The  $\text{PEC}_{\text{local(water)}}$  is calculated for a generic site (parameters and emissions as defined by the TGD):

Daily emission of nonylphenol ethoxylate	2.46 kg/day
$C_{\text{localinf}}$ to wwtp	1.23 mg/l NPEO
$C_{\text{localeff}}$ from wwtp	0.0308 mg/l NP
$C_{\text{localwater}}$	3.05 $\mu\text{g/l}$ NP
$C_{\text{localwater,ann}}$	0.13 $\mu\text{g/l}$ NP
$\text{PEC}_{\text{local}}$	3.65 $\mu\text{g/l}$
$\text{PEC}_{\text{local, ann}}$	0.73 $\mu\text{g/l}$

Nonylphenol ethoxylate use in industrial and institutional cleaning

The  $PEC_{local(water)}$  is calculated for a generic site (parameters and emissions as defined by the TGD):

Daily emission of nonylphenol ethoxylate	20.7 kg/day
$C_{localinf}$ to wwtp	10.35 mg/l NPEO
$C_{localeff}$ from wwtp	0.259 mg/l NP
$C_{localwater}$	25.7 $\mu$ g/l NP
$C_{localwater,ann}$	14.1 $\mu$ g/l NP
$PEC_{local}$	26.3 $\mu$ g/l
$PEC_{local, ann}$	14.7 $\mu$ g/l

Nonylphenol ethoxylate use in the leather processing industry

The  $PEC_{local(water)}$  is calculated for an average size site and a large scale site using default release estimations:

Daily emission of nonylphenol ethoxylate	67.5 kg/day	(large)
	13.5 kg/day	(small)
$C_{localinf}$ to wwtp	33.8 mg/l NPEO	(large)
	6.75 mg/l NPEO	(small)
$C_{localeff}$ from wwtp	0.845 mg/l NP	(large)
	0.169 mg/l NP	(small)
$C_{localwater}$	83.8 $\mu$ g/l NP	(large)
	16.7 $\mu$ g/l NP	(small)
$C_{localwater,ann}$	45.9 $\mu$ g/l NP	(large)
	9.15 $\mu$ g/l NP	(small)
$PEC_{local}$	84.4 $\mu$ g/l NP	(large)
	17.3 $\mu$ g/l NP	(small)
$PEC_{local, ann}$	46.5 $\mu$ g/l NP	(large)
	9.74 $\mu$ g/l NP	(small)

Nonylphenol ethoxylate use in the metal extraction, refining and processing industry

The  $PEC_{local(water)}$  is calculated for a generic site (parameters and emissions as defined by the TGD):

Daily emission of nonylphenol ethoxylate	114 kg/day
$C_{localinf}$ to wwtp	57 mg/l NPEO
$C_{localeff}$ from wwtp	1.43 mg/l NP
$C_{localwater}$	141 $\mu$ g/l NP
$C_{localwater,ann}$	38.7 $\mu$ g/l NP
$PEC_{local}$	141 $\mu$ g/l
$PEC_{local, ann}$	39.2 $\mu$ g/l

Nonylphenol ethoxylate use in the mineral fuel and oil industry

The  $PEC_{local}$  from nonylphenol ethoxylate use in additive manufacture and blending operations is calculated using data supplied in a survey of ATC (Additive Technical Committee) members.



The  $C_{\text{localwater}}$  is calculated at between 1-35  $\mu\text{g/l}$  depending upon the company. This gives a  $\text{PEC}_{\text{local}}$  of 1.6-35.6  $\mu\text{g/l}$ .

During use the product is effectively destroyed.

#### Nonylphenol ethoxylate use in the photographic industry

The  $\text{PEC}_{\text{local(water)}}$  is calculated for a large scale user and a small scale user. The release estimations are based upon TGD default values.

Daily emission of nonylphenol ethoxylate	1.24 kg/day	(large)
	0.008 kg/day	(small)
$C_{\text{localinf}}$ to wwtp	0.62 mg/l NPEO	(large)
	0.004 mg/l NPEO	(small)
$C_{\text{localeff}}$ from wwtp	15.5 $\mu\text{g/l}$ NP	(large)
	0.1 $\mu\text{g/l}$ NP	(small)
$C_{\text{localwater}}$	1.54 $\mu\text{g/l}$ NP	(large)
	0.0099 $\mu\text{g/l}$ NP	(small)
$C_{\text{localwater,ann}}$	1.26 $\mu\text{g/l}$ NP	(large)
	0.008 $\mu\text{g/l}$ NP	(small)
$\text{PEC}_{\text{local}}$	2.14 $\mu\text{g/l}$	(large)
	0.61 $\mu\text{g/l}$	(small)
$\text{PEC}_{\text{local, ann}}$	1.86 $\mu\text{g/l}$	(large)
	0.60 $\mu\text{g/l}$ NP	(small)

#### Nonylphenol ethoxylate use in the polymers industry

The  $\text{PEC}_{\text{local(water)}}$  is calculated for a generic site (parameters and emissions as defined by the TGD).

Daily emission of nonylphenol ethoxylate	1 kg/day
$C_{\text{localinf}}$ to wwtp	0.5 mg/l NPEO
$C_{\text{localeff}}$ from wwtp	0.0125 mg/l NP
$C_{\text{localwater}}$	1.24 $\mu\text{g/l}$ NP
$C_{\text{localwater,ann}}$	1.02 $\mu\text{g/l}$ NP
$\text{PEC}_{\text{local}}$	1.84 $\mu\text{g/l}$
$\text{PEC}_{\text{local, ann}}$	1.62 $\mu\text{g/l}$

#### Nonylphenol ethoxylate use in the pulp, paper and board industry

The  $\text{PEC}_{\text{local(water)}}$  is calculated using information on the use of nonylphenol ethoxylates from the ESD on the industry in the TGD.

Daily emission of nonylphenol ethoxylate	12.5 kg/d
$C_{\text{localinf}}$ to wwtp	6.25 mg/l NPEO
$C_{\text{localeff}}$ from wwtp	0.16 mg/l NPEO
$C_{\text{localwater}}$	15.9 $\mu\text{g/l}$ NP
$C_{\text{localwater,ann}}$	4.4 $\mu\text{g/l}$ NP (100 days use)
	13.2 $\mu\text{g/l}$ NP (300 days use)
$\text{PEC}_{\text{local}}$	16.5 $\mu\text{g/l}$

PEC <sub>local, ann</sub>	5.9 µ/l (100 days use)
	13.8 µg/l NP (300 days use)

### Nonylphenol ethoxylate use in the textile processing industry

The PEC<sub>local(water)</sub> is calculated for a generic scenario as defined in the use category document on surfactants.

Daily emission of nonylphenol ethoxylate	280 kg/day
C <sub>localinf</sub> to wwtp	140 mg/l
C <sub>localeff</sub> from wwtp	3.5 mg/l
C <sub>localwater</sub>	0.35 mg/l
C <sub>localwater,ann</sub>	0.19 mg/l
PEC <sub>local</sub>	350 µg/l
PEC <sub>local, ann</sub>	190 µg/l

### Nonylphenol ethoxylate use in the paints, lacquers and varnishes industry

The PEC<sub>local(water)</sub> is calculated using industry data for emulsion paint production and a generic site (parameters and emissions as defined by the TGD) for paint use.

#### *Emulsion paint production*

Daily emission of nonylphenol ethoxylate	4 kg/day
C <sub>localinf</sub> to wwtp	2 mg/l NPEO
C <sub>localeff</sub> from wwtp	0.05 mg/l NP
C <sub>localwater</sub>	4.96 µg/l NP
C <sub>localwater,ann</sub>	3.39 µg/l NP
PEC <sub>local</sub>	5.56 µg/l
PEC <sub>local, ann</sub>	3.99 µg/l

#### *Paint use*

Daily emission of nonylphenol ethoxylate	0.008 kg/day	(domestic emulsion)
	0.01 kg/day	(industrial)
C <sub>localinf</sub> to wwtp	0.004 mg/l NPEO	(domestic emulsion)
	0.005 mg/l NPEO	(industrial)
C <sub>localeff</sub> from wwtp	0.1 µg/l NP	(domestic emulsion)
	0.125 µg/l NP	(industrial)
C <sub>localwater</sub>	0.01 µg/l NP	(domestic emulsion)
	0.012 µg/l NP	(industrial)
C <sub>localwater,ann</sub>	0.01 µg/l NP	(domestic emulsion)
	0.008 µg/l NP	(industrial)
PEC <sub>local</sub>	0.60 µg/l	(domestic emulsion)
	0.60 µg/l	(industrial)
PEC <sub>local, ann</sub>	0.60 µg/l	(domestic emulsion)
	0.60 µg/l	(industrial)

Information supplied by a paint manufacturer gives a loss of 0.5% nonylphenol ethoxylate during paint production. The resultant C<sub>localwater</sub> from this site was calculated as 0.39 µg/l taking

into account local conditions. This information supports the information supplied in the EPDLA survey.

### Nonylphenol ethoxylate use in the civil and mechanical engineering industry

The  $PEC_{local(water)}$  is calculated for a generic site (parameters and emissions as defined by the TGD).

Daily emission of nonylphenol ethoxylate	24.8 kg/day
$C_{localinf}$ to wwtp	12.4 mg/l NPEO
$C_{localeff}$ from wwtp	0.31 mg/l NP
$C_{localwater}$	30.75 $\mu$ g/l NP
$C_{localwater,ann}$	2.53 $\mu$ g/l NP
$PEC_{local}$	31.3 $\mu$ g/l
$PEC_{local, ann}$	3.12 $\mu$ g/l

#### **3.1.2.1.2 Calculation of $PEC_{regional(water)}$ and $PEC_{continental(water)}$**

The PEC for the region is calculated using the EUSES model; the printout is given in Appendix 2. The inputs to the regional and continental environments are detailed in Section 3.1.1.1.3 and include direct releases of nonylphenol and indirect releases due to breakdown of nonylphenol ethoxylate.

In the model, it is assumed that 2.5% of the nonylphenol ethoxylate released to wastewater treatment plant would eventually be converted and released to surface waters as nonylphenol. Based on the emissions estimated in **Tables 3.3** and **3.4**, the amount of nonylphenol released to surface water as a result of use of nonylphenol ethoxylates is estimated as 2,690 kg/day in the continental model and 299 kg/day in the regional model.

From EUSES a  $PEC_{regional_{surface\ water}}$  of 0.60  $\mu$ g/l and a  $PEC_{continental_{surface\ water}}$  of 0.066  $\mu$ g/l are calculated.

#### **3.1.2.1.3 Calculation of Predicted Environmental Concentration for Sewage Treatment Plants ( $PEC_{stp}$ )**

The  $PEC_{stp}$  is taken as equal to the  $C_{local_{eff}}$ . The  $C_{local_{eff}}$  is calculated in Section 3.1.2.1.1 for all the release scenarios.

#### **3.1.2.1.4 Calculation of $PEC_{sediment}$**

The  $PEC_{sediment}$  can be derived from the  $PEC_{local(water)}$  according to equation 35 of the TGD using the suspended matter-water partitioning coefficient method as given in the TGD.

Details of the calculated  $PEC_{sediment}$  are given in **Table 3.8** below. The regional and continental PECs are calculated using EUSES.

### 3.1.2.1.5 Summary of calculated PECs for surface water

Table 3.8 Summary of calculated concentrations for water and sediment

Life Cycle Stage	PEC <sub>stp</sub> (C <sub>localeff</sub> )	C <sub>localwater</sub>	PEC <sub>localwater</sub>	PEC <sub>localsediment</sub> (wet weight)
Direct releases of nonylphenol				
Nonylphenol Production Sites A B C* D	<1 µg/l(m)	<0.2 µg/l (m) <0.0208 µg/l(m) <0.019 µg/l	<0.60 µg/l <0.60 µg/l	<23.5 µg/kg <70.4 µg/kg <70.4 µg/kg
Nonylphenol ethoxylate production sites B* C 1+2 C 3 D 1 D 2 E* F* G*	7.29, 2.55 mg/l 2.98 mg/l 15 µg/l 13.8 µg/l	0.54-3.02µg/l(m) 0.26 mg/l 0.30 mg/l 1.49 µg/l 1.36 µg/l	0.26 mg/l 0.30 mg/l 2.09 µg/l 1.96 µg/l	63.4-355 µg/kg 30.5 µg/kg 35.2 mg/kg 245 µg/kg 230 µg/kg
Nonylphenol/ formaldehyde resin production	15.75-26.25 µg/l	1.6-2.6 µg/l	2.2-3.2 µg/l	258-376 µg/kg
TNPP production*				
Epoxy resin manufacture	0.46 µg/l	0.05 µg/l	0.65 µg/l	76 µg/kg
Production of other plastic stabilisers	28 µg/l	2.78 µg/l	3.38 µg/l	397 µg/l
Phenolic oxime production	0.318 mg/l (m)	0.004 µg/l	0.60 µg/l	70.4 µg/kg
Indirect releases of nonylphenol due to the breakdown of nonylphenol ethoxylates				
Formulation	12.5, 31, 125 µg/l	1.24, 3.08, 12.4 µg/l	1.84, 3.68, 13.0µg/l	216, 432, 1,526 µg/kg
Pesticide application	n/a	0.08-0.33 µg/l	0.68-0.93 µg/l	79.8-109 µg/kg
Captive use by chemical industry	51 µg/l	0.02 µg/l	0.62 µg/l	73 µg/kg
Electrical engineering applications	30.8 µg/l	3.05 µg/l	3.65 µg/l	428 µg/kg
Industrial and institutional cleaning	259 µg/l	25.7 µg/l	26.3 µg/l	3.09 mg/kg
Leather processing	169-845 µg/l	16.7-83.8 µg/l	17.3-84.4 µg/l	2.03-9.91 mg/kg
Metal processing and extraction	1.43 mg/l	141 µg/l	141 µg/l	1.66 mg/kg
Mineral fuel and oil industry	10-350 µg/l	1-35 µg/l (m)	1.6-35.6 µg/l	0.19-4.18 mg/kg
Photographic industry	0.1-15.5 µg/l	0.009-1.54 µg/l	0.61-2.14 µg/l	71.6-251 µg/kg
Polymer production	12.5 µg/l	1.24 µg/l	1.84 µg/l	216 µg/kg
Pulp, paper and board industry	160 µg/l	15.9 µg/l	16.5 µg/l	1.94 mg/kg

Table 3.8 continued overleaf

**Table 3.8** continued Summary of calculated concentrations for water and sediment

Life Cycle Stage	PEC <sub>stp</sub> (C <sub>localeff</sub> )	C <sub>localwater</sub>	PEC <sub>localwater</sub>	PEC <sub>localsediment</sub> (wet weight)
Textile processing	3.5 mg/l	350 µg/l	350 µg/l	41.1 mg/kg
Paint Production	0.05 mg/l	4.96 µg/l	5.5 µg/l	653 µg/kg
Domestic use	0.1 µg/l	0.01 µg/l	0.60 µg/l	70.4 µg/kg
Industrial use	0.125 µg/l	0.012 µg/l	0.60 µg/l	70.4 µg/kg
Civil engineering	0.31 mg/l	30.75 µg/l	31.3 µg/l	3.67 mg/kg
Regional and Continental PECs due to direct emissions of nonylphenol and the breakdown of nonylphenol ethoxylates				
Regional			0.60 µg/l	103 µg/kg
Continental			0.072 µg/l	13.1 µg/kg

m = measured levels

\* = no emission to water

### 3.1.2.2 Measured levels in water

A variety of extraction techniques and quantification methods may be used to determine concentrations of nonylphenol, depending upon the type of sample being analysed. The most frequently used extraction technique for environmental samples appears to be steam distillation; other techniques include using hexane and methylene chloride as extraction solvents. Quantification of samples is usually by HPLC (High Performance Liquid Chromatography) or GC (Gas Chromatography) using either UV or MS (Mass Spectrometer) detectors. Details about analytical techniques and the detection limits are given below where appropriate.

Nonylphenol can be difficult to analyse for in water, it has a low solubility, and may be adsorbed to the surface of the glassware. Varineau (1996) reported the results of a round robin analysis to determine the effect of analytical methodology on reported nonylphenol/nonylphenol ethoxylate levels in the environment. Blind samples were sent to principal researchers in the nonylphenol area for analysis. The initial conclusion of the study was that analytical methodology was not a likely source for the variation seen in the levels of NP/NPE in environmental samples.

A large number of measured levels of nonylphenol in various water systems is available. The range of levels and typical concentrations reported are described in detail in the subsequent sections. Some of the measured levels reflect the concentrations of nonylphenol near to point sources (e.g. wastewater treatment plant) and so are probably representative of local concentrations of nonylphenol as a result of specific uses of nonylphenol ethoxylates rather than widespread use. Also, given that the use of nonylphenol ethoxylates in domestic detergents in most European countries will have reduced in recent years (due to the industry led voluntary agreement), some of the older measurements (notably the data from the Glatt River in Switzerland) may not reflect the current levels of nonylphenol, particularly where the major source was thought to be from nonylphenol ethoxylate use in detergents.

#### 3.1.2.2.1 Surface waters

In the USA a survey of nonylphenol concentrations in 30 rivers has been conducted (Naylor et al., 1992; Radian Corporation, 1990). Samples for analysis were extracted by steam distillation and formalin added as a preservative. Quantification was by HPLC and the detection limit was 0.107

µg/l. The sampling sites were chosen from the EPA river reach database according to random selection criteria to cover three situations: 5 reaches with identified industrial effluents; 14 reaches having a wastewater treatment plant with less than median dilution; and 11 reaches having one or more treatment plant effluents with more than median dilution. The sites were chosen to allow the results to be projected across the USA with a high degree of confidence. The concentration of nonylphenol in surface waters was below the detection limit in 17 rivers. Concentrations in the other rivers were between <0.11 to 0.64 µg/l, and the average value was 0.12 µg/l.

A number of studies have measured the concentration of nonylphenol in the Glatt river in Switzerland (Ahel et al., 1981; Ahel et al., 1994; Ahel and Giger, 1985; Schaffner et al., 1987; Ahel et al., 1996). Ahel et al. (1981) reported nonylphenol concentrations in the Glatt river between 1-2.8 µg/l with a average concentration of 1.8 µg/l. In a later study concentrations were reported between ≤0.3 µg/l and 45 µg/l. Of the 110 samples analysed, 92 were between 1-10 µg/l and one was above 10 µg/l. The concentration of nonylphenol in a surface water sample taken from below an effluent discharge was reported as 3 µg/l (Ahel and Giger, 1985). In all the studies samples were extracted by steam distillation and quantified by HPLC. Schaffner et al. (1987) reported the concentration of nonylphenol in the Glatt river as 4.1 µg/l. Ahel et al. (1996) reported the concentration of nonylphenol in the Glatt river as 2.7 µg/l (range 0.7-26 µg/l, 16 samples). The detection limit for the method used was quoted as 0.5 µg/l in the Ahel and Giger (1985) paper.

Since these measurements were made controls on the use of nonylphenol and nonylphenol ethoxylate have been implemented in Switzerland. Recent work by Giger (1998) indicates that the levels of nonylphenol in the Glatt river have significantly decreased. The average concentration of nonylphenol in the Glatt river was found to be 0.18 µg/l (range 0.1-0.3 µg/l). In the rivers Thur and Thine the average concentrations (and ranges) were found to be 0.17 µg/l (range 0.09-0.27 µg/l) and 0.04 µg/l (below detection limit to 0.13 µg/l).

Ahel (1991) measured the concentration of nonylphenol in the River Sava in Croatia. Samples were taken from an industrial region which received untreated municipal and industrial wastewaters. Nonylphenol concentrations were between 0.1-1 µg/l. The sampling and analysis technique used was the same as reported in Ahel and Giger (1985).

Blackburn and Waldock (1995) measured the concentration of nonylphenol in 6 rivers in the United Kingdom. Samples for analysis were extracted using a C18 solid phase extraction column and quantified by GC/MS. The detection limit for this method was 0.03 to 0.2 µg/l in water. Nonylphenol concentrations were measured as total extractable nonylphenol (TENP) and dissolved nonylphenol (DNP). The rivers for sampling were chosen to give a wide range of potential nonylphenol inputs and concentrations. The highest concentration of nonylphenol was measured in the River Aire, which receives a high input of industrial surfactants from the textile industry. The lowest concentrations were measured in the River Wye at a remote upland site in a mainly agricultural area. The following concentrations were measured: River Aire TENP <1.6-180 µg/l, DNP <1.6-53 µg/l; River Thames TENP 0.8-2.3 µg/l, DNP 0.6-1.3 µg/l; River Lea TENP 0.5-12 µg/l, DNP 0.2-9.0 µg/l; River Wye TENP 0.2-2.7 µg/l, DNP <0.2-0.9 µg/l; River Ouse TENP 0.6-5.3 µg/l, DNP <0.5-1.3 µg/l. The concentration of nonylphenol in the River Arun at a drinking water abstraction point was <0.2 µg/l.

The concentration of nonylphenol and nonylphenol ethoxylates have been measured in a lake in Eastern Finland. The lake receives inputs from a sewage treatment plant which treats wastewater from a car import and washing business which uses nonylphenol ethoxylate surfactants. The

concentration of nonylphenol in the lake water 1 km from the sewage treatment plant was 0.1-0.8 µg/l. The background concentration of nonylphenol in the lake was reported as 0.01 µg/l (Suoanttila, 1996).

Zellner and Kalbfus (1997) published recent monitoring data from a survey in Bavarian rivers. For the monitoring of nonylphenol concentrations in water, as well as in sediments and sludge from wastewater treatment plants, a specific analytical method using gas chromatography/mass spectrometry was used. The detection limit of the method was 1 ng/l. Downstream of wastewater treatment plants the nonylphenol concentrations were found to be in the range of 0.1-0.4 µg/l, depending on population density and level of industrialisation. At other locations of the rivers the concentrations were much lower in the range of 0.01-0.08 µg/l.

The concentrations of several substances including nonylphenol have been measured in Hessian rivers, sewage and sewage sludge from 1991 to 1995 by the Hessian Landesanstalt für Umwelt (Fooker et al., 1995). The concentration of nonylphenol was measured at 5 locations. At each location the concentration was below 0.5 µg/l (detection limit).

The Bund-/Länderausschuß für Umweltchemikalien (BLAU, 1995) reviewed the available information on nonylphenol concentrations in the environment in Germany. The nonylphenol concentration in the River Main was monitored throughout the years 1989-1991. The nonylphenol concentration in the water (March 1990) was in the range of 0.007 to 3.3 µg/l (47 samples, 90<sup>th</sup> percentile = 0.08 µg/l). One year later (June 1991) the concentrations were in the range of 0.009 to 1.3 µg/l (54 samples, 90<sup>th</sup> percentile = 0.18 µg/l). The average concentrations were found to be 0.038 µg/l (June 1989, 32 samples), 0.052 µg/l (March 1990, 46 samples) and 0.12 µg/l (June 1991, 54 samples).

#### **3.1.2.2.2 Seawater**

Blackburn and Waldock (1995) measured the concentration of nonylphenol in estuarine waters around the UK. Samples for analysis were extracted using a C18 solid phase extraction column and quantified by GC/MS. The detection limit for the method used was 0.03-0.2 µg/l. Nonylphenol concentrations were measured as total extractable nonylphenol (TENP) and dissolved nonylphenol (DNP). The highest concentrations were observed in the Tees estuary at 0.08-3.1 µg/l DNP and 0.09-5.2 µg/l TENP. The Tees estuary is a heavily industrialised area receiving wastewaters from a range of industries. In other estuaries concentrations were below <0.08 µg/l DNP at 8 sampling points and between <0.08-0.32 µg/l TENP at 20 sampling points. The concentration of nonylphenol in seawater near the outfall from a tanker washing operation was reported as 27 µg/l.

#### **3.1.2.2.3 Groundwater**

It should be noted that in this Section the reported levels are not groundwater levels resulting from infiltration of rainwater through soil but are due to infiltration of riverwater to groundwater.

Ahel (1991) measured the concentration of nonylphenol in groundwater near the River Sava in Croatia. Nonylphenol was not detected in samples 120 m from the river or next to and 30m from a municipal landfill. Nonylphenol was detected at between 0.1-1 µg/l in samples taken 3m and 15m from the river at a site receiving industrial wastewater. Samples were extracted for analysis by steam distillation and quantified by HPLC. The detection limit of the method used was not quoted.

Schaffner et al. (1987) reported the concentration of nonylphenol in groundwater near the River Glatt. The average concentrations of nonylphenol in groundwater were 1.0 µg/l (range 0.14-3.1 µg/l, 17 samples), 0.5 µg/l (range <0.1-1.4 µg/l, 17 samples), 0.5 µg/l (range 0.1-1.5 µg/l, 17 samples) and 0.3 µg/l (range 0.1-1.1 µg/l, 17 samples) 2.5m, 5m, 7m and 14 m respectively from the river. The method used for sample extraction and analysis was that reported by Ahel and Giger (1985).

Ahel et al. (1996) also reported the concentration of nonylphenol in groundwater near the River Glatt. Sample extraction and analysis were by the method described in Ahel and Giger (1985). The concentrations of nonylphenol in groundwater were 0.96 µg/l 2.5m from the river (range <0.1-29 µg/l, 16 samples), 0.40 µg/l 5m from the river (range <0.1-4.4 µg/l, 16 samples), 0.44 µg/l 7m from the river (range <0.1-3.4 µg/l, 16 samples), and 0.20 µg/l 13m from the river (range <0.1-33 µg/l, 16 samples).

#### **3.1.2.2.4 Effluent from industrial processes**

Paxéus (1996) measured the concentrations of a range of organic pollutants including nonylphenol in effluent from light vehicle washing and heavy vehicle washing. The concentration of nonylphenol in the effluent from light vehicle washing ranged from 0.01 to 4 mg/l (mean 0.6 mg/l, median 0.26 mg/l). The concentration of nonylphenol in the effluent from heavy vehicle washing ranged from 0.1 to 0.8 mg/l (mean 0.43 mg/l, median 0.41 mg/l).

#### **3.1.2.2.5 Wastewater treatment plant**

Naylor et al. (1992) measured the concentration of nonylphenol in sewage treatment plant influent, effluent and sludge in the USA. All the sewage treatment plants studied used activated sludge digestion. Samples for analysis were extracted by steam distillation and quantified by HPLC. The detection limit for the method used was 0.1 µg/l. Nonylphenol was measured in the influent of a WWTP which receives water from a chemical manufacturing plant (nonylphenol production on-site) at concentrations of 400-800 µg/kg. Nonylphenol concentrations in the effluent were between 23-74 µg/kg. Nonylphenol concentrations in the sludge produced from sewage treatment plants were also measured. The highest concentrations were 2,800 µg/kg and 1,800 µg/kg from a sewage treatment plant receiving wastewaters from cleaning product manufacture and domestic wastewater. The concentration of nonylphenol in sewage sludges from wood pulp mills was between 19-43 µg/kg and 740 µg/kg. All concentrations in sewage sludge are on a dry weight basis.

Giger et al. (1984) analysed sewage sludge samples from mixed digesters during sludge transfer. Samples for analysis were extracted by steam distillation and quantified by GC, MS/GC and HPLC. All the concentrations are reported on a dry weight basis. The detection limit for the method used was not quoted. The concentration of nonylphenol in anaerobically stabilised sludge was 0.45-2.53 g/kg (mean 1.01 g/kg, 30 samples). The concentration of nonylphenol in eight samples, taken from the same digester, over a 10 month period was 0.81-1.49 g/kg (mean 1.18 g/kg). The concentration of nonylphenol in aerobically stabilised sludge was 0.08-0.5 g/kg (mean 0.28 g/kg, 30 samples). The concentration of nonylphenol in activated sludge was 0.09-0.15 g/kg and the concentration of nonylphenol in mixed primary and secondary sludge was 0.04-0.14 g/kg.

Ahel et al. (1981) measured the concentration of nonylphenol in secondary sewage effluent in Switzerland. Samples for analysis were extracted by steam distillation and quantified by HPLC.



The detection limit for the method used was not quoted. Nonylphenol concentrations in the effluent were 14-63  $\mu\text{g/l}$  (mean 40  $\mu\text{g/l}$ ) and 13-42  $\mu\text{g/l}$  (mean 26  $\mu\text{g/l}$ ), from the two sites surveyed. The higher values were from a municipal sewage treatment plant serving a heavily populated area.

Ahel and Giger (1985) surveyed municipal wastewaters and sewage sludges from the Zürich area in Switzerland. Samples for analysis were extracted by steam distillation and quantified by HPLC. The detection limit for the method used was 0.5  $\mu\text{g/l}$  for nonylphenol in water. The concentration of nonylphenol in the raw wastewater was 14  $\mu\text{g/l}$ . The concentration of nonylphenol in the effluent from the water treatment plant was 8  $\mu\text{g/l}$  and the resulting concentration in the receiving waters was 3  $\mu\text{g/l}$ . The concentration of nonylphenol in the effluent from the anaerobic sludge digester was 467  $\mu\text{g/l}$ . The concentration of nonylphenol in the anaerobically digested sludge was measured as 1,000 mg/kg (dry weight) and the concentration of nonylphenol in activated sludge was 128 mg/kg (dry weight).

Blackburn and Waldock (1995) measured the concentration of nonylphenol in wastewater treatment plant effluent in the UK. Samples for analysis were extracted using a C18 solid phase extraction column and quantified by GC/MS. The detection limit for the method used was 0.03 to 0.2  $\mu\text{g/l}$ . The concentration of nonylphenol in the effluent from a sewage treatment plant receiving wastewaters from an industrial area was 330  $\mu\text{g/l}$  (total extractable nonylphenol (TENP)). The concentration of nonylphenol in effluents from sewage treatment plants receiving mainly domestic wastewaters and operating secondary treatment was 0.2-2.9  $\mu\text{g/l}$  (TENP) and 0.1-1.4  $\mu\text{g/l}$  (dissolved nonylphenol (DNP)). The concentration of nonylphenol in effluents from sewage treatment plants receiving mainly domestic wastewaters and operating primary treatment only was 6.7  $\mu\text{g/l}$  (TENP) and 2-5.4  $\mu\text{g/l}$  (DNP).

Brunner et al. (1988) measured the concentration of nonylphenol in sewage treatment plant influent, effluent and sewage sludge. Samples were analysed by HPLC with formaldehyde added as a preservative. The detection limit for the method used was not quoted in the paper. Nonylphenol was measured in the influent of one sewage treatment plant. The total concentration of nonylphenol was 21  $\mu\text{g/l}$ , the dissolved concentration of nonylphenol was 20  $\mu\text{g/l}$  and the total concentration on particles was 2.3 mg/kg (dry weight). Nonylphenol was measured in the effluent from a sewage plant. The total concentration of nonylphenol in the effluent from the primary clarifier was 15  $\mu\text{g/l}$ , the total amount on particulates was 2.9 mg/kg (dry weight) and the total dissolved nonylphenol was 14  $\mu\text{g/l}$ . The total concentration of nonylphenol in the effluent from the secondary clarifier was 2.7  $\mu\text{g/l}$ , the total amount on particulates was 2.7 mg/kg (dry weight) and the total dissolved nonylphenol was 2.7  $\mu\text{g/l}$ . The concentration of nonylphenol in anaerobically digested sewage sludge was between 0.9-2.2 g/kg (dry weight) in samples taken from 25 plants. The concentration of nonylphenol in sludges treated by aerobic sludge stabilisation was between 0.12-0.65 g/kg (dry weight) in samples taken from four plants. The concentration of nonylphenol in activated sludge was 150  $\mu\text{g/l}$  (total concentration), 74 mg/kg (dry weight) and 0.8  $\mu\text{g/l}$  (dissolved nonylphenol) in samples taken from one plant. The concentration of nonylphenol in digested sludge was 78,000  $\mu\text{g/l}$  (total concentration), 1,500 mg/kg (dry weight) and 9  $\mu\text{g/l}$  (dissolved nonylphenol) in samples taken from one plant. The concentration of nonylphenol in raw sewage sludge was 2,850  $\mu\text{g/l}$  (total concentration), 190 mg/kg (dry weight) and 3  $\mu\text{g/l}$  (dissolved nonylphenol) in samples taken from one plant.

Lee and Peart (1995) measured the concentration of nonylphenol in sewage treatment plant effluent and sludge at five sites in a metropolitan area of Canada. Samples were analysed by in-situ acetylation of nonylphenol and GC/MS. The detection limit for nonylphenol was quoted as 0.1 µg/l for water and 0.1 µg/g for sludge and sediment. The concentration in primary effluents was between 4-30 µg/l. The concentration in the final effluents before chlorination was 1.0-15.1 µg/l and in the final effluents after chlorination was 0.8-15.0 µg/l. The concentration in sewage treatment plant sludges was 137-470 µg/g.

Clark et al. (1991) measured the concentration of a number of organic pollutants in wastewater from three publicly owned treatment works in the USA (New Jersey area). Samples from the wastewater were prepared for analysis by liquid/liquid extraction, acid/base extraction and adsorption on a XAD-2 resin column. Quantification was by GC/MS and HPLC/MS. The samples were taken for analysis after wastewater treatment. The first treatment works examined was in a rural area receiving mainly domestic wastewater, the concentration of nonylphenol was between 1-4 µg/l. The second treatment works studied was in an industrial area receiving approximately 27% industrial wastewater. The main industries present were pharmaceutical, paper processing and chemical manufacturing and the concentration of nonylphenol was between 4-5 µg/l. The third treatment works studied was in an industrial area receiving approximately 18% industrial wastewater, the main industries present were textile and dye manufacturing and the concentration of nonylphenol was 1.4 µg/l.

Williams and Varineau (1996) measured the concentration of nonylphenol in biosolids and sludges arising from wastewater treatment plants. Nonylphenol was extracted from the samples by steam distillation and quantified by HPLC. Concentrations of nonylphenol in the anaerobic digester feed were between 3-960 mg/kg (dry weight) and in the anaerobic digester sludge outlet 380-1,030 mg/kg (dry weight). The concentration of nonylphenol in aerobic sludges was between 1-175 mg/kg (dry weight).

The concentrations of several substances including nonylphenol have been measured in Hessian rivers, sewage and sewage sludge from 1991 to 1995 by the 'Hessian Landesanstalt für Umwelt' (Fooker et al., 1995). The mean concentration of nonylphenol in sewage sludge of domestic WWTP was about 25 mg/kg dry weight (range 6-52.1 mg/kg dry weight). The concentration of nonylphenol was determined in 3 effluents of industrial wastewater treatment plants. The concentrations were 1.5 µg/l, 2.9 µg/l and below the detection limit of 0.5 µg/l.

The concentration of nonylphenol and nonylphenol ethoxylates have been measured in a lake in Eastern Finland as reported in Section 3.1.2.2.1. The lake receives inputs from a sewage treatment plant which treats wastewater from a car import and washing business which uses nonylphenol ethoxylate surfactants. The concentration of nonylphenol before wastewater treatment was 100-200 µg/l (nonylphenol ethoxylate concentration 30,000-70,000 µg/l). After wastewater treatment the concentration had dropped to 4-34 µg/l nonylphenol (4,600-12,900 µg/l nonylphenol ethoxylate) (Suoanttila, 1996).

In 1995 the "Bund-/Länderausschuß für Umweltchemikalien" (BLAU, 1995) reviewed the available information on nonylphenol concentrations in the environment in Germany. Nonylphenol concentrations in sludge from domestic and industrial wastewater treatment plants in Brandenburg (Eastern Germany) were determined between October 1993-May 1994. The concentrations were in the range of <1 to 214 mg/kg dry weight in domestic wastewater treatment plants and in the range of <1 to 39 mg/kg dry weight in industrial wastewater treatment plants.

The Danish EPA has conducted a series of studies on the use of waste products in agriculture (Environmental Project No 366). As part of the study, the concentrations of nonylphenol and nonylphenol ethoxylates (with 1 or 2 ethoxylate groups) in sewage sludges typically applied to soil were measured. Nonylphenol was detected in 3 out of 11 samples taken. The average concentration in solids was 34.18 µg/kg dry weight and the highest measured level was 130 µg/kg dry weight (the rest of the samples were below the detection limit 20 µg/kg dry weight). Nonylphenol was not detected in the aqueous extracts suggesting that it is preferentially adsorbed to solids in the sludge.

### 3.1.2.2.6 Sediment

Naylor et al. (1992) analysed sediment samples from 30 rivers in the USA. Samples for analysis were extracted by steam distillation and quantified by HPLC. Formalin was added to the samples prior to quantification as a preservative. The detection limit of the method used was 2.93 µg/kg. The average concentration of nonylphenol in sediment was 162 µg/kg and the range of concentrations measured was <2.9 to 2,960 µg/kg. Nonylphenol was not detected in 6 of the rivers sampled.

Ahel et al. (1994) measured nonylphenol concentrations in sediments in the Glatt river in Switzerland. The sampling and analysis technique used was the same as that used in Ahel and Giger (1985). The range of concentrations found was between 0.51-5.61 mg/kg.

Lee and Peart (1995) measured the concentrations of nonylphenol in sediment samples taken downstream from a pulp and paper mill outflow and from near a sewage treatment plant outflow in Canada. Samples for analysis were extracted in-situ by acetylation of nonylphenol and quantified by GC/MS. The detection limit for nonylphenol in water was quoted as 0.1 mg/kg for sludge and sediment. The nonylphenol concentrations in sediment downstream from a pulp and paper mill outflow were 0.29-1.28 mg/kg. The nonylphenol concentrations in sediment near the outflow of a sewage treatment plant were 1.29-41.1 mg/kg.

Marcomini et al. (1990) measured nonylphenol levels in sediment samples taken from the Lagoon of Venice in Italy. The samples were extracted by steam distillation and quantified by HPLC. The detection limit of the method used was 1 µg/kg (dry weight). Formaldehyde was added to the samples prior to quantification as a preservative. The mean concentration of nonylphenol in the sediment samples was 14 µg/kg (dry weight), the range of concentrations measured was 5-42 µg/kg (dry weight).

The concentrations of nonylphenol and nonylphenol ethoxylates have been measured in sediments in a lake in Eastern Finland. The lake receives inputs from a sewage treatment plant which treats wastewater from a car import and washing business which uses nonylphenol ethoxylate surfactants. The concentration of nonylphenol in sediment 1 km from sewage treatment plant was 180-890 µg/kg (dry weight). The background concentration of nonylphenol in sediment in the lake was reported as 0.43 µg/kg (dry weight) (Suoanttila, 1996).

In 1995 the "Bund-/Länderausschuß für Umweltchemikalien" (BLAU, 1995) reviewed the available information on nonylphenol concentrations in the environment in Germany. In March 1991 the concentrations of nonylphenol in sediments were found to be in the range of 56-14,827 µg/kg dry weight (23 locations, 90 percentile = 9.5 mg/kg). In June 1991 the concentrations were in the range of 22-13,187 µg/kg dry weight (23 locations, 90 percentile = 7.7 mg/kg dry weight). In 1994 the nonylphenol concentration in the suspended matter in the river Main and several

other Hessian surface waters was 170-3,333 µg/kg dry weight (11 samples, average concentration = 800 µg/kg dry weight, 90 percentile = 2.7 mg/kg dry weight). In sediment of Lake Constance nonylphenol concentrations were found to be in the range of <3 to 214 mg/kg dry weight (10 locations, average concentration = 50 µg/kg dry weight, 90<sup>th</sup> percentile = 80 µg/kg dry weight) in June 1991.

### 3.1.2.2.7 Comparison of PECs with measured data

**Table 3.7** summarises the calculated PECs for surface water due to nonylphenol and nonylphenol ethoxylate use. The PECs for nonylphenol production, nonylphenol ethoxylate production and phenolic oximes production are based upon data supplied by industry. The amount of data supplied varies from company to company, so default parameters have been used where applicable. The main areas where this may lead to inaccuracies are in the operating parameters of the treatment plants and the dilution of the effluent in the receiving waters. For production site A where measured levels of nonylphenol in the receiving waters are available the concentration of nonylphenol is low (< 0.2 µg/l). This is lower than if the PEC had been calculated using the release estimations supplied by the company. The remaining PECs are calculated using limited data on nonylphenol or nonylphenol ethoxylate use and the emission tables in Appendix 1 Chapter 3 of the TGD or emission scenario documents.

The measured levels in surface waters are summarised in section 3.1.2.2.1. Naylor et al. (1992) reported concentrations in USA surface waters between <0.11 µg/l (detection limit) and 0.64 µg/l with an average value of 0.12 µg/l. Ahel and co-workers have reported concentrations of nonylphenol from the Glatt river in Switzerland from the 1980s to 1997. The most recent work has shown a significant decrease in surface water concentrations from the early 1980s. The most recent measurements suggest that the average concentration of nonylphenol in the river is 0.18 µg/l (0.1 to 0.3 µg/l). Higher levels in surface waters have been recorded by Blackburn and Waldock with the highest levels observed in surface waters receiving a high level of industrial effluent. The background concentration of nonylphenol in a lake in Finland was reported as 0.01 µg/l with levels rising to 0.1-0.8 µg/l 1 km from a wastewater treatment plant receiving effluent from a car import and washing business. Zellner and Kalbfus have reported data for Bavarian rivers, concentrations of nonylphenol downstream from wastewater treatment plant were found to be in the range of 0.1-0.4 µg/l and at other sites 0.01 to 0.08 µg/l. In Hessian rivers the concentration of nonylphenol was found to be below the detection limit (0.5 µg/l). In the river Main in Germany nonylphenol concentrations of 0.007 to 3.3 µg/l and 0.009 to 1.3 µg/l have being reported.

Based upon these data background concentrations of nonylphenol in surface waters would appear to be relatively low when compared to calculated levels (0.12 µg/l USA; 0.18 µg/l Glatt river; 0.01 µg/l Finnish Lake water; 0.01 to 0.08 µg/l Bavarian rivers; <0.5 µg/l Hessian rivers). A background concentration of nonylphenol of 0.2 µg/l therefore appears to be realistic based upon measured data. The PEC<sub>regional</sub> which is calculated based upon default releases is 0.6 µg/l which, while higher, is of the same magnitude. The recent measured data are typical of areas where the use of ethoxylates has been controlled to some extent, but may not be representative of areas where widespread use still occurs. Therefore the calculated PEC<sub>regional</sub> will be used in the risk assessment, as this is taken as representing an area with widespread use of nonylphenol or nonylphenol ethoxylates.

For seawater, only one set of measurements is available. It is therefore not possible to comment on the representative nature of these data. As with the surface water data, the data available

suggest that higher levels are observed in areas receiving a high level of effluent from industries using either nonylphenol or nonylphenol ethoxylates.

The groundwater levels reported should be used with care as they relate to river water infiltration into groundwater.

The concentration of nonylphenol in the effluent from light vehicle washing (0.01 to 4 mg/l) and heavy vehicle washing (0.1 to 0.8 mg/l) is reported by Paxéus (1996). The  $PEC_{local}$  for public domain uses a concentration of nonylphenol in the effluent to a wastewater treatment plant of 8.7 mg/l, about twice the highest concentration reported here.

The data on measured levels in wastewater treatment plants again show wide variations in nonylphenol concentration depending upon the inputs to the sewage treatment plant. As with the other data reported, wastewater treatment plants receiving effluents from industries which use nonylphenol or nonylphenol ethoxylates generally show higher levels of nonylphenol. The calculated levels in wastewater covered a similar range of concentrations to those measured.

A wide range of sediment concentrations is reported. As with the other data, the concentrations appear to vary widely depending upon the inputs to the receiving waters. The calculation levels again were similar to those measured.

The higher levels reported in waters receiving effluent from industrial activities which use nonylphenol or nonylphenol ethoxylate products suggest that local hotspots may be occurring. These local hotspots are likely to be dependent upon the particular industries in an area. The measured levels downstream of wastewater treatment plants receiving industrial effluents are generally lower than the  $PEC_{local}$  calculated for specific industries. This suggests that the PEC calculations are overestimating the concentrations in receiving waters. The measured data however are not comprehensive enough to have covered receiving waters from all the different industry types which use nonylphenol or nonylphenol ethoxylates. Therefore the calculated PECs will be used in the risk characterisation section despite the concerns over the assumptions made in generating the data.

### **3.1.3 Terrestrial compartment**

#### **3.1.3.1 Calculated PEC for soil**

PECs can be calculated for natural soil, agricultural soil and grassland using equations 36-52 in the TGD. The method takes into account direct releases to soil, application of sewage sludge containing the chemical and atmospheric deposition. For nonylphenol and nonylphenol ethoxylates no direct releases to soil are expected except for use in agricultural products. Soil concentrations are expected to arise due to atmospheric deposition and application in sewage sludge. Of these the concentrations due to atmospheric deposition are expected to be negligible due to the amounts released and the atmospheric behaviour of nonylphenol. The calculated soil concentrations are therefore due to application in sewage sludge. This is to be expected when the behaviour of nonylphenol and nonylphenol ethoxylates in wastewater treatment plants is considered. For nonylphenol 34.4% of the nonylphenol released to a wastewater treatment plant is removed on sewage sludge (default estimation; EUSES). For nonylphenol ethoxylates it is estimated that 19.5% of nonylphenol ethoxylates input into a wastewater treatment plant are removed as nonylphenol in the sludge (See Appendix 1).

EUSES has been used to calculate the PECs for soil. For uses of nonylphenol the PECs have been calculated from the emissions to wastewater treatment plants. Where releases are given as values after wastewater treatment an input release to the wastewater treatment plant has been calculated. For nonylphenol ethoxylates the fraction of nonylphenol in the sludge due to release of nonylphenol ethoxylates is taken as 19.5%. This release figure assumes anaerobic treatment, which not all wastewater treatment plants will use. From the available data (Appendix 1), although it is not possible to estimate the amount of nonylphenol in sludge from purely aerobic treatment plants, it is clear that much less of the nonylphenol ethoxylate is converted to nonylphenol on the sludge at such plants. Therefore using this fraction to estimate the concentrations in sludge will be an overestimation. The calculated concentration in sludge has then been put into EUSES to give the resulting concentrations in soil.

### Regional and Continental PECs due to nonylphenol and nonylphenol ethoxylate use

$$\begin{aligned} \text{PEC}_{\text{continentalagri,soil}} &= 0.0271 \text{ mg/kg wet wt} \\ \text{PEC}_{\text{continentalnat,soil}} &= 2.39 \cdot 10^{-6} \text{ mg/kg wet wt} \\ \text{PEC}_{\text{continentalpore water}} &= 2.86 \cdot 10^{-4} \text{ mg/kg wet wt} \\ \text{PEC}_{\text{regionalagri,soil}} &= 0.265 \text{ mg/kg wet wt} \\ \text{PEC}_{\text{regionalnat,soil}} &= 1.44 \cdot 10^{-5} \text{ mg/kg wet wt} \\ \text{PEC}_{\text{regionalpore water}} &= 2.8 \cdot 10^{-3} \text{ mg/kg wet wt} \end{aligned}$$

### Nonylphenol production

#### *Site A*

There are no indirect emissions to soil as sludge from the on-site treatment plant is incinerated.

#### *Site B*

Sludge from the on-site treatment plant is applied to agricultural land in accordance with local regulations (no limit is set for the amount of nonylphenol applied).

$$\begin{aligned} \text{PEC}_{\text{localagri,soil}} &= 0.0242 \text{ mg/kg wet wt. (averaged over 30 days)} \\ \text{PEC}_{\text{localagri,soil}} &= 0.0204 \text{ mg/kg wet wt. (averaged over 180 days)} \\ \text{PEC}_{\text{localgrassland,soil}} &= 7.94 \cdot 10^{-3} \text{ mg/kg wet wt. (averaged over 180 days)} \end{aligned}$$

#### *Site C*

There are no indirect emissions to soil as sludge from the on-site treatment plant is incinerated.

#### *Site D*

There are no indirect emissions to soil as sludge from the on-site wastewater treatment plant is disposed of to a controlled landfill.

### Production of nonylphenol ethoxylates

Company A - See production above

Company B - No indirect emissions to soil – no on-site wastewater treatment.

Company C - Sites 1 and 2 (The sludge from the on-site industrial wastewater treatment plant is incinerated. No information on fate of sludges at the municipal wastewater treatment plant is available, therefore a worst-case assumption of sewage sludge application to agricultural soil is assumed)

$PEC_{\text{local,agri,soil}} = 15.5 \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 13 \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 5.06 \text{ mg/kg wet wt. (averaged over 180 days)}$

Company C - Site 3 (No information on fate of sludges, therefore a worst-case assumption of sewage sludge application to agricultural soil is assumed)

$PEC_{\text{localagri,soil}} = 18 \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 15.2 \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 5.9 \text{ mg/kg wet wt. (averaged over 180 days)}$

Company D – Site 1 (No information on fate of sludges, therefore a worst-case assumption of sewage sludge application to agricultural soil is assumed)

$PEC_{\text{localagri,soil}} = 1.27 \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 1.07 \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 0.416 \text{ mg/kg wet wt. (averaged over 180 days)}$

Company D – Site 2 (No information on fate of sludges, therefore a worst-case assumption of sewage sludge application to agricultural soil is assumed)

$PEC_{\text{localagri,soil}} = 1.17 \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 0.982 \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 0.382 \text{ mg/kg wet wt. (averaged over 180 days)}$

Companies E, F and G – There are no indirect emissions to soil as the wastewater is incinerated.

#### Use of nonylphenol in polymers industry

##### *Phenol/formaldehyde resins production*

$PEC_{\text{localagri,soil}} = 0.159 \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 0.134 \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 0.0522 \text{ mg/kg wet wt. (averaged over 180 days)}$

##### *TNPP Production*

There are no indirect emissions to soil as wastewater from production plants is incinerated.

##### *Epoxy resin production*

$PEC_{\text{localagri,soil}} = 2.77 \cdot 10^{-3} \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 2.34 \cdot 10^{-3} \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 9.17 \cdot 10^{-4} \text{ mg/kg wet wt. (averaged over 180 days)}$

*Other plastic stabilisers*

$PEC_{\text{localagri,soil}} = 0.17 \text{ mg/kg wet wt. (averaged over 30 days)}$   
 $PEC_{\text{localagri,soil}} = 0.143 \text{ mg/kg wet wt. (averaged over 180 days)}$   
 $PEC_{\text{localgrassland,soil}} = 0.0555 \text{ mg/kg wet wt. (averaged over 180 days)}$

Production of phenolic oximes

There are no indirect emissions to soil as the sludge from on-site treatment plant is disposed of to landfill.

Formulation of nonylphenol ethoxylates*Large-scale formulator*

$PEC_{\text{localagri,soil}} = 10.6 \text{ mg/kg wet wt. (averaged over 30 days)}$   
 $PEC_{\text{localagri,soil}} = 8.95 \text{ mg/kg wet wt. (averaged over 180 days)}$   
 $PEC_{\text{localgrassland,soil}} = 3.51 \text{ mg/kg wet wt. (averaged over 180 days)}$

*Medium-scale formulator*

$PEC_{\text{localagri,soil}} = 2.67 \text{ mg/kg wet wt. (averaged over 30 days)}$   
 $PEC_{\text{localagri,soil}} = 2.25 \text{ mg/kg wet wt. (averaged over 180 days)}$   
 $PEC_{\text{localgrassland,soil}} = 0.905 \text{ mg/kg wet wt. (averaged over 180 days)}$

*Small-scale formulator*

$PEC_{\text{localagri,soil}} = 1.07 \text{ mg/kg wet wt. (averaged over 30 days)}$   
 $PEC_{\text{localagri,soil}} = 0.899 \text{ mg/kg wet wt. (averaged over 180 days)}$   
 $PEC_{\text{localgrassland,soil}} = 0.359 \text{ mg/kg wet wt. (averaged over 180 days)}$

Captive use of nonylphenol ethoxylates by the chemical industry

$PEC_{\text{localagri,soil}} = 4.33 \text{ mg/kg wet wt. (averaged over 30 days)}$   
 $PEC_{\text{localagri,soil}} = 3.64 \text{ mg/kg wet wt. (averaged over 180 days)}$   
 $PEC_{\text{localgrassland,soil}} = 1.42 \text{ mg/kg wet wt. (averaged over 180 days)}$

Electrical and electronic industry

$PEC_{\text{localagri,soil}} = 2.61 \text{ mg/kg wet wt. (averaged over 30 days)}$   
 $PEC_{\text{localagri,soil}} = 2.20 \text{ mg/kg wet wt. (averaged over 180 days)}$   
 $PEC_{\text{localgrassland,soil}} = 0.853 \text{ mg/kg wet wt. (averaged over 180 days)}$

Industrial and institutional cleaning

$PEC_{\text{localagri,soil}} = 21.9 \text{ mg/kg wet wt. (averaged over 30 days)}$   
 $PEC_{\text{localagri,soil}} = 18.5 \text{ mg/kg wet wt. (averaged over 180 days)}$   
 $PEC_{\text{localgrassland,soil}} = 7.18 \text{ mg/kg wet wt. (averaged over 180 days)}$



Leather industry

$PEC_{\text{localagri,soil}} = 14.3, 71.6 \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 12.1, 60.3 \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 4.68, 23.4 \text{ mg/kg wet wt. (averaged over 180 days)}$

Manufacture and blending of additives in the fuel industry

The disposal practices of the members of the ATC vary considerably. Not all members use nonylphenol or nonylphenol ethoxylates. Of those that do, some incinerate their wastes, while others dispose of their wastes to wastewater treatment plants. Of those plants disposing of their wastes to wastewater none report the subsequent disposal of sludges to agricultural soil. However as the survey did not cover all sites within the EU, this disposal route cannot be ruled out. Losses from the manufacture and blending of additive components are likely to be in line with losses due to captive use within the chemical industry (i.e. both are synthesis processes). The concentrations in soil calculated due to captive use in the chemical industry will be taken as applicable for this use as well.

Metal extraction and finishing industry

$PEC_{\text{localagri,soil}} = 121 \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 102 \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 39.5 \text{ mg/kg wet wt. (averaged over 180 days)}$

Photographic industry

$PEC_{\text{localagri,soil}} = 0.00903, 1.31 \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 0.0076, 1.11 \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 0.00296, 0.43 \text{ mg/kg wet wt. (averaged over 180 days)}$

Polymer industry

$PEC_{\text{localagri,soil}} = 1.06 \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 0.893 \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 0.347 \text{ mg/kg wet wt. (averaged over 180 days)}$

Pulp and paper industry

$PEC_{\text{localagri,soil}} = 13.3 \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 11.2 \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 4.34 \text{ mg/kg wet wt. (averaged over 180 days)}$

Textile industry

$PEC_{\text{localagri,soil}} = 297 \text{ mg/kg wet wt. (averaged over 30 days)}$

$PEC_{\text{localagri,soil}} = 250 \text{ mg/kg wet wt. (averaged over 180 days)}$

$PEC_{\text{localgrassland,soil}} = 97.1 \text{ mg/kg wet wt. (averaged over 180 days)}$

### Paint industry (Production)

$PEC_{\text{localagri,soil}} = 4.24$  mg/kg wet wt. (averaged over 30 days)  
 $PEC_{\text{localagri,soil}} = 3.57$  mg/kg wet wt. (averaged over 180 days)  
 $PEC_{\text{localgrassland,soil}} = 1.39$  mg/kg wet wt. (averaged over 180 days)

### Paint industry (Domestic use)

$PEC_{\text{localagri,soil}} = 0.0085$  mg/kg wet wt. (averaged over 30 days)  
 $PEC_{\text{localagri,soil}} = 0.00716$  mg/kg wet wt. (averaged over 180 days)  
 $PEC_{\text{localgrassland,soil}} = 0.00279$  mg/kg wet wt. (averaged over 180 days)

### Paint industry (Industrial use)

$PEC_{\text{localagri,soil}} = 0.0106$  mg/kg wet wt. (averaged over 30 days)  
 $PEC_{\text{localagri,soil}} = 0.00894$  mg/kg wet wt. (averaged over 180 days)  
 $PEC_{\text{localgrassland,soil}} = 0.00348$  mg/kg wet wt. (averaged over 180 days)

### Civil and mechanical industry

$PEC_{\text{localagri,soil}} = 26.3$  mg/kg wet wt. (averaged over 30 days)  
 $PEC_{\text{localagri,soil}} = 22.1$  mg/kg wet wt. (averaged over 180 days)  
 $PEC_{\text{localgrassland,soil}} = 8.6$  mg/kg wet wt. (averaged over 180 days)

### Use of nonylphenol ethoxylates in agriculture

As nonylphenol ethoxylates are used in pesticides which are applied directly to soil, a different approach than that used for the applications described above is required. Information supplied by industry to calculate surface water concentrations (Section 3.1.2.1.1) assumed 4% drift of the pesticide application to surface waters downstream of pesticide application. This suggests that 96% of the pesticide is applied to soil. The amount of nonylphenol ethoxylate applied is reported as 48-192 g/ha, this is equivalent to 4.8-19.2 mg/m<sup>2</sup>. As a worst case the higher application rate will be considered. The concentration in soil of the nonylphenol ethoxylate can be obtained by dividing by the mixing depth for agricultural soil (0.2 m), which gives a soil concentration of 96 mg/m<sup>3</sup> nonylphenol ethoxylate. To convert this to mg/kg dry weight the concentration is divided by the bulk density of soil (1,700 kg/m<sup>3</sup>). This gives a concentration of nonylphenol ethoxylate in soil of 56.5 µg/kg dry weight. In the soil the nonylphenol ethoxylate will break down slowly to nonylphenol, which will itself subsequently undergo degradation. If a worst-case scenario is assumed, that nonylphenol ethoxylate breaks down instantly to nonylphenol, and taking an average side-chain length of 7, the concentration of nonylphenol is 23.4 µg/kg. This concentration is based upon one application per year. In practice there may be multiple applications during the year or applications of other products containing nonylphenol ethoxylates. However the assumption of complete production of nonylphenol from nonylphenol ethoxylate is already a significant overestimate, so for the purpose of the current calculation only one application per year is considered. Multiple applications will be considered in the risk characterisation. The fraction of nonylphenol accumulating per year is calculated as 0.416. This gives a concentration after 10 years application of 40 µg/kg. The concentration in agricultural soil averaged over 30 days is 38.6 µg/kg and over 180 days is 32.5 µg/kg after the initial application.

For veterinary medicine products application rates have been calculated for application of parlour washings containing teat dip formulation, direct irrigation of water containing teat dip formulation to fields and spreading of sheep dip on land. The application rate for parlour washings containing teat dip formulation is  $12.5 \text{ mg/m}^2$  nonylphenol ethoxylate to agricultural soil. Application to soil occurs every two weeks, but this could be considered as continuous input, at a rate of  $0.9 \text{ mg/m}^2/\text{day}$ . This gives a concentration in soil after 10 years of  $1.1 \text{ mg/kg}$  NPEO or  $0.46 \text{ mg/kg}$  NP. The application rate for direct irrigation of water containing teat dip formulation is  $0.6 \text{ mg/m}^2/\text{day}$  nonylphenol ethoxylate to agricultural soil. This gives a concentration in soil after 10 years of  $0.73 \text{ mg/kg}$  NPEO or  $0.30 \text{ mg/kg}$  NP. The application rate for sheep dips is  $400 \text{ mg/m}^2$  nonylphenol ethoxylate to agricultural soil. Using the method described above for pesticides the resultant concentration of nonylphenol in soil is  $0.5 \text{ mg/kg}$  nonylphenol. This concentration is based upon one application per year. In practice there may be multiple applications during the year or applications of other products containing nonylphenol ethoxylates. The fraction of nonylphenol accumulating per year is calculated as 0.416. This gives a concentration after 10 years application of  $0.85 \text{ mg/kg}$ . The concentration averaged over 30 days is  $0.82 \text{ mg/kg}$  and over 180 days is  $0.69 \text{ mg/kg}$ .

In calculating the PECs for soil due to agricultural use of products containing nonylphenol ethoxylates several assumptions have been made. These assumptions are likely to give rise to worst-case PECs. Since in practice the breakdown of the ethoxylate in the environment will be gradual.

### 3.1.3.2 Measured levels

Marcomini et al. (1992) measured the levels of nonylphenol in sludge amended soil and sludge-only landfills. The study looked at the behaviour of nonylphenol in grassland treated with sewage sludge (Section 3.1.1.2.3.). Soil samples were collected from the upper 5 cm of planted grassland that had received anaerobically digested sludge at an average application rate of 13.5 tonnes/ha year (dry weight). The sludge was applied to the surface soil as a liquid spread four to six times per year. Samples were dried at  $60^\circ\text{C}$ , pulverised to a particle size of  $<300 \mu\text{m}$  and stored in the dark at  $4^\circ\text{C}$ . Nonylphenol was analysed by extraction with hexane and quantification by HPLC with a UV-fluorescence detector. The initial concentration of nonylphenol in the soil was  $4.7 \text{ mg/kg}$ , but this had dropped to  $0.46 \text{ mg/kg}$  dry weight after 322 days. The concentration of nonylphenol in grassland soil that had not been treated with sewage sludge was  $<0.02 \text{ mg/kg}$  (dry weight). The study also looked at nonylphenol concentrations in sludge-only landfill sites. The concentration of nonylphenol in the sludge samples ranged from 4-37  $\text{mg/kg}$  (dry weight) for raw sewage sludges and 7-375  $\text{mg/kg}$  (dry weight) for digested sludges.

The Danish EPA has conducted a series of studies on the use of waste products in agriculture (Environmental Project No 366). As part of the study the concentration of nonylphenol ethoxylates (with 1 or 2 ethoxylate groups) in compost were measured. The compost was based upon green household waste. The concentration of nonylphenol ethoxylates in the compost was  $780 \mu\text{g/kg}$  dry weight. As only one sample was taken it is uncertain how representative it is. The concentration of nonylphenol ethoxylates in cattle slurry was also measured. In slurry from a conventional farm the concentration was  $64 \mu\text{g/l}$  ( $1,050 \mu\text{g/kg}$  dry weight) and in slurry from an organic farm the concentration was  $45 \mu\text{g/l}$  ( $1,160 \mu\text{g/kg}$  dry weight).

Krogh et al. (1996) (as included in personal communication from Danish EPA) detected nonylphenol and nonylphenol ethoxylates in non-contaminated soils in Denmark. The

concentration of nonylphenol and nonylphenol ethoxylates was 0.007 mg/kg in a clayey soil and 0.003 mg/kg in a sandy soil.

The Danish EPA reports that levels of nonylphenol in soil after sludge application are typically 0.3-1.0 mg/kg but that they can go up to 4.7 mg/kg. These measured levels are of the same order as a number of those calculated, but the PECs for some industries are much higher.

### 3.1.4 Atmospheric compartment

There are no reported measurements of nonylphenol in the atmosphere. Considering the low vapour pressure of nonylphenol, and its tendency to adsorb to soils and sediments it would be expected that atmospheric concentrations of nonylphenol would be low. PECs for the air compartment have been estimated from the release values given in Section 3.1.1.1, using EUSES (see Appendix 2) and are shown below. The local PECs are calculated for direct release of nonylphenol only. Indirect releases of nonylphenol from wastewater treatment plants treating nonylphenol or nonylphenol ethoxylate containing wastes are virtually zero. Indirect emissions of nonylphenol due to the breakdown of nonylphenol ethoxylates have been considered in the regional and continental models only. In these models it has been assumed that the nonylphenol ethoxylate has a chain length of 7 and breaks down instantaneously in the atmosphere to nonylphenol.

PEC <sub>continentalair</sub>	= $5.21 \cdot 10^{-7}$ mg/m <sup>3</sup>
PEC <sub>regionalair</sub>	= $3.14 \cdot 10^{-6}$ mg/m <sup>3</sup>
PEC <sub>localair</sub> (Production of nonylphenol)	= 8.37 µg/m <sup>3</sup> (emission episode) Site A = 6.88 µg/m <sup>3</sup> (annual average) Site A = Emissions to air incinerated Site B = Emissions to air incinerated Site C = Emission to air incinerated Site D
PEC <sub>localair</sub> (Production of nonylphenol ethoxylate)	= 0.136 µg/m <sup>3</sup> (emission episode) Company B = 0.112 µg/m <sup>3</sup> (annual average) Company B = 0.0278 µg/m <sup>3</sup> (emission episode) Company C (1,2) = 0.0228 µg/m <sup>3</sup> (annual average) Company C (1,2) = 0.316 µg/m <sup>3</sup> (emission episode) Company C (3) = 0.0849 µg/m <sup>3</sup> (annual average) Company C (3) = 0.0334 µg/m <sup>3</sup> (emission episode) Company D (1) = $9.14 \cdot 10^{-5}$ µg/m <sup>3</sup> (annual average) Company D (1) = 0.0019 µg/m <sup>3</sup> (emission episode) Company D (2) = $5.33 \cdot 10^{-6}$ µg/m <sup>3</sup> (annual average) Company D (2) = 0.0083 µg/m <sup>3</sup> (emission episode) Company E = 0.00685 µg/m <sup>3</sup> (annual average) Company E = 0.222 µg/m <sup>3</sup> (emission episode) Company F = 0.183 µg/m <sup>3</sup> (annual average) Company F
PEC <sub>localair</sub> (Phenol/formaldehyde resins)	= 0.042 µg/m <sup>3</sup> (emission episode) = 0.0343 µg/m <sup>3</sup> (annual average)
PEC <sub>localair</sub> (TNPP production)	= Emissions to air incinerated
PEC <sub>localair</sub> (Epoxy resins)	= 0.0007 µg/m <sup>3</sup> (emission episode) = 0.000194 µg/m <sup>3</sup> (annual average)
PEC <sub>localair</sub> (Plastic stabilisers)	= 0.003 µg/m <sup>3</sup> (emission episode) = $8/16 \cdot 10^{-6}$ µg/m <sup>3</sup> (annual average)
PEC <sub>localair</sub> (Production of phenolic oximes)	= Emissions to air incinerated

Other uses do not lead to direct nonylphenol emissions to air.

### 3.1.5 Non compartment specific effects relevant for the food chain (Secondary poisoning)

Uptake experiments are described in Section 3.1.1.3.4. Bioconcentration factors for fish were 10-1,300 (with most values >100) on a whole body fresh weight basis. The value calculated from the log Kow in EUSES is of the same order (1,280). Section 3.1.1.3.4 also has levels in fish measured by Ahel et al. (1993) in the Glatt River in Switzerland. These range from <0.03 to 1.6 mg/kg dry weight. The average concentration of nonylphenol in the river during the sampling period was 3.9 µg/l.

EUSES has been used to calculate the concentration of nonylphenol in fish and earthworms (**Table 3.9**) and daily human intake due to indirect exposure to nonylphenol in the environment (see Section 4). The regional concentration of nonylphenol in fish calculated by EUSES was of a similar order compared to those measured by Ahel et al. (1993). Much higher values were calculated for local concentrations based on the default emissions to water.

Ahel et al. (1993) also reported levels in samples from ducks taken from the Glatt River; the highest value was 1.2 mg/kg dry weight in muscle.

A further possible route of exposure for higher animals which might be considered is the consumption of plants which have been sprayed with pesticide containing nonylphenol ethoxylates.

An application rate of 20 mg/m<sup>2</sup> (see Section 3.1.1.1.2) to leaves of 2 mm thickness gives 20 mg to 2 · 10<sup>-3</sup> m<sup>3</sup> leaf, giving a concentration of 10<sup>4</sup> mg/m<sup>3</sup>. Taking the density of plant material as 700 kg/m<sup>3</sup> from the TGD gives a concentration of 14 mg/kg. This is nonylphenol ethoxylate; assuming this is converted entirely to nonylphenol gives a concentration of 6 mg/kg.

There are a number of worst-case assumptions in this estimate (e.g. complete breakdown to nonylphenol, animals eat only from contaminated leaves); as these are combined then this is likely to be a significant over-estimate.

Table 3.9 PEC for Secondary Poisoning

Life Cycle Stage	Concentration in fish for predators (mg/kg wet weight)	Concentration in earthworms (mg/kg wet weight)
Direct releases of nonylphenol		
Nonylphenol production		
Site A	7.95	n/a
Site B	0.775	1.82
Site C	n/a	n/a
Site D	0.764	n/a
Nonylphenol ethoxylate production		
Company B	2.34	n/a
Company C	134, 156	84.7, 98.5
Company D	1.55, 1.48	8.52, 7.95
Company E	n/a	n/a
Company F	n/a	n/a
Company G	n/a	n/a
Phenol/formaldehyde resin production	2.14	2.55
TNPP production	n/a	n/a
Epoxy resin production	0.787	1.71
Production of other plastic stabilisers	2.23	2.6
Phenolic oximes production	0.766	n/a
Indirect releases of nonylphenol from the breakdown of ethoxylates		
Formulation of nonylphenol ethoxylates	1.42, 2.4, 7.3	7.51, 16, 58.7
Agriculture - pesticide application veterinary medicine use	0.79*	1.9 6.1
Captive use by the chemical industry	0.774	24.9
Electrical engineering industry	2.37	15.7
Industrial and institutional cleaning	14.3	120
Leather processing	9.59, 44.9	78.6, 386
Metal extraction	75.3	651
Mineral fuel and oil (Manufacture and blending)	2.38	24.9
Photographic industry	0.769, 1.57	1.74, 8.75
Polymer industry	1.42	7.38
Pulp, paper and board industry	8.93	72.9
Textile processing	184	1,600
Paints, lacquers and varnishes	3.38 (Manufacturing) 0.769 (Domestic use) 0.77 (Industrial use)	24.5 (Manufacturing) 1.74 (Domestic use) 1.75 (Industrial use)
Civil engineering	17	143
Regional	0.764	1.69

\* - calculated from average water concentration over 30 days from application, assuming half-life for removal from water of 2.5 days.

## 3.2 EFFECTS ASSESSMENT: HAZARD IDENTIFICATION AND DOSE (CONCENTRATION) - RESPONSE (EFFECT ASSESSMENT)

### 3.2.1 Aquatic compartment (including sediment)

#### 3.2.1.1 Toxicity test results

##### 3.2.1.1.1 Criteria for validation

Studies are classed as valid if they fully describe the test material used, the test organism, the test method and conditions and if the endpoint concentration is based upon measured levels. Where only some of these criteria are described the tests may be used with care or considered not valid. Studies marked ‘use with’ care can be used to support valid studies. For some studies a ‘lack of data’ marking is given. In these cases the original paper has not been received but only a citation. However the results from these non-validated studies are higher than those from the studies already checked so validating such references will not change the outcome of the PNEC derivation.

##### 3.2.1.1.2 Fish

**Table 3.9** summarises the toxicity test results for fish exposed to nonylphenol. This section considers toxic effects; endocrine effects are considered in Section 3.2.1.1.7.

#### Acute toxicity

The lowest 96-hour LC<sub>50</sub> reported from a fully valid study is 0.128 mg/l for the freshwater species, the fathead minnow (*Pimephales promelas*) (Brooke, 1993a). It has not been possible to validate the data from some of the remaining studies on freshwater species. As the study with the lowest LC<sub>50</sub> is already validated, validating the remainder of the data set will not change the value used in calculating a PNEC<sub>aquatic organisms</sub>.

The lowest 96-hour LC<sub>50</sub> reported for seawater species is 0.017 mg/l for the winter flounder (*Pleuronectes americanus*) (Lussier et al.). This study is given a validity marking of ‘use with care’ because only a summary report is available. The lowest value from a valid study is a 96-hour LC<sub>50</sub> of 0.31 mg/l for sheepshead minnow (*Cyprinodon variegatus*) (Ward and Boeri, 1990d).

#### Long-term toxicity

A long-term study on fathead minnow (*Pimephales promelas*) embryos (Ward and Boeri, 1991b) gives a 33-day LOEL<sub>survival</sub> of 0.014 mg/l and a 33-day NOEL<sub>survival</sub> of 0.0074 mg/l (LOEL and NOEL are taken to be equivalent to LOEC and NOEC respectively). Brooke (1993b) reports the results from a 28-day study on fathead minnow (*Pimephales promelas*); a 28-day NOEC<sub>mortality</sub> of 0.0775 mg/l and a 28-day LOEC<sub>mortality</sub> of 0.193 mg/l are reported. Both of these studies are valid.

Ashfield et al. (1998) reported a study of the effect of prolonged exposure to nonylphenol on growth of female juvenile rainbow trout. Details of the study are included in Section 3.2.1.1.7, as it also investigated possible endocrine disrupting effects. Concentrations were not measured and were widely spaced at lower concentrations, so the results are only supportive, but they indicate a NOEC between 1 and 10 µg/l.

### 3.2.1.1.3 Aquatic invertebrates

**Table 3.11** summarises the toxicity of nonylphenol to aquatic invertebrates. From the data presented, the lowest acute toxicity value from a fully valid study for freshwater aquatic invertebrates is a 96-hour EC<sub>50</sub> of 0.0207 mg/l for the amphipod *Hyaella azteca* (Brooke et al., 1993a). The lowest acute toxicity value for *Daphnia magna* from a fully valid study is a 48-hour EC<sub>50(Immobilisation)</sub> of 0.085 mg/l (Brooke, 1993a). For marine invertebrates the lowest value from a validated study is a 96-hour LC<sub>50</sub> of 0.043 mg/l for the mysid *Mysidopsis bahia* (Ward and Boeri, 1990c). For seawater species lower values are reported in studies by Lussier et al., though these studies are to be used with care as only limited data are given in the test report. The lowest value reported by Lussier et al. is a 96-hour LC<sub>50</sub> of 0.038 mg/l for the Coot Clam (*Mulinia lateralis*).

The chronic toxicity of nonylphenol (>95% 4-nonylphenol) to the midge *Chironomus tentans* has been studied in a semi-static system (Kahl et al., 1997). In the test, midge larvae (<24h old) were introduced into open test chambers, containing 5 ml of 146 µm washed sand, held within tanks held at 23°C, pH 7.73, with a dissolved oxygen concentration of 7.04 mg/l. The larvae were exposed to nominal nonylphenol concentrations of 12.5-200 µg/l, with renewal of the test system every 12 hours. Samples of the test solution were analysed for nonylphenol on days 0, 4, 11, 18, 25, 42, 48 and 53. The results indicated that, immediately after renewal, the concentration in the test tanks for the first 18 days of the test were generally within 20% of the nominal value. However, by the last sampling date the concentrations were around 50% of the nominal value. It was also found that the measured concentrations in the actual test chambers were around 50% of that in the tank in which they were held. These effects on the actual exposure concentration were accounted for when the overall effect and no effect concentrations were determined. The test looked at various end-points including survival and growth at 20 days (4th instar life stage); survival from 4th instar through emergence and subsequent reproduction (total exposure time was 53 days). The only statistically significant effect seen was a reduction in survival at 20 days at the highest concentration tested, giving a NOEC of 42 µg/l and LOEC of 91 µg/l for these effects, based on the measured concentrations in the test chambers. No significant effects were seen on larval growth (at day 20), organism survival past day 20, emergence success or pattern, sex ratio, fecundity or egg viability at any treatment level. There was an increased incidence of irregular-shaped egg-masses observed, particularly at the highest exposure concentration, but the biological significance this effect is unknown. The NOEC for this effect was in the range 15-45 µg/l.

Other long-term toxicity data are reported for marine and freshwater invertebrates. The lowest value from a fully valid study on freshwater organisms is a 21-day NOEC<sub>surviving offspring</sub> of 24 µg/l for *Daphnia magna* (Comber et al., 1993). For seawater species a 21-day NOEC<sub>length</sub> of 3.9 µg/l is reported for the mysid *Mysidopsis bahia* (Ward and Boeri, 1991c). This test is considered valid for use in the risk assessment. A 21-day NOEC<sub>reproduction</sub> for *Daphnia magna* of 0.001 mg/l is reported by Kopf (1997). However, although the study was carried out according to the current guidelines, the interval between test concentrations is considered too great to allow a NOEC to be defined. Thus this test is taken as showing the NOEC to be between 1 and 10 µg/l.



Table 3.10 Toxicity of nonylphenol to fish

Freshwater species											
Species	Chemical tested	Age/Size	Stat/Flow	Temp (°C)	Dissolved oxygen (mg/l)	Hardness (mg CaCO <sub>3</sub> /l)	pH	Endpoint	Concentration (mg/l)	Reference	Validity
Fathead minnow <i>Pimephales promelas</i>	nonylphenol (91% 4-nonylphenol; 4% 2-nonylphenol; 5% dinonylphenol)	31-35 days 220 mg	flow	24.6 ± 1.4	Mean 7.4 Range 4.6-8.8	Mean 44.9 Range 42.2-46.6	6.9-7.7	96hr LC <sub>50</sub> 96hr LOEC <sub>lethargy</sub> 96hr LOEC <sub>loss of equilibrium</sub>	0.135 (m) 0.187 (m) 0.098 (m)	Holcombe et al (1984)	Valid
	nonylphenol, 4- branched CAS No. 84852-15-3	embryos <24 hrs old	flow	25 ± 1.5	7.1 - 8.2	160-180 mg/l	7.4-8.1	33 day LOEC <sub>survival</sub> 33 day NOEC <sub>survival</sub>	0.014 (m) 0.0074 (m)	Ward and Boeri (1991b)	Valid
	nonylphenol	25-35 days	flow					96hr LC <sub>50</sub> 96hr EC <sub>50</sub>	0.128 (m) 0.096 (m)	Brooke (1993a)	Valid
	nonylphenol							96hr LC <sub>50</sub>	0.51	Waldock and Thain (1991)	Lack of data
	nonylphenol	30 day	flow					96hr NOEC <sub>mortality</sub> 96hr LOEC <sub>mortality</sub> 28 day NOEC <sub>mort</sub> 28 day LOEC <sub>mort</sub>	0.0831 (m) 0.23 (m) 0.0775 (m) 0.193 (m)	Brooke (1993b)	Valid
Bluegill <i>Lepomis macrochirus</i>	nonylphenol	< 1 year	flow					96hr LC <sub>50</sub> 96hr EC <sub>50</sub>	0.209 (m) 0.203 (m)	Brooke (1993a)	Valid
	nonylphenol	10-12 weeks	flow					96hr NOEC <sub>mortality</sub> 96hr LOEC <sub>mortality</sub> 28 day NOEC <sub>mort</sub> 28 day LOEC <sub>mort</sub>	0.0865 (m) 0.211 (m) 0.0595 (m) 0.126 (m)	Brooke (1993b)	

Table 3.10 continued overleaf

Table 3.10 continued Toxicity of nonylphenol to fish

Freshwater species											
Species	Chemical tested	Age/Size	Stat/Flow	Temp (°C)	Dissolved oxygen (mg/l)	Hardness (mg CaCO <sub>3</sub> /l)	pH	Endpoint	Concentration (mg/l)	Reference	Validity
Killifish <i>Oryzias latipes</i>	4-nonylphenol	0.2 g	stat			25	7.0	96hr LC <sub>50</sub>	0.4	Yoshimura (1986)	Lack of data
Stickleback <i>Gasterostrus aculeatus</i>	nonylphenol							48hr LC <sub>50</sub>	1.4	Granmo (1991)	Lack of data
Brook trout <i>Salvelinus fontinalis</i>	nonylphenol							96hr LC <sub>50</sub>	0.145	Armstrong and Kingsbury (1979)	Lack of data
Rainbow trout <i>Oncorhynchus Mykiss</i>	nonylphenol	fingerling						96hr LC <sub>50</sub>	0.23	Armstrong and Kingsbury (1979)	Lack of data
	nonylphenol	45 days post hatch	flow					96hr LC <sub>50</sub> 96hr EC <sub>50</sub>	0.221 0.109	Brooke (1993a)	Valid
	nonylphenol	embryo juvenile						24hr LC <sub>50</sub>	0.48	Ernst et al. (1980)	Lack of data
Golden orfe <i>Leuciscus idus melanotus</i>	nonylphenol	6 ± 2 cm	stat	20 ± 2	> 5 mg/l		7.2-7.3	48hr LC <sub>50</sub>	0.56 (n)	Hüls (1996f)	Use with care
Atlantic salmon <i>Salmo salar</i>	nonylphenol	juvenile	flow					96hr LC <sub>50</sub>	0.13-0.16 mg/l	McLeese et al. (1981)	Use with care
		juvenile	stat					96hr LC <sub>50</sub>	0.19 mg/l	McLeese et al. (1981)	Use with care

Table 3.10 continued overleaf

Table 3.10 continued Toxicity of nonylphenol to fish

Saltwater species											
Species	Chemical tested	Age/Size	Stat/Flow	Temp (°C)	Dissolved oxygen (mg/l)	Salinity o/oo	pH	Endpoint	Concentration (mg/l)	Reference	Validity
Cod Gadus morhua	nonylphenol			17				96hr LC <sub>50</sub> 15 day LC <sub>50</sub>	3 0.1	Swedmark et al. (1971)	Lack of data
Guppy Poecilia reticulata	4-nonylphenol	3 weeks old	stat	25		28	8	96hr LC <sub>50</sub> 96hr NOEC	0.44 (n) 0.18 (n)	Personal communication	Use with care
Hook nose Agonus cataphractus	nonylphenol							96hr LC <sub>50</sub>	0.3	Etnier (1985)	Lack of data
Sheepshead minnow Cyprinodon variegatus	nonylphenol, 4- branched CAS No. 84852-15-3	juvenile	flow	22 ± 2	7.0 - 8.8	15-17	7.4-8.1	96hr LC <sub>50</sub> 96hr NOEC	0.31 (m) 0.24 (m)	Ward and Boeri (1990d)	Valid
	4-nonylphenol CAS No. 84852-15-3		flow					96hr LC <sub>50</sub>	0.142 (m)	Lussier et al	Use with care
Winter flounder Pleuronectes americanus	4-nonylphenol CAS No. 84852-15-3		stat					96hr LC <sub>50</sub>	0.017 (n)	Lussier et al	Use with care
Inland silversides Menidia beryllina	4-nonylphenol CAS No. 84852-15-3		flow					96hr LC <sub>50</sub>	0.069 (m)	Lussier et al	Use with care

stat – static system      flow – flow through system      n – nominal concentration      m-measured concentration

Table 3.11 Toxicity of nonylphenol to aquatic invertebrates

Freshwater											
Species	Chemical tested	Age/Size	Stat/Flow	Temp (°C)	Dissolved oxygen (mg/l)	Hardness mg CaCO <sub>3</sub> /l	pH	Endpoint	Concentration (mg/l)	Reference	Validity
Water flea <i>Daphnia magna</i>	4-nonylphenol	24 hrs old	stat	20			8 ± 0.2	24hr EC <sub>50</sub> 24hr EC <sub>0</sub> 24hr EC <sub>100</sub>	0.18 (n) 0.09 (n) 0.34 (n)	Bringmann and Kühn (1982)	Use with care
	nonylphenol							48hr EC <sub>50</sub>	0.44	Monsanto (1985)	Lack of data
	nonylphenol (91.8% nonylphenol, 86.1% 4-nonylphenol)	<24 hrs old	stat	20 ± 1		180 ± 20	8.25 ± 0.25	24hr LC <sub>50</sub> 48hr LC <sub>50</sub> 7 day LC <sub>50</sub> 14 day LC <sub>50</sub> 21 day LC <sub>50</sub> 21 day NOEC <sub>surviving offspring</sub> 21 day NOEC <sub>length</sub>	0.30 (m) <sup>c</sup> 0.19 (m) <sup>c</sup> 0.12 (m) <sup>c</sup> 0.12 (m) <sup>c</sup> 0.10 (m) <sup>c</sup> 0.024 (m) <sup>c</sup> 0.039 (m) <sup>c</sup>	Comber et al. (1993) <sup>c</sup>	Valid
	nonylphenol	<24 hrs old	stat					48hr EC <sub>50</sub>	0.085	Brooke (1993a)	Valid
	nonylphenol 25154-52-3	<24 hrs old	stat	20 ± 1		294	7.5	24hr EC <sub>50</sub> (immobilisation) 48hr EC <sub>50</sub> (immobilisation)	0.218 (n) 0.14 (n)	Hüls (1992c)	Valid
	nonylphenol CAS No. 25154-52-3	<24 hrs old	semi-stat	20 ± 1				21 day NOEC <sub>reproduction</sub>	≥ 0.1 (n)	Hüls (1992a)	Valid
	nonylphenol CAS No. 25154-52-3	<24 hrs old	semi-static	20 ± 1				21 day NOEC <sub>reproduction</sub> LOEC <sub>reproduction</sub>	0.1 (n) 0.14 (n)	Hüls (1992b)	Valid
	nonylphenol		static					21 day NOEC <sub>reproduction</sub>	0.001 (n)	Kopf (1997)	Use with care
Water flea <i>Daphnia pulex</i>	nonylphenol							48hr EC <sub>50</sub>	0.14-0.19	Ernst et al. (1980)	Lack of data
Water flea <i>Ceriodaphnia dubia</i>	nonylphenol			25				48hr EC <sub>50</sub>	Mean 0.47 (n)	Ankley et al. (1990)	Use with care

Table 3.11 continued overleaf

Table 3.11 continued Toxicity of nonylphenol to aquatic invertebrates

Freshwater											
Species	Chemical tested	Age/Size	Stat/Flow	Temp (°C)	Dissolved oxygen (mg/l)	Hardness (mg CaCO <sub>3</sub> /l)	pH	Endpoint	Concentration (mg/l)	Reference	Validity
Water flea <i>Ceriodaphnia dubia</i>	nonylphenol CAS No. 84852-15-3 (>95% 4-nonylphenol)	1st instar <24 hrs old	stat	24-25	6.4-7.9	144-172	8.3-8.6	96hr LC <sub>50</sub> 96hr EC <sub>50</sub> 7 day LC <sub>50</sub> 7 day EC <sub>50</sub> 7 day NOEC <sub>survival</sub> 7 day LOEC <sub>survival</sub> 7 day NOEC <sub>reproduction</sub> 7 day LOEC <sub>reproduction</sub>	0.276 (m) 0.069 (m) 0.258 (m) 0.0992 (m) 0.202 (m) 0.377 (m) 0.0887 (m) 0.202 (m)	England (1995)	Valid
Clam <i>Anodonta cataractae</i>	nonylphenol	adult 15 g	stat	10				6 day LC <sub>50</sub>	5.0 (n) 1.7 (m)	McLeese et al. (1980b)	Use with care
Annelid <i>Lumbriculus variegatus</i>	nonylphenol CAS No. 25154-52-3	adult 0.005 g	flow					96hr LC <sub>50</sub> 96hr EC <sub>50</sub> (inacitivity)	0.342 (m) 0.268 (m)	Brooke et al. (1993a)	Valid
Snail <i>Physella virgata</i>	nonylphenol CAS No. 25154-52-3	adult 476±218 mg	flow					96hr LC <sub>50</sub> 96hr EC <sub>50</sub> (inacitivity)	0.774 (m) 0.378 (m)	Brooke et al. (1993a)	Valid
Dragonfly <i>Ophiogomphus</i> sp.	nonylphenol CAS No. 25154-52-3		flow					96hr EC <sub>50</sub> (loss of equilibrium)	0.596 (m)	Brooke et al. (1993a)	Valid
Damselfly <i>Ischnura elegans</i>	Nonylphenol		Static					96hr EC <sub>50</sub> 96hr LC <sub>50</sub>	0.057 (m) 0.108 (m)	Sims et al. (1997)	Use with care
Freshwater shrimp <i>Gammarus pulex</i>	Nonylphenol		Static					96hr EC <sub>50</sub> 96hr LC <sub>50</sub>	0.0127 (m) 0.0246 (m)	Sims et al (1997)	Use with care
Painted shrimp <i>Hyalella azteca</i>	nonylphenol CAS No. 25154-52-3		flow					96 hr EC <sub>50</sub> (loss of mobility)	0.0207 (m)	Brooke et al.. (1993a)	Valid
Painted shrimp <i>Hyalella azteca</i>	nonylphenol CAS No. 84852-15-3 (>95% 4-nonylphenol)	juvenile 2-3 mm	flow	21	1.4-8.0	152-158	7.9-8.7	96hr LC <sub>50</sub> 96hr EC <sub>50</sub>	0.17 (m) 0.15 (m)	England and Bussard (1994)	Valid

Table 3.11 continued overleaf

Table 3.11 continued Toxicity of nonylphenol to aquatic invertebrates

Seawater											
Species	Chemical tested	Age/Size	Stat/Flow	Temp (°C)	Dissolved oxygen (mg/l)	Salinity (o/oo)	pH	Endpoint	Concentration (mg/l)	Reference	Validity
Clam <i>Mya arenaria</i>	nonylphenol	adult 20 g	stat	10				15 day LC <sub>50</sub>	> 1 (n) > 0.7 (m)	McLeese et al. (1980b)	Use with care
Coot Clam <i>Mulinia lateralis</i>	4-nonylphenol CAS No. 84852-15-3		stat					96hr LC <sub>50</sub>	0.038 (n)	Lussier et al.	Use with care
Mussel <i>Mytilus edulis</i>	nonylphenol CAS No. 25154-52-3	adult 40-50 mm	semi-stat	17 ± 1		32		96hr LC <sub>50</sub> 15 day LC <sub>50</sub> 35 day LC <sub>50</sub>	3 (n) 0.5 (n) 0.14 (n)	Granmo et al. (1989)	Use with care
Crustacean <i>Nitocra spinipes</i>	nonylphenol							96hr LC <sub>50</sub>	0.118 0.139	Wahlberg et al. (1990) <sup>d</sup>	Not valid
Brown shrimp Crangon	4-nonylphenol							96hr LC <sub>50</sub>	0.6	Granmo (1991)	Lack of data
crangon	nonylphenol							96hr LC <sub>50</sub>	0.42	Waldock and Thain (1991)	Lack of data
Sand shrimp Crangon	nonylphenol	adult 1.3 g	stat	10				96hr LC <sub>50</sub>	0.4 (n) 0.3 (m)	McLeese et al. (1980b)	Use with care
septemspinosa			stat					96hr LC <sub>50</sub>	0.3 (m)	McLeese et al. (1981)	Use with care
Grass shrimp <i>Palaemonetes pugio</i>	4-nonylphenol CAS No. 84852-15-3		flow					96hr LC <sub>50</sub>	0.059	Lussier et al.	Use with care
Lobster <i>Homarus</i>	nonylphenol	20 g	stat	10				96hr LC <sub>50</sub>	0.2 (n) 0.17 (m) <sup>a</sup>	McLeese et al. (1980b)	Use with care
americanus	4-nonylphenol CAS No. 84852-15-3		stat					96hr LC <sub>50</sub>	0.071 (n)	Lussier et al.	Use with care

Table 3.11 continued overleaf

Table 3.11 continued Toxicity of nonylphenol to aquatic invertebrates

Seawater											
Species	Chemical tested	Age/Size	Stat/Flow	Temp (°C)	Dissolved oxygen (mg/l)	Salinity (o/oo)	pH	Endpoint	Concentration (mg/l)	Reference	Validity
Mysid Mysidopsis bahia	nonylphenol CAS No. 84852-15-3 (4-nonylphenol, branched)	< 24 hrs old	flow	23.8- 25.3	6.5-7.8	20	7.3-8.2	96hr LC <sub>50</sub> 96hr NOEC	0.043 (m) 0.018 (m)	Ward and Boeri (1990c)	Valid
			stat	23.3- 26.4	5-8.5	20-21	7.5-8.2	28 day LOEC <sub>length</sub> 28 day NOEC <sub>length</sub>	0.0067 (m) 0.0039 (m)	Ward and Boeri (1991c)	Valid
	4-nonylphenol CAS No. 84852-15-3		flow					96hr LC <sub>50</sub>	0.06 (m)	Lussier et al.	Use with care
Mud crab Dyspanopeus sayi	4-Nonylphenol CAS No. 84852-15-3		flow					96hr LC <sub>50</sub>	0.2 (m)	Lussier et al.	Use with care
Amphipod Leptocheirus plumulosus	4-nonylphenol CAS No. 84852-15-3		flow					96hr LC <sub>50</sub>	0.062 (m)	Lussier et al.	Use with care
Benthic (Sediment dwelling) organisms											
Midge Chironomus tentans	nonylphenol	larvae	flow	20 ± 1		138-158	7.7-8.3	14 day LC <sub>50</sub>	0.119	England and Bussard (1993)	Valid

stat – static system flow – flow through system n – nominal concentration m-measured concentration

Table 3.12 Toxicity of nonylphenol to aquatic algae and plants

Species	Chemical	Experimental conditions	Endpoint/Effect	Concentration (mg/l)	Reference	Validity
<b>Freshwater species</b>						
Duckweed Lemna minor	nonylphenol CAS No. 25154-52-3		96hr NOEC 96hr LOEC(Frond production)	0.901 (m) 2.08 (m)	Brooke et al. (1993a)	Valid
Green alga Chlorella pyrenoidosa	nonylphenol		Growth reduction 24hr LC <sub>50</sub> 24hr LC100	0.025-7.5 1.5 25	Weinberger and Rea (1981)	Lack of data
Green alga Scenedesmus subspicatus	nonylphenol	UBA GLP	72hr EC50 (Cell growth) 72hr EC10 (Cell growth)	1.3 0.5	Hüls (1996d)	Valid
	nonylphenol CAS No. 2515-52-3	EN 28692/ISO 8692 DIN 38412 9	72hr EC50 (Biomass) 72hr EC <sub>10</sub> (Biomass) 72hr EC <sub>50</sub> (Growth rate) 72 hr EC10 (Growth rate)	0.0563 0.0033 0.323 0.0251	Kopf (1997)	Valid
Flagellate Chlamydomonas reinhardii	nonylphenol	Ultrastructure examined under electron microscope	Cell membrane disorganisation; distorted flagellae	0.5-0.7	Weinberger and Rea (1981)	Lack of data
	nonylphenol		Inhibition of photosynthesis 55% 100%	0.5 0.75	Moody and Weinberger (1983)	Lack of data
Alga Selenastrum capricornutum	nonylphenol CAS No. 25154-52-3		96hr NOEC 96hr LOEC (Cell production)	0.694 (m) 1.480 (m)	Brooke et al. (1993a)	Valid
	nonylphenol CAS No. 84852-15-3 (95% 4-nonylphenol)	Temp 23.2-23.7 °C pH 7.4-7.5 to 8.2-8.9	96hr EC50 (Cell growth)	0.41 (m)	Ward and Boeri (1990b)	Valid
<b>Saltwater species</b>						
Marine alga Skeletonema costatum	nonylphenol CAS No. 84852-15-3 (95% 4-nonylphenol)	Temp 21-22 °C pH 7.9-8.1 to 8.3-9.6 Salinity 30 o/oo	96hr EC50 (Cell growth)	0.027 (m)	Ward and Boeri (1990a)	Valid

m-measured concentration



### 3.2.1.1.4 Aquatic algae and plants

**Table 3.12** summarises the toxicity of nonylphenol to aquatic algae.

Algal studies are multigenerational. The Technical Guidance Document recommends that 72-hour (or longer) EC<sub>50</sub> values are considered as equivalent to a short-term result, and that a 72-hour (or longer) NOEC is considered as a long-term result. From **Table 3.10** the lowest 72-hour EC<sub>50</sub> value for freshwater species is 0.0563 mg/l for the alga *Scenedesmus subspicatus* based upon change in biomass (Kopf, 1997). The lowest 96-hour EC<sub>50</sub> value for saltwater species is 0.027 mg/l for the alga *Skeletonema costatum*, based upon biomass (Ward and Boeri, 1990a). Both these values are from valid studies and are taken as short-term test results.

The Technical Guidance Document states that for long-term studies an EC<sub>10</sub> may be taken as a long-term NOEC if no long-term NOEC is available. A 72-hour EC<sub>10</sub> value of 0.0033 mg/l based upon biomass is reported for the freshwater alga *Scenedesmus subspicatus* (Kopf, 1997). This value will be taken as equivalent to a long-term NOEC.

Prasad (1989) studied the effects of nonylphenol on the macrophytes *Lemna minor* L. and *Salvinia molesta* Mitchell. Cultures of *Lemna minor* and *Salvinia molesta* were treated with nonylphenol for 4 to 9 days. Observations were made on frond number, vigour, and phytotoxicity. In *Lemna minor* inhibition of frond production was noticed after 2 days at 0.5 mg/l, 2.5 mg/l and 5 mg/l nonylphenol. Photosynthetic activity was curtailed after 4 days. Reductions in growth were observed in lower concentrations of nonylphenol (0.125-0.5 mg/l) and bleaching, chlorosis and mortality observed at nonylphenol concentrations of 0.5-2.5 mg/l. The authors concluded that nonylphenol most likely interfered with photosynthesis and cell division. In *Salvinia* cultures, frond production was reduced by day 3 of exposure (nonylphenol concentrations of 2.5-25 mg/l), and by days 6 and 9 the cultures showed extreme phytotoxicity and started dying. The use of <sup>14</sup>C-nonylphenol confirmed that the cultures were absorbing nonylphenol and that the observed phytotoxicity was due to systemic injury.

### 3.2.1.1.5 Micro-organisms

Cultures of the bacterium *Pseudomonas putida* showed an EC<sub>10</sub> of >10 mg/l for oxygen consumption when exposed to 4-nonylphenol for 30 minutes (Knie et al., 1983). The sporostatic effect of 4-nonylphenol was investigated in the bacterium *Bacillus megaterium* (Lewis and Jurd, 1972). Fifty percent inhibition of spore germination was seen following exposure to 10 mg/l for 2 hours. A two-hour exposure to 32 mg/l (close to the reported solubility of 40 mg/l) led to >99% inhibition. However following longer exposure of 24 hours to a saturated solution of nonylphenol, there was no inhibition of germination of spores

In an inhibition of activated sludge respiration test (OECD Test Guideline 209) an EC<sub>50</sub> of 950 mg/l was reported for nonylphenol (Hüls, 1999a). The sludge used in the test was taken from a sewage treatment plant treating predominantly domestic sewage. The EC<sub>50</sub> value was determined by linear regression of the available data. The value is higher than the water solubility of nonylphenol and is probably based on the tendency of nonylphenol to adsorb to the activated sludge used as inoculum.

### 3.2.1.1.6 Amphibians

Ward and Boeri (1992) studied the toxicity of nonylphenol to the tadpole *Rana catesbiana*. The test method and material used are fully described and the test can be considered valid. In the test, tadpoles were exposed for up to 30 days to nonylphenol in a sediment/water system. Nonylphenol was added to the sediment in the test vessels and dilution water added on a flow through basis. Nonylphenol concentrations were measured in the sediment and water throughout the test. Nonylphenol concentrations were found to be highest in the test water at the beginning of the test, decreasing significantly during the first 10 days of the test and more gradually during the last 20 days of the test. The tadpoles used in the study were all stage VI through IX, as characterised by the presence of hind paddles and respiration by gills. The 30-day LC<sub>50</sub> was 260 mg/kg dry weight and the 30 day EC<sub>50</sub> was 220 mg/kg dry weight. At 10, 20 and 30 days the lowest observed effect level (LOEL) was 390 mg/kg dry weight and the no observed effect level (NOEL) was 155 mg/kg dry weight. The authors noted that the levels of nonylphenol in the water were high enough to cause the observed toxicity and it is not possible to attribute the toxic effect to either water or sediment exposure.

### 3.2.1.1.7 Endocrine disruption

The oestrogenic effect of nonylphenol on fish and Daphnids has been studied by a number of authors. Generally the work shows that nonylphenol and nonylphenol ethoxylates do exhibit oestrogenic activity. For nonylphenol ethoxylates the activity was found to increase with decreasing chain length, with nonylphenol showing the greatest activity. Most of the tests indicate that oestrogenic effects may start to occur at around 10-20 µg/l.

Vitellogenin production by isolated hepatocytes from rainbow trout (*Oncorhynchus mykiss*) has been used as an *in vitro* test system for oestrogenic activity of nonylphenol and several nonylphenol ethoxylates (Jobling and Sumpter, 1993). Vitellogenin is a yolk protein normally produced in response to oestrogen in female trout. The relative potency of nonylphenol to oestradiol-17β was 0.0000090. The mean EC<sub>50</sub> for the test was measured at 16.15 µM nonylphenol (3.56 mg/l).

White et al. (1994) reported that nonylphenol can stimulate vitellogenin secretion, *in vitro*, at concentrations of 10<sup>-6</sup> M (0.2 mg/l) and above in hepatocytes from rainbow trout (*Oncorhynchus mykiss*). The authors also found that nonylphenol showed competitive displacement of oestrogen from its receptor site in rainbow trout (*Oncorhynchus mykiss*).

Jobling et al. (1996) exposed two-year-old male rainbow trout (*Oncorhynchus mykiss*) to nonylphenol at 30 µg/l (nominal concentration) in a flow through system for 3 weeks. Measured concentrations of nonylphenol were 36.81± 2.4 µg/l throughout the experiment. Exposure was conducted in May, when growth of the testes was at an early stage. Blood samples were taken at the beginning and end of the exposure period. After three weeks, the fish were killed and testicular weight measured. Nonylphenol was found to stimulate production of vitellogenin, by a factor of 100 to 1,000 times compared to controls. Statistically significant reductions in testis size, expressed as gonadosomatic index (GSI) were also noted. Histological examination of the testes showed that control fish had actively developed testes with a predominance of spermatocytes type A. The fish exposed to nonylphenol had a significantly higher proportion of spermatogonia type A than controls. A second experiment was conducted in November, when the testes were more developed, to establish a dose-response for the two effects using nonylphenol. A significant stimulation of blood vitellogenin levels was seen after exposure to

20.3 µg/l but not at 5.02 µg/l, which was the NOEC for this effect. A significant reduction in GSI relative to controls was seen at 54.3 µg/l but not at 20.3 µg/l which was the NOEC for testicular growth.

Baldwin et al. (1997) investigated the effects of exposure of *Daphnia magna* to nonylphenol in a 3-week assay designed to look at the effects on the metabolism of the steroid hormone testosterone and any resulting effects on reproduction. Both acute and long-term exposures were used in the test. In acute tests, adult (10-day-old) female daphnids were exposed to nonylphenol (25, 50 or 100 µg/l) for 48 hours. After the acute exposure, the daphnids were then exposed to <sup>14</sup>C testosterone for a further 16 hours and analysed for total radioactivity. The presence of radiolabelled metabolites in the water was also determined. Effects of exposure to nonylphenol on reproduction were investigated in a 3-week static renewal toxicity test. Again, after the three-week exposure, the daphnids were exposed to <sup>14</sup>C testosterone for a further 16 hours to investigate the effects on steroid hormone metabolism.

After 48-hour exposure to nonylphenol at 100 µg/l, a significant increase ( $p=0.01$ ) over the controls was seen in the accumulation of <sup>14</sup>C testosterone and/or its metabolites in the daphnids. No significant effect was seen at nonylphenol concentrations of 25 or 50 µg/l. More detailed investigation of the metabolic elimination products indicated that the increased accumulation of androgens in the daphnids was a result of a decrease in the production of the major testosterone elimination product (testosterone-glucose) and an increase in the production of reduced/hydrogenated metabolites that are preferentially retained in the daphnids. These effects were seen at all exposure concentrations and were concentration related (although the effects were not always statistically significant at nonylphenol concentrations of 25 µg/l). It was concluded that nonylphenol is capable of significantly perturbing components of androgen metabolism in daphnids at concentrations of  $\leq 25$  µg/l. In the 3-week reproduction assay, nonylphenol concentrations of up to 100 µg/l had no effect on survival of parental daphnids. The number of off-spring produced was reduced on exposure to 50 or 100 µg/l, but this reduction was only statistically significant ( $p=0.05$ ) at 100 µg/l. The reproductive chronic value derived from these data was 71 µg/l (geometric mean of the NOEC and LOEC for reproduction) and this concentration was estimated to reduce the elimination of testosterone by approximately 50%. The results indicate that nonylphenol can cause effects on steroid hormone metabolism that may contribute to its reproductive toxicity (Baldwin et al., 1997).

The effects of nonylphenol exposure on both the asexual and sexual reproduction of *Daphnia galeata mendotae* have been studied over 30-day exposure (Shurin and Dodson, 1997). Four parameters (averaged over a female's lifetime) were examined: a) number of female offspring; b) number of male offspring; c) number of ephippia and d) number of developmentally abnormal male and female offspring. The laboratory conditions used induced the production of all three types of offspring (males, females and ephippia) and the exposure media were renewed every 48 hours. The nonylphenol concentrations used were 10, 50 and 100 µg/l. The results from the test were complicated due to the fact that different responses were seen in the solvent control (acetone at 80 µg/l) and the medium control. The daily production of female offspring/adult was found to increase over that seen in the medium control at the high concentrations (50 and 100 µg/l) of nonylphenol, but a similar increase was seen in the solvent control. No effects were seen on the daily production of male offspring/adult at any concentration and a slight decrease in the number of ephippia/adult was seen at high doses of nonylphenol. This latter effect was thought to be a result of increased adult mortality at the high nonylphenol concentrations. The daily production of deformed live offspring/adult was found to be related to nonylphenol exposure as a clear dose-response curve was seen and no such deformed offspring were seen in the two

controls. The deformed offspring were of similar size to normal offspring but had forward curled tail spines and lacked, or had severely reduced, terminal setae on their second antennae, which reduced the swimming ability of the organism. This deformity was seen in 11% of live young at a nonylphenol concentration of 10 µg/l, and only animals that were prenatally exposed to nonylphenol exhibited this deformity.

Gray and Metcalfe (1997) investigated the sexual development of male and female Japanese Medaka (*Oryzias latipes*) exposed to nonylphenol from hatch to 3 months of age. The test used was a static renewal system (renewal every 72 hours for first month and then every 48 hours) using 30 fish per exposure concentration and exposure was initiated 1 or 2 days post hatch. The nominal concentrations used were 10, 50 and 100 µg/l, but analysis indicated that these concentrations fell over the 48-hour or 72-hour renewal period and the mean measured concentration over the renewal period was around 55% of the nominal for 72-hour renewal and 66% for 48-hour renewal. Between 18 and 20 of the original 30 fish in each treatment and control survived to the end of the 3-month exposure period. A statistically significant increase in mean body weight and length was found for the fish in the 10 and 50 µg/l groups when compared with controls. This was not apparent in the 100 µg/l treatment group. Histological examination indicated that males in the 50 and 100 µg/l had developed testis-ova, characterised by the presence of both testicular and ovarian tissue in the gonad. The incidence of this was 6 out of 12 males (50%) in the 50 µg/l treatment and 6 out of 7 males (86%) in the 100 µg/l treatment. No incidence of testis-ova was found in the control group (12 males) or the 10 µg/l treatment (10 males). The LOEC for this effect was therefore 50 µg/l. At 100 µg/l the authors suggested that sex reversal (male to female) may also be occurring as the ratio of males to females was different to that seen in controls or the 10 and 50 µg/l treatments, however this could also be due to different mortality patterns in the various treatments (i.e. greater mortality in male fish at 100 µg/l). It was also noted in the paper that the Japanese Medaka has a relatively unique process of gonadal differentiation and development and it is not clear how these results relate to possible effects in other fish species.

Nimrod and Benson (1996) investigated the induction of serum vitellogenin in Channel Catfish (*Ictalurus punctatus*) by 17β-estradiol, several synthetic oestrogens and several suspected xenoestrogens including nonylphenol. Juvenile fish (65-95 g) were exposed to each substance by intraperitoneal injection. After 7 days, the serum vitellogenin level was determined. Fish exposed to nonylphenol at doses of 79 mg/kg and 237 mg/kg showed elevated serum vitellogenin levels when compared to controls. The response of individual fish was found to be very variable and the mean serum vitellogenin levels found in control, low dose and high dose groups were 0.3±0.4 mg/ml, 3.6±3.4 mg/ml and 9.5±5.7 mg/ml respectively, however, this was only significantly different (p<0.05) from controls in the high dose (237 mg nonylphenol/kg) fish. The response from nonylphenol was much lower than that found with 17β-estradiol by a factor of around 5,000 (i.e. a 500 times higher dose of nonylphenol resulted in a 10 times lower serum vitellogenin level compared with that seen with 17β-estradiol).

Christensen et al. (1995) dosed male flounders (*Platichthys flesus*) with nonylphenol by four intraperitoneal injections over a period of two weeks. Vitellogenin was detected in plasma of fish dosed with 10 mg/kg wet weight. Effects were also seen on plasma lipids (increase), protein (increase) and ninhydrin positive substances (decrease). Toxic effects (cell damage), as indicated by increased activity of the plasma enzyme GPT was also found.

Elevated levels of blood vitellogenin have been found in rainbow trout (*Oncorhynchus mykiss*) exposed *in vivo* to nonylphenol for 3 weeks. The nonylphenol concentrations used were in the

range 0.24-54.3  $\mu\text{g/l}$ . The levels of blood vitellogenin were found to be significantly elevated at concentrations of 20.3  $\mu\text{g/l}$  (1  $\mu\text{g}$  vitellogenin/ml; a ten fold increase over controls) and 54.3  $\mu\text{g/l}$  (100  $\mu\text{g}$  vitellogenin/ml; a 1,000 fold increase over controls) (Harries et al., 1995).

The effects of nonylphenol on steroid metabolising enzymes from the liver have been studied using Atlantic Salmon (*Salmo salar*) (Arukwe et al., 1997). Groups of 6 fish (approximately 1 year old and between 75 and 120 g in weight) were injected intraperitoneally with either 1, 5, 25 or 125 mg/kg bodyweight of nonylphenol (consisting of 85% para- isomers, and around 8-13% phenol, 1% tripropylene and 1% dinonylphenol) and then maintained at 10°C and 34‰ salinity for 2 weeks. Similar groups of fish were dosed with 5 mg/kg body weight of estradiol-17 $\beta$  as positive control and the carrier solvent (vehicle control group). After the 2-week period, various assays were carried out using liver microsomes collected from the exposed and control fish. The nonylphenol treatments caused an increase in the 6 $\beta$ -, 16 $\alpha$ - and 17 $\alpha$ -hydroxylase activities in liver microsomes from the 1 mg/kg body weight groups (the increase was only statistically significant ( $p < 0.05$ ) compared with vehicle controls for the 6 $\beta$ -activity). With increasing dose of nonylphenol, there was an apparent dose related decrease in the hydroxylase activities of liver microsomes compared to vehicle controls. This decrease was statistically significant for 6 $\beta$ -hydroxylase in the 25 mg nonylphenol/kg body weight group and for all activities in the 125 mg nonylphenol/kg body weight group. Reductions compared with vehicle controls were also seen in the 7-ethoxyresorufin-O-deethylase (EROD) activity (23-70% reductions were seen but they were only statistically significant in the 125 mg nonylphenol/kg body weight groups) and the UDP-glucuronosyltransferase activities (decrease was not statistically significant). Immunochemical analysis of CYP1A, CYP2K-like and CYP3A-like proteins showed statistically significant 18%, 47% and 30% reductions in enzyme-linked immunosorbent assay absorbance levels respectively compared with vehicle controls in the 125 mg nonylphenol/kg body weight group. Plasma levels of estradiol-17 $\beta$  were found to be lowered by 24-43% compared with vehicle controls, but this decrease was only statistically significant in the 1 and 5 mg nonylphenol/kg body weight treated groups. The report concluded that nonylphenol might increase the activity of steroid-metabolising enzymes at low concentrations but decrease the activity of these enzymes at high concentrations.

Ashfield et al. (1998) investigated the effects of prolonged exposure to nonylphenol on growth and gonado(ovo)somatic index of female juvenile rainbow trout (*Oncorhynchus mykiss*). Groups of 200 fish were exposed to 3 concentrations of 4-<sup>t</sup>nonylphenol using a flow-through system from hatch to early sexual maturity (approximately 1 month after hatch). Two series of experiments were conducted. In the first series, exposure to nonylphenol (nominal concentrations 1, 10 and 50  $\mu\text{g/l}$ ) was for 22 days from hatch, and monitoring of the fish was continued for a further 86 days. In the second series, exposure to nonylphenol (nominal concentrations 1, 10 and 30  $\mu\text{g/l}$ ) was for 35 days from hatch, with monitoring of fish continuing for a further 431 days. In all tests, the water had a pH of 6.5, a hardness of 12.5 mg/l as  $\text{CaCO}_3$ , a temperature of 7-13°C and was continuously aerated to maintain the dissolved oxygen level. The stock nonylphenol solutions were made up in methanol/water mixture and each exposure solution had around 0.0005% methanol present (the same amount of methanol was added to the control). In the tests no significant difference was seen in total mortality between controls and treated fish. At the end of the first series of tests, fish that had been exposed to 1 and 50  $\mu\text{g/l}$  showed a statistically significant ( $p < 0.001$  and  $p < 0.01$  at the two concentrations respectively) lower body weight relative to controls (the 10  $\mu\text{g/l}$  group was not significantly different from the control group). In the second series of experiments, by day 55 the mean weights and lengths of fish exposed to 30  $\mu\text{g/l}$  were significantly ( $p < 0.05$  for weight,  $p < 0.01$  for length) lower than in the control group. The 10  $\mu\text{g/l}$  group showed no significant effect on weight at this time, but the length was

significantly reduced ( $p < 0.05$ ) compared with controls. These differences in weight and length became more pronounced at day 84, with significantly lower weights in the 10  $\mu\text{g/l}$  ( $p < 0.001$ ) and 30  $\mu\text{g/l}$  ( $p < 0.01$ ) groups. The significantly reduced body weight seen in the 30  $\mu\text{g/l}$  group continued up until the experiment ended on day 466, but the fish exposed to 10  $\mu\text{g/l}$  showed a significantly elevated bodyweight ( $p < 0.05$ ) compared with controls from day 300 onwards. The fish body weight in the 1  $\mu\text{g/l}$  group was not significantly different from controls at any time during the experiment. At the end of the experiment, the ovosomatic index ( $\text{OSI} = (100 \times \text{gonad weight} / [\text{bodyweight} - \text{gonad weight}])$ ) was determined, and this was found to be significantly ( $p < 0.05$ ) elevated in the 30  $\mu\text{g/l}$  group. The paper concluded that significant effects on growth of the fish had occurred during the test, although the mechanism by which nonylphenol caused these effects was unclear.

### 3.2.1.1.8 Field Studies

The fate and effects of nonylphenol have been studied using littoral enclosures. In the test, 18 enclosures (4.7-8 m) were constructed in a 2-hectare freshwater pond in Minnesota, USA. Each enclosure consisted of three plastic walls, with the fourth side being 4 metres of natural shoreline. The enclosures had an average surface area of  $13.4 \pm 3.3 \text{ m}^2$ , an average depth of  $1.0 \pm 0.2 \text{ m}$  (average maximum depth of  $2.1 \pm 0.4 \text{ m}$ ) and an average water volume of  $32.0 \pm 6.4 \text{ m}^3$ . The enclosures were allocated into 3 blocks of 6 units, with each block consisting of two controls and 1 each exposed to nonylphenol concentrations of 3, 30, 100 and 300  $\mu\text{g/l}$ . The nonylphenol used in the test had the following composition: 96.43% p-nonylphenol, 3.19% o-nonylphenol, 0.21% dialkylphenols, 0.012% phenol and 0.16% nonene. Nonylphenol was added to the enclosures 11 times, with two days between applications (i.e. total of 20 days). The nonylphenol was added as an aqueous solution at a depth of 20-120 cm below the surface of the enclosure, with gentle mixing down to a depth of approximately 1 m. Samples were collected and analysed 39 hours after each application and the results of these analyses were used to calculate the succeeding application rates to ensure that the water concentration was as close as possible to the required nominal value. The measured water levels refer to total (i.e. dissolved + particulate) nonylphenol concentrations, as the sampling/extraction method does not appear to include a filtration step. The average peak nonylphenol concentrations in the water phase (measured 2 hours after applications and thus taken to represent the maximum concentration present) were  $5 \pm 4 \mu\text{g/l}$ ,  $23 \pm 11 \mu\text{g/l}$ ,  $76 \pm 21 \mu\text{g/l}$  and  $243 \pm 41 \mu\text{g/l}$ , corresponding to the nominal exposure concentrations of 3, 30, 100 and 300  $\mu\text{g/l}$  respectively. There was also evidence that the application method used did not completely mix the nonylphenol at depths below around 1.4 m, where the concentrations found were lower than the mean levels measured. After the 11th application of nonylphenol, the concentration in the water phase decreased rapidly, with around 50% dissipation within  $\leq 1.2$  days (mean value 0.74 days), although the actual water concentration in the 300  $\mu\text{g/l}$  treatment remained above 10  $\mu\text{g/l}$  for 34 days. At the same time the sediment concentrations increased (Heinis et al., 1999). The concentrations measured in the various phases during the test are summarised in **Table 3.13**.

Table 3.13 Summary of measured concentrations in various phases found in the field study.

Nominal treatment level <sup>a</sup> (water)	Measured water concentration during application phase <sup>b</sup>		Measured water concentration at times after application phase	Maximum concentration in macrophytes	Maximum concentration in sediment	Mean sediment pore water concentration
	2 h	39 h				
3 µg/l	5.44± 3.65	2.20± 1.27	not detected after day 27			
30 µg/l	23.4± 11.3	8.86± 1.78	not detected after day 41	11.5 mg/kg dry wt, on day 22, falling to 4.71 mg/kg dry wt at day 56	2.74 mg/kg dry wt at day 20 falling to 1.15 mg/kg dry wt at day 24, 0.31 mg/kg dry wt at day 76, 0.24 mg/kg at day 318	Trace amounts (0.15-0.20 µg/l) during application period (day 1-20)
100 µg/l	75.7± 20.8	27.2±5.0	0.22 µg/l at day 98			
300 µg/l	243± 40.7	105±24.3	0.59 µg/l at day 98	139 mg/kg dry wt, on day 21, falling to 94 mg/kg dry wt on day 34, 3.87 mg/kg dry wt on day 56 and 3.26 mg/kg dry wt between days 56 and 318.	27.4 mg/kg dry wt at day 48, falling to 4.90 mg/kg dry wt at day 76, 4.90 mg/kg dry wt. at day 318 and 1.97 mg/kg dry wt at day 440.	18.6 µg/l, over days 3-35

a - refers to nominal concentration maintained in water during the first 20 days

b - refers to mean measured concentration in water either 2 hours or 39 hours after application during first 20 days

The first applications of nonylphenol occurred on July 8. After application of nonylphenol ceased on day 20 (July 28), the effects of nonylphenol on the ecosystem present in the enclosure were monitored up until day 440. Various effects were seen during the test and these are summarised in the following paragraphs and **Table 3.14**.

#### Zooplankton (O'Halloran et al., 1999)

Zooplankton in the enclosures was collected at regular intervals from 9 days before the first nonylphenol application until day 83 (63 days after the last nonylphenol application). After collection, the abundance of the various organisms was determined by counting (the detection limit of the method used corresponded to 84-168 organisms/m<sup>2</sup>), and the effects of the nonylphenol on the zooplankton community were assessed based on changes observed in population abundances and taxonomic composition.

In the experiment, a total of 45 taxa were identified from the 18 enclosures over the 9 sampling dates. The most abundant group present was Cladocera (dominated by members of *Chydoridae* and *Daphnidae*) and the total abundance in the pre-application and control enclosures ranged from 7,381 to 265,446 organisms/m<sup>2</sup>. Copepods ranged in abundance from 22,142 to 112,873 organisms/m<sup>2</sup> and were dominated by cyclopoids. The peak abundance of both cladoceran and copepod populations occurred between days 34 and 51 (August 12-27) of the experiment. Ostracod abundance ranged between 84-46,428 organisms/m<sup>2</sup>, with the peak abundance being seen on day 34. Of the 45 taxa identified, 32 were found at high enough abundance on several sampling days to carry out a statistical analysis.

All cladoceran and copepod taxa were significantly ( $p < 0.05$ ) reduced in number in the enclosures exposed to 243  $\mu\text{g/l}$  nonylphenol when compared to controls, and some of the more sensitive taxa were significantly reduced in number at two lower nonylphenol concentrations (76  $\mu\text{g/l}$  and 23  $\mu\text{g/l}$ ). Ostracod and rotifer taxa appeared to be less sensitive, with effects being seen at nonylphenol concentrations of 243  $\mu\text{g/l}$  and  $\geq 76$   $\mu\text{g/l}$  respectively. The maximum reduction in abundance generally occurred within 1 to 7 days of the last nonylphenol application, and recovery to control abundance generally occurred within 7 to 28 days of the last nonylphenol application. However, some particularly sensitive taxa e.g. *Acroperus* and *Calanoida* did not recover in the 76  $\mu\text{g/l}$  or 243  $\mu\text{g/l}$  treatments by the end of the study. The maximum acceptable toxicant concentration (MATC geometric mean of NOEC and LOEC) for the study was derived as  $\sim 10$   $\mu\text{g/l}$ .

#### Benthic macroinvertebrates (Schmude et al., 1999)

The detection limit for the sampling method used was 37-55 organisms/ $\text{m}^2$  and a total of 25 taxa were identified. The most abundant groups present in the enclosures were Chironomidae, Oligochaeta and Mollusca, with Chironomidae generally representing  $>90\%$  of the organisms found. The first sampling date for the treated enclosures was day 25, i.e. 5 days after the last application of nonylphenol. Generally, the oligochaete and chironomid groups showed a similar sensitivity to nonylphenol, with both being significantly reduced in number following 243  $\mu\text{g/l}$  treatments and the abundance of both groups generally recovered to control levels within 4-6 weeks. Molluscs were found to be significantly reduced in number throughout most of the study in the 243  $\mu\text{g/l}$  treatments. The NOEC and LOECs derived from the experiment were 23  $\mu\text{g/l}$  and 76  $\mu\text{g/l}$  based in the mean water concentrations in the enclosures over the first 20 days of the test.

#### Fish (Liber et al., 1999)

This part of the study looked at the effects on nonylphenol on the growth and survival of juvenile bluegill sunfish (*Lepomis macrochirus*). This species was not native to the pond and so 150 juvenile bluegills were added to each enclosure after the removal of the endemic fish population. The average length and weight of the introduced fish was  $9.0 \pm 0.9$  cm and  $12.0 \pm 3.4$  g respectively. The bluegill populations in the various enclosures were sampled (minimum of 10 fish per sample) once before the first nonylphenol application and seven times after the first nonylphenol application (days 5-6, 13-14, 19-20, 26-27, 40, 54 and 70-71) and growth was used as the main endpoint for assessing effects. No significant ( $p < 0.05$ ) difference was found in mean lengths and weights of fish from the nonylphenol-treated enclosures when compared to controls at any time during the study. Capture success was used as an indication of reduced bluegill survival. Capture success in the 243  $\mu\text{g/l}$  treated enclosures was lower (although not statistically significant ( $p > 0.05$ )) than in controls from day 19 onwards, and by day 54 the mean capture success in this group was 88% lower (significant at  $p < 0.001$ ) than in controls. These findings indicated that at the end of the assessment period (day 70-71) the bluegill populations in the 243  $\mu\text{g/l}$  treatment (83% reduction compared with controls) and also possibly the 76  $\mu\text{g/l}$  treatment (56% reduction compared with controls) had been adversely effected, but the reductions in capture success seen were not significantly different from controls ( $p < 0.05$ ) due to low capture success in one of the control groups. The cumulative mortality seen in the enclosures supported these findings as 74 dead fish were found in the 243  $\mu\text{g/l}$  treatments, with 68 of these occurring between days 11 to 22, and the mean mortality seen in the 76  $\mu\text{g/l}$  group was also greater (but not statistically significant) than in controls. For comparison, the 28 day mortality NOEC for



Table 3.14 Effects observed on zooplankton and macroinvertebrate populations

Taxon	NOEC <sup>a</sup>	LOEC <sup>a</sup>	Maximum reduction relative to controls	Time to recovery (days after last nonylphenol application)
ZOOPLANKTON				
Cladocera	76	243	77	14
Alona	76	243	48	8
Chydorus	76	243	79	14
Pleuroxus	76	243	99	31
Ceriodaphnia	23	76	91	43
Simocephalus	76	243	96	14
Acroperus	23	76	99	>63
Bosmina	76	243	98	1
Kurzia	76	243	99	43
Copepoda	76	243	86	31
Acanthocyclops	76	243	94	31
Eucyclops	76	243	92	31
Macrocyclus	76	243	97	43
Calanoida	5	23	90	>63
Mesocyclops	76	243	98	31
Diacyclops	76	243	92	31
Paracyclops	5	23	91	43
Harpacticoid	76	243	98	31
Rotifera	243	>243	-	-
Monostyla	243 <sup>b</sup>	>243	-	-
Polyarthra	243	>243	-	-
Lecane	243 <sup>b</sup>	>243	-	-
Trichocerca	23	76	73	63
Keratella	76	243	80	28
Euchlanis	76 <sup>b</sup>	243	88	34
Pleosoma	243	>243	-	-
Conochilus	243	>243	-	-
Colurella	76	243	85	31
Platyias	76	243	91	43
Lepadella	243 <sup>b</sup>	>243	-	-
Testudinella	76	243	95	≥31
Trichotria	76	243	82	1
Brachionus	243 <sup>b</sup>	>243	-	-
Notholca	76	243	93	1
Myytilina	243 <sup>b</sup>	>243	-	-
Ostracoda	76	243	82	14
All zooplankton	76	243	67	28
Macroinvertebrates				
Chironomidae				
Tanytarsini	76	243		53
Chironomini	243	>243		-
Oligochaeta				
Naididae	23	76		75
Tubificidae	243	>243		-
Mollusca				
Bivalvia	23	76		-
Gastropoda	76	243		>399 >111 but ≤299

a - based on average concentration measured in water during the 20-day exposure period - exposure may have occurred via other phases (see Table 3.11 above for details of the concentrations found in the various phases in the enclosures).

b - showed a significant increase in abundance relative to controls within 7-30 days of last application.

bluegills in a flow through assay was 59.5 µg/l and the LOEC 126 µg/l (Brooke 1993b, see **Table 3.10**). Bioconcentration factors of 10-614 (mean 87±124) were determined on a fish wet weight basis for fish from the 5 µg/l and 23 µg/l groups. These are comparable with other values reported for fish (Section 3.1.1.3.5).

#### Summary of field studies

Overall, the lowest NOEC derived in the study was 5 µg/l (for two species of Copepod). Generally the effect levels determined in the study for the various organisms agree reasonably well with the laboratory generated data.

When considering this study in terms of the risk assessment, several factors should be taken into account. Although the study is very comprehensive and well carried out, the actual study design means that the water concentrations were maintained only for the first 20 days of the study. While this time is probably adequate to observe effects on reproduction (and hence abundance) of some invertebrate species, this is not the case with some of the other organisms studied, particularly fish and some macroinvertebrates. Also, in the case of fish, only juvenile fish were added to the systems and only gross endpoints (growth and mortality) were observed, which means that some of the more sensitive life stages (e.g. larval stages) were not considered and the test system does not cover possible reproductive (or oestrogenic) effects. Another consequence of the test system used is that some effects were seen days or weeks after the initial 20 day period where the water concentrations were maintained (for instance the maximum reduction in zooplankton). This opens up the possibility that the same effects may occur at lower concentrations if the exposure was maintained throughout the test (for instance the long recovery period for some species exposed at 243 µg/l may indicate that they are still being affected by lower concentrations, as measurable concentrations of nonylphenol were still present for up to 98 days after the last application). Another consideration is that for benthic macroinvertebrates, the paper assumes exposure was mainly due to overlying water, as the concentration there was generally much higher than in pore water. However, as the organisms were generally collected from within the sediment the effects could have been due to the porewater, resulting in lower effect concentrations. A final consideration is that given the natural variation inherent in such a test system, very large changes in population abundance have to occur for them to be statistically significant when compared to the variation in control populations. Although the system used is suitable for detecting gross changes in populations, it is doubtful that such a system is sufficiently sensitive to detect small changes in the populations that could become significant with continued exposure.

Taken as a whole, the field study provides good supporting data for that generated in the laboratory studies, but cannot on its own be used as the basis for deriving a PNEC to protect the aquatic compartment.

### 3.2.1.2 Calculation of Predicted No Effect Concentration (PNEC)

**Table 3.15** summarises the lowest reliable toxicity values of nonylphenol for aquatic species.

Table 3.15 Summary of aquatic toxicity

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

#### 3.2.1.2.1 Surface water

The PNEC<sub>water</sub> is calculated using the assessment factors detailed in the TGD. For nonylphenol short-term and long-term data are available for both freshwater and seawater species for three trophic levels.

Short-term studies are available for fish, aquatic invertebrates and algae. The most sensitive species appears to be the freshwater invertebrate *Hyaella azteca* with a 96-hour EC<sub>50</sub> of 0.0207 mg/l. Long-term studies are also reported for fish, aquatic invertebrates and algae. The most sensitive species in long-term studies appears to be the freshwater algae *Scenedesmus subspicatus* with a 72-hour EC<sub>10</sub>(Biomass) of 3.3 µg/l. As long-term NOECs from at least three species representing three trophic levels are available an assessment factor of 10 may be used. Applying this to the long-term NOEC for algae gives a PNEC<sub>water</sub> of 0.33 µg/l.

For nonylphenol a mesocosm study is available which studied the effects on species from several trophic levels. Generally the effect levels determined in the study for various organisms agree reasonably well with the laboratory data. However, there are several aspects of the experiment design that suggest that the system used, while suitable for detecting gross changes in populations, is not sufficiently sensitive to detect small changes in populations that could become significant with continued exposure. The field study is therefore taken as supporting data in generating the PNEC, but cannot be used as the basis for deriving a PNEC to protect the aquatic compartment.

The  $PNEC_{water}$  is calculated using all the aquatic toxicity data present on nonylphenol. Data exist indicating toxicity at lower concentrations than the concentrations at which oestrogenic effects are observed. Therefore, the calculated PNEC should be protective for oestrogenic effects in fish as well.

### 3.2.1.2.2 Sewage treatment plants

A limited data set is reported for micro-organisms. From the data reported the most relevant data for deriving a  $PNEC_{micro-organisms}$  is the  $EC_{50}$  of 950 mg/l from the OECD 209 inhibition of activated sludge respiration study. The TGD recommends that an assessment factor of 100 is applied to an  $EC_{50}$  from an activated sludge respiration study, which gives a  $PNEC_{micro-organisms}$  of 9.5 mg/l.

### 3.2.1.2.3 Sediment

The TGD states that an equilibrium partitioning method may be used to estimate the  $PNEC_{sed}$ . In using this method it is assumed that sediment-dwelling organisms and water column organisms are equally sensitive to nonylphenol and that the concentration of nonylphenol in sediment, interstitial water and benthic organisms is at thermodynamic equilibrium. The formula 54 of the TGD is used to derive the  $PNEC_{sed}$  from the  $PNEC_{water}$

## 3.2.2 Terrestrial compartment

### 3.2.2.1 Terrestrial effect data

A wide range of mammalian toxicity test results is reported. These tests are reviewed in section 4 (human health). Limited toxicity data for other terrestrial organisms are reported in a Danish EPA report. These data are summarised in **Tables 3.16** and **3.17** below.

Table 3.16 Toxicity to terrestrial plants

Species	Test substance	Soil type	Endpoint and effect concentration (wet weight)	Reference
Lettuce ( <i>Lactuca sativa</i> )	4-nonylphenol	Agricultural loam	7 day $EC_{50}$ (Growth) 559 mg/kg 14 day $EC_{50}$ (Growth) 625 mg/kg	Hulzebos et al. (1993)
Sorghum ( <i>Sorghum bicolor</i> )	nonylphenol	Grit/loam soil	21 day NOEC (Growth) 100 mg/kg 21 day $EC_{50}$ (Growth) 1,000 mg/kg	Windeatt and Tapp (1987)
Sunflower ( <i>Helianthus rodeo</i> )			21 day NOEC (Growth) 100 mg/kg 21 day $EC_{50}$ (Growth) 1,000 mg/kg	
Soya ( <i>Glycine max</i> )			21 day NOEC (Growth) 100 mg/kg 21 day $EC_{25}$ (Growth) 1,000 mg/kg	

Table 3.17 Toxicity to terrestrial invertebrates

Species	Test substance	Soil type	Endpoint and effect concentration (wet weight)	Reference
Springtails ( <i>Folsomia fimetaria</i> )	nonylphenol	sandy soil	21 day EC10 (Reproduction) 27 mg/kg 21 day EC50 (Reproduction) 39 mg/kg	Holm
	4-nonylphenol in sludge		21 day EC10 (Reproduction) 48 mg/kg 21 day EC50 (Reproduction) 59 mg/kg	
	nonylphenol	LUFA soil	21 day EC10 (Reproduction) 24 mg/kg 21 day EC50 (Reproduction) 66 mg/kg 21 day EC10 (Mortality) 75 mg/kg 21 day EC50 (Mortality) 151 mg/kg	Krogh et al. (1996)
Earthworms ( <i>Apporec-todea calignosa</i> )	LUFA soil	21 day EC10 (Mortality) >40 mg/kg 21 day EC50 (Growth) 23.9 mg/kg 21 day EC10 (Reproduction) 3.44 mg/kg 21 day EC50 (Reproduction) 13.7 mg/kg		

In degradation experiments (See Section 3.1.2.2.3) Trocmé et al. (1988) studied the fate of nonylphenol in a simplified soil system and its effect on microbial activity. The authors found that CO<sub>2</sub> production was reduced at 1,000 mg/kg nonylphenol while no effects were observed at 100 mg/kg nonylphenol over a 40 day period. Kirchmann et al. (1991) studied the biodegradation of 4-n-nonylphenol in soil. The authors found that upon addition of 500 mg/kg nonylphenol microbial respiration was significantly enhanced, whereas no stimulation was observed upon addition of 10 mg/kg nonylphenol to the soil over a 100 day period. For nitrogen mineralisation they found no effect upon addition of 10 or 500 mg/kg nonylphenol, whereas a temporary reduction in nitrification was observed at 500 mg/kg.

### 3.2.2.2 Calculation of PNEC<sub>soil</sub>

For nonylphenol there are limited terrestrial effects data. The Technical Guidance Document recommends that when toxicity data are available for a producer, a consumer and/or a decomposer the PNEC<sub>soil</sub> should be calculated using assessment factors and that there is no need to calculate a PNEC using the equilibrium partitioning method. For nonylphenol there are toxicity data for terrestrial micro-organisms, plants and invertebrates, so the PNEC<sub>soil</sub> should be calculated from these data using assessment factors.

The most sensitive species group appears to be the terrestrial invertebrates with a 21-day EC<sub>50</sub> (reproduction) of 13.7 mg/kg and a 21-day EC<sub>10</sub> (reproduction) of 3.44 mg/kg reported for earthworms (*Apporec-todea calignosa*). As long-term tests are available for species from three trophic levels an assessment factor of 10 will be used on the NOEC for the species showing the most sensitive end point. In this case a 21-day EC<sub>10</sub> (reproduction) is reported for earthworms which can be taken as equivalent to a NOEC. Applying a factor of 10 to this value gives a PNEC<sub>soil</sub> of 0.3 mg/kg wet wt.

### 3.2.3 Atmosphere

There are no data on the effects of nonylphenol through aerial exposure of non-mammalian organisms. Biotic or abiotic effects are unlikely to occur because of the limited direct release, low volatility and rapid atmospheric degradation of nonylphenol. Nonylphenol is not expected to be a greenhouse gas. It is unlikely to move from the troposphere to the stratosphere and contribute to ozone depletion, and neither is it thought to contribute to low-level ozone formation.

### 3.2.4 Non compartment specific effects relevant to the food chain (secondary poisoning)

Nonylphenol has been shown to bioconcentrate in aquatic species.

No toxicity data are available on avian species; thus a PNEC is derived from laboratory mammal data. From Section 4, a NOAEL of 15 mg/kg body weight was found for reproductive effects. Using the conversion factor of 20 from Appendix VII of the TGD and a further factor of 3 to allow for the fact that calorific content of a laboratory diet is higher than the diet of fish-eating mammals and birds, this NOAEL is equivalent to a daily dose of 100 mg/kg food. The TGD recommends the use of an assessment factor of 10 on reproductive studies. Therefore the  $PNEC_{oral}$  is 10 mg/kg food.

## 3.3 RISK CHARACTERISATION

In view of the large number of different life cycle stages, the environment conclusions for nonylphenol are tabulated in section 5.1.

### 3.3.1 Aquatic compartment (including sediment)

Nonylphenol enters the aquatic compartment directly as nonylphenol or as the breakdown product of nonylphenol ethoxylates. In this assessment predicted environmental concentrations have been calculated using default release estimations from the Technical Guidance Document, use category documents, information supplied by industry and from consultation with end users. The quantities used in calculating these values have been derived from an industry survey of nonylphenol and nonylphenol ethoxylate producers in 1994. Updated figures covering 1997 have been supplied by industry. While there can be a reasonable level of confidence in the total amounts of nonylphenol and nonylphenol ethoxylates used in each application, there is less information readily available on the use and release of nonylphenol and nonylphenol ethoxylates at the local scale.

The regional  $PEC_{surface\ water}$  is calculated as 0.60 µg/l. When compared to the PNEC of 0.33 µg/l the PEC/PNEC ratio is 1.8 indicating concern for the aquatic compartment.

The measured data suggest that local concentrations may be higher where waters are receiving inputs from industries which use either nonylphenol or nonylphenol ethoxylates. Some of the current measured data represent areas where some uses have already been restricted or banned. The measured data are not comprehensive enough to allow all the possible uses of nonylphenol to be accounted for, and therefore the calculated PECs are used to indicate the levels arising from different industries.

As the regional concentration gives a PEC/PNEC ratio greater than 1 the PEC/PNEC ratio for the local PECs will also be greater than 1. This is because the regional concentration is added to the local concentrations to take account of background levels. **Table 3.17** gives details of local concentrations before the regional concentration is added and compares these values to the PNEC for aquatic organisms. This enables those uses that are only a problem due to the addition of the regional concentration to be identified.

The concentration of nonylphenol in the influent and effluent of wastewater treatment plants has been calculated for the uses detailed above. The  $C_{local,eff}$  is taken as the  $PEC_{stp}$  for risk assessment purposes. The  $PNEC_{stp}$  is calculated as 9.5 mg/l. When the  $PEC_{stp}$  is compared with

the  $PEC_{stp}$  a  $PEC/PNEC$  ratio  $<1$  is obtained for the all life cycle stages of nonylphenol and nonylphenol ethoxylate use (See **Table 3.18**).

Nonylphenol in water courses is strongly adsorbed to sediments and sludges. The  $PNEC_{sediment}$  is 0.039 mg/kg. This has been calculated from the  $PNEC_{water}$  using an equilibrium partition method. The predicted levels in sediments from local sources are shown in **Table 3.18**, along with the resulting  $PEC/PNEC$  ratios. These suggest that nonylphenol may have adverse effects on sediment dwelling species although the assessment could be refined with test data.

During consultation with industry and end users of nonylphenol and nonylphenol ethoxylate products it has become apparent that use and disposal patterns can vary within an industry sector. For some use scenarios of the nonylphenol ethoxylates it was found that not all companies active in a particular industry use nonylphenol ethoxylates in their products. Other companies were found to be phasing the chemicals out of their product ranges and replacing them with alternatives. The disposal patterns of companies were found to vary greatly with disposal to wastewater after treatment and incineration of wastes being the most common methods reported. This means that for several of the industry sectors, covered a reasonable worst-case assumption is presented that may only cover a few sites within the EU. The remainder of the sites may be operating within acceptable parameters. This is shown in the calculations for nonylphenol and nonylphenol ethoxylate production plants, where the majority of sites give a local concentration in water below the  $PNEC_{water}$  (before accounting for background levels). The sites that show a concentration higher than the  $PNEC$  are those which were unable to obtain additional data on their releases to water.

In order to refine the assessment in general, further information would be required on the use of nonylphenol and nonylphenol ethoxylates at specific sites within the EU for specific industries. For most applications this would present considerable problems, as there are a large number of companies within an industry sector. In addition not all the companies within an industry sector are likely to use nonylphenol or nonylphenol ethoxylates. Therefore it is not considered possible to refine the exposure estimates for the industries within a reasonable time period.

### **Conclusions to the risk assessment for the aquatic compartment:**

- (i) There is a need for further information and/or testing.

This conclusion applies to the aquatic (sediment) compartment for all life cycle stages (except production of tri-(4-nonylphenyl) phosphite (TNPP) and the use of veterinary medicine products containing nonylphenol ethoxylates). The  $PNEC$  for sediment was derived from that for aquatic organisms. It could therefore be revised by performing toxicity tests on sediment organisms. However, the requirement for further testing should await the outcome of the risk reduction strategy for the aquatic (surface water) compartment, since the sediment  $PECs$  will be directly affected by any measures to reduce concentrations in water.

- (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those, which are being applied already.

This conclusion applies to the aquatic (surface water and sediment) compartment for production of TNPP and the use of veterinary medicine products containing nonylphenol ethoxylates, and to micro-organisms in wastewater treatment plants for all life cycle stages.

Table 3.18 Comparison of calculated concentrations for water and sediment and PNECs for water, sediment and micro-organisms

Life Cycle Stage	PEC <sub>stp</sub> (Clocaeff)	PEC <sub>stp</sub> / PNEC <sub>micro-organisms</sub>	Clocalwater	Clocalwater/ PNEC <sub>water</sub>	PEC <sub>localwater</sub>	PEC <sub>localwater</sub> / PNEC <sub>water</sub>	PEC <sub>localsediment</sub> (wet weight)	PEC <sub>sediment</sub> / PNEC <sub>sediment</sub>
Direct releases of nonylphenol								
Nonylphenol Production Sites								
A	n/a	n/a	n/a	n/a	<0.2 µg/l (m)	<0.6	<23.5 µg/kg	0.6
B	n/a	n/a	<0.0208 µg/l (m)	<0.006	<60 µg/l	<1.8	<70.4 µg/kg	1.8
C	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
D	<1 µg/l (m)	0.0001	<0.019 µg/l	<0.06	<0.60 µg/l	<1.8	<70.4 µg/kg	1.8
Nonylphenol ethoxylate production sites								
B	n/a	n/a	n/a	n/a	3.02 µg/l (m)	9.15	355 µg/kg	9.1
C 1+2	2.55, 7.29 mg/l	0.27, 0.77	0.26 mg/l	787	0.26 mg/l	787	30.5 mg/kg	782
C 3	2.98 mg/l	0.31	0.30 mg/l	909	0.30 mg/l	909	35.2 mg/kg	903
D 1	30 µg/l	0.003	1.49 µg/l	4.52	2.09 µg/l	6.33	245 µg/kg	6.28
D 2	15 µg/l	0.0015	1.36 µg/l	4.09	1.95 µg/l	5.91	230 µg/kg	5.87
E	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
F	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
G	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Production of nonylphenol/ formaldehyde resin	15.75-26.25 µg/l	0.002-0.003	1.6-2.6 µg/l	3.09-7.9	2.2-3.2 µg/l	4.9-9.7	258-376 µg/kg	3.05-9.6
Production of TNPP	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Production of epoxy resin	0.46 µg/l	0.00005	0.05 µg/l	0.15	0.65 µg/l	1.97	76 µg/kg	1.94
Production of other plastic stabilisers	28 µg/l	0.003	2.78 µg/l	8.42	3.38 µg/l	11.3	397 µg/l	11.2
Phenolic oxime production	0.318 mg/l (m)	0.033	0.004 µg/l	0.01	0.60 µg/l	1.79	70.4 µg/kg	1.78
Indirect releases of nonylphenol due to the breakdown of nonylphenol ethoxylates								
Formulation	12.5, 31, 125 µg/l	0.001, 0.003, 0.013	1.24, 3.08, 12.4 µg/l	3.76, 9.33, 37.6	1.84, 3.68, 13.0 µg/l	5.79, 11.12, 39.4	216, 433, 1,526 µg/kg	5.7, 13.1, 39.1

Table 3.18 continued overleaf



**Table 3.18 continued** Comparison of calculated concentrations for water and sediment and PNECs for water, sediment and micro-organisms

Life Cycle Stage	PEC <sub>stp</sub> (Clocaleff)	PEC <sub>stp</sub> / PNEC <sub>micro-organisms</sub>	Clocalwater	Clocalwater/ PNEC <sub>water</sub>	PEC <sub>localwater</sub>	PEC <sub>localwater</sub> / PNEC <sub>water</sub>	PEC <sub>localsediment</sub> (wet weight)	PEC <sub>sediment</sub> / PNEC <sub>sediment</sub>
Agriculture (pesticide application)	n/a	n/a	0.08-0.33 µg/l	0.24-1	0.68-0.93 µg/l	2-2.8	79.8-109 µg/kg	2.02-2.77
Captive use by chemical industry	51 µg/l	0.005	0.02 µg/l	0.06	0.62 µg/l	1.88	73 µg/kg	1.87
Electrical engineering industry	30.8 µg/l	0.003	3.05 µg/l	9.24	3.65 µg/l	11.0	428 µg/kg	10.9
Industrial and institutional cleaning	259 µg/l	0.027	25.7 µg/l	77.9	26.3 µg/l	79.7	3.09 mg/kg	79.2
Leather processing	169-845 µg/l	0.018-0.089	16.7-83.8 µg/l	50.6-254	17.3-84.4 µg/l	52.4-255.8	2.03-9.91 mg/kg	52.1
Metal extraction and processing	1.43 mg/l	0.15	141 µg/l	427	141 µg/l	427	1.66 mg/kg	42.6
Mineral fuel and oil industry	n/a	n/a	1-35 µg/l (m)	3-106	1.6-35.6 µg/l	4.8-108	0.19-4.18 mg/kg	4.87-10.7
Photographic industry	0.1-15.5 µg/l	0.00001-0.0016	0.009-1.54 µg/l	0.03-4.67	0.61-2.14 µg/l	2.06-6.45	71.6-251 µg/kg	2.05-6.41
Polymer industry	12.5 µg/l	0.0013	1.24 µg/l	3.76	1.84 µg/l	5.55	216 µg/kg	5.51
Pulp, paper and board industry	160 µg/l	0.017	15.9 µg/l	48	16.5 µg/l	50	1.94 mg/kg	49.7
Textile industry	3.5 mg/l	0.37	350 µg/l	1,060	350 µg/l	1,060	41.1 mg/kg	1,053
Paint Production Domestic use Industrial use	0.05 mg/l 0.1 µg/l 0.125 µg/l	0.005 0.00001 0.00001	4.96 µg/l 0.01 µg/l 0.012 µg/l	15 0.03 0.04	5.5 µg/l 0.60 µg/l 0.60 µg/l	16.7 1.8 1.8	653 µg/kg 70.4 µg/kg 70.4 µg/kg	16.6 1.81 1.81
Civil engineering	0.31 mg/l	0.033	30.75 µg/l	93	31.3 µg/l	94.8	3.67 mg/kg	94.1
Regional and Continental PECs due to direct emissions of nonylphenol and the breakdown of nonylphenol ethoxylates								
Regional					0.60 µg/l	1.78	103 µg/kg	2.64
Continental					0.072 µg/l		13.1 µg/kg	

- (iii) There is a need for limiting the risks; risk reduction measures that are already being applied shall be taken into account.

This conclusion applies to the aquatic (surface water) compartment for the following life cycle stages (as well as to regional concentrations derived from all sources):

- Production of nonylphenol;
- Production of phenol/formaldehyde resins;
- Production of epoxy resins;
- Production of other plastic stabilisers;
- Production of phenolic oximes;
- Production of nonylphenol ethoxylates;
- Formulation of nonylphenol ethoxylates; and
- Nonylphenol ethoxylate use in all applications (i.e. agriculture\*; captive use by the chemical industry; civil engineering; electrical engineering; industrial and institutional cleaning; leather processing; metal extraction and processing; mineral fuel and oil industry; paint production and use; photographic industry; polymer industry; pulp, paper and board industry; textile industry).

For nonylphenol and nonylphenol ethoxylate production sites not all of those sites considered give rise to a PEC/PNEC ratio greater than 1.

For the following uses a PEC/PNEC ratio greater than 1 is only obtained because the regional PEC (0.60 µg/l) is added to the local concentration to give the local PEC:

- Production of nonylphenol (Sites B and D);
- Production of epoxy resins;
- Production of phenolic oximes;
- Use of nonylphenol ethoxylates in agriculture (pesticide formulations);
- Captive use of nonylphenol ethoxylates by the chemical industry;
- Use of photographic materials containing nonylphenol ethoxylates by small scale photographic processors; and
- Use of domestic and industrial emulsion paints containing nonylphenol ethoxylates.

The available information on measured levels is not sufficient to identify which uses of nonylphenol or nonylphenol ethoxylates give rise to concern. It is noted that the voluntary removal of nonylphenol ethoxylates from domestic detergents has led to a noticeable reduction in measured concentrations. However levels which give rise to concern have still been measured recently. Therefore at this stage the conclusion has to apply to all areas. It should be noted that if the contribution made by the use of nonylphenol ethoxylates in industrial and institutional cleaning and the textile industry was removed, the calculated regional PEC would be in the order of 0.2 µg/l. This is in the range of levels measured in areas that reduced or banned the use of nonylphenol ethoxylates in domestic and/or industrial cleaning products. It should also be noted that, as well as nonylphenol, other toxic products such as nonylphenol carboxylates and short chain nonylphenol ethoxylates could be formed by the breakdown of nonylphenol ethoxylates in the environment. These are not addressed in the assessment.

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\* This does not apply to use in veterinary medicines.

It is recognised that the reliance on default values implies that it should be possible to refine the PECs. However, as noted above this is not considered to be feasible in a reasonable time frame. The conclusion is that measures are required to continue the reduction in levels of nonylphenol in the aquatic compartment.

### *Uncertainties*

There are a number of uncertainties in the risk characterisation for the aquatic environment (including sediment). Firstly, as already discussed, a number of emission scenarios are based upon default estimations. This may result in significant variations between predicted concentrations and actual environmental concentrations.

Secondly, the results of biodegradation studies show a wide variation in test results. The reasons for this are discussed fully in Section 3.1.1.2.4 but included possible toxicity of nonylphenol to micro-organisms in the test system, a level of adaptation of the micro-organisms to nonylphenol and varying isomer composition of the nonylphenol. Therefore the actual half-life for nonylphenol in the environment could be different (longer or shorter) than the estimated values depending on the prevailing conditions.

Thirdly, in the PEC calculations some of the calculated levels are higher than the water solubility limit of nonylphenol. This could mean that actual concentrations are over-estimated for these scenarios, but no correction for this has been applied in the calculations.

Finally, a recent assessment of the risks to the aquatic environment by the US EPA concluded that the current use pattern of nonylphenol and nonylphenol ethoxylates in the USA does not lead to widespread concern. However there are likely to be local 'hotspots' where effects might be seen. The reasons for the differences between the EPA conclusions and those in this risk assessment appear to be largely methodological. A discussion of the main differences is included in Appendix 3.

### **3.3.2 Terrestrial compartment**

Direct releases of nonylphenol to the terrestrial compartment are unlikely to occur given its production method and use pattern. The exception is the use of nonylphenol ethoxylates in pesticide formulations. The calculated PECs do imply high concentrations of nonylphenol in all the soil types due to the application of sewage sludge. In calculating the PECs default estimations based upon the TGD and information on use supplied by industry have been used.

Nonylphenol is strongly adsorbed to sludge in the wastewater treatment process, and this may then be applied to agricultural land. Nonylphenol in sewage treatment plants can come from direct discharges of nonylphenol or from the breakdown of products containing nonylphenol, such as nonylphenol ethoxylates, in the WWTP. High concentrations of nonylphenol may therefore occur in soils where sewage sludge is applied. This is reflected in the high-calculated PEC values.

Nonylphenol released to soil either directly or indirectly will be strongly bound to the soil. It is therefore unlikely to enter groundwater or be transported a considerable distance.

There is limited information available on the effects of nonylphenol on soil dwelling species. A  $PNEC_{soil}$  of 0.3 mg/kg was calculated using terrestrial toxicity data. A comparison of the

calculated PEC/PNEC ratios indicates that for most uses there is a level of concern for the terrestrial environment (**Table 3.19**).

The reported levels in soil (arising from sludge application) range from 0.3-4.7 mg/kg following application. This would give PEC/PNEC ratios of 1 to 15.6. The background concentration, measured in soil with no sludge application, was <0.02 mg/kg; this is lower than the PNEC<sub>soil</sub>.

#### **Conclusion to risk assessment for terrestrial compartment:**

- ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those, which are being applied already.

This conclusion applies to the following life cycle stages (as well as to regional soil concentrations derived from all sources):

- Production of nonylphenol;
- Production of nonylphenol/formaldehyde resins;
- Production of epoxy resins;
- Production of TNPP;
- Production of other plastic stabilisers;
- Production of phenolic oximes;
- Use of nonylphenol ethoxylates in agriculture (pesticide formulations); and
- Domestic and industrial use of paint containing nonylphenol ethoxylates.

- iii) There is a need for limiting the risks; risk reduction measures that are already being applied shall be taken into account.

This conclusion applies to the following:

- Production of nonylphenol ethoxylates;
- Formulation of nonylphenol ethoxylates;
- Use of nonylphenol ethoxylates in agriculture (veterinary medicines);
- Captive use of nonylphenol ethoxylates by the chemical industry;
- Use of nonylphenol ethoxylates in civil engineering;
- Use of nonylphenol ethoxylates in electrical engineering;
- Use of nonylphenol ethoxylates in industrial and institutional cleaning;
- Use of nonylphenol ethoxylates in leather processing;
- Use of nonylphenol ethoxylates in metal extraction and processing;
- Use of nonylphenol ethoxylates in the mineral fuel and oil industry;
- Production of paint containing nonylphenol ethoxylates;
- Use of nonylphenol ethoxylates in the photographic industry;
- Use of nonylphenol ethoxylates in the polymer industry;
- Use of nonylphenol ethoxylates in the pulp, paper and board industry; and
- Use of nonylphenol ethoxylates in the textile industry.

Table 3.19 PEC/PNEC ratios for the terrestrial compartment

Source	PEC <sub>local</sub> <sub>agri,soil</sub> (mg/kg wet wt) (Averaged over 30 days)	PEC/PNEC
Direct release of nonylphenol		
Nonylphenol production sites		
A	n/a	n/a
B	0.0242	0.08
C	n/a	n/a
D	n/a	n/a
Nonylphenol ethoxylates production sites		
B	n/a	n/a
C	15.5, 15.2	51.7, 50.7
D	1.27, 1.17	4.23, 3.9
E	n/a	n/a
F	n/a	n/a
G	n/a	n/a
Production of nonylphenol/formaldehyde resin	0.159	0.53
Production of TNPP	n/a	n/a
Production of epoxy resins	0.0028	0.009
Production of other plastic stabilisers	0.17	0.57
Phenolic oximes production	n/a	n/a
Indirect releases of nonylphenol due to the breakdown of nonylphenol ethoxylates		
Formulation	1.07 (Small scale) 2.67 (Medium scale) 10.6 (Large scale)	3.57 (Small scale) 8.9 (Medium scale) 35.3 (Large scale)
Use in agriculture: Pesticide application Veterinary medicine use	0.0386 0.46, 0.30, 0.82	0.13* 1.5, 1, 2.7
Captive use by the chemical industry	4.33	14.4
Electrical engineering industry	2.61	8.7
Industrial and institutional cleaning	21.9	73
Leather processing	14.3 (Average user), 71.6 (Large user)	42.7 (Average user) 239 (Large user)
Metal extraction and processing	121	403
Mineral fuel and oil industry	4.33	14.4
Photographic industry	0.009 (Small processor) 1.31 (Large processor)	0.03 (Small processor) 4.37 (Large processor)
Polymer industry	1.06	3.53
Pulp, paper and board industry	13.3	44.3
Textile industry	297	990

Table 3.19 continued overleaf

Table 3.19 continued PEC/PNEC ratios for the terrestrial compartment

Source	PEC <sub>local</sub> <sub>agri,soil</sub> (mg/kg wet wt) (Averaged over 30 days)	PEC/PNEC
Paint Production Domestic use Industrial use	4.24 0.0085 0.0106	14.1 0.028 0.035
Civil engineering	26.3	87.7
Regional	0.265	0.88

\* - the calculation of the PEC for this scenario was based on a single application of pesticide, from which all of the NPEO broke down to NP. It is possible that multiple application will occur. However it is calculated that up to 7 simultaneous applications would not give a PEC/PNEC ratio >1, so it is considered that there is no concern based on a worst-case assessment.

### Uncertainties

There are a number of uncertainties in the risk characterisation for the terrestrial environment.

Firstly, as already discussed, a number of emission scenarios are based upon default estimations. They also assume that sludge from wastewater treatment plants treating nonylphenol ethoxylate is applied to agricultural soil which will not always be the case.

Secondly, the results of biodegradation studies show a wide variation in test results. The reasons for this are discussed in Section 3.1.1.2.4. Therefore the actual half-life for nonylphenol in the environment could be different (longer or shorter) than the estimated values depending on the prevailing conditions.

Thirdly, measured and calculated values for adsorption coefficient are different. The reasons for this are discussed in Section 3.1.1.3.1. Evidence from measured levels indicates that adsorption to soil may be governed by factors other than organic carbon content and the calculated levels used in the PEC calculations do not take this into account.

Finally, in the PEC calculations it is assumed that nonylphenol ethoxylates are converted instantly into nonylphenol in sludge whereas in the environment this will be a gradual process.

### 3.3.3 Atmosphere

Nonylphenol is not released in any significant quantities to the atmosphere. In the atmosphere nonylphenol is relatively short lived, based upon its reaction with hydroxyl radicals. It is therefore unlikely to be transported very far from its point of emission. It is unlikely to move from the troposphere to the stratosphere and contribute to ozone depletion. Nonylphenol is not thought to contribute to low-level ozone formation nor act as a greenhouse gas. Biotic effects are unlikely.

#### Conclusion to risk assessment for atmospheric compartment:

- ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those, which are being applied already.

This conclusion applies to all life cycle stages for nonylphenol.

### 3.3.4 Non compartment specific effects relevant for the food chain (Secondary poisoning)

Nonylphenol shows a high bioconcentration potential in aquatic organisms. In Section 3.1.5 a PNEC<sub>oral</sub> of 10 mg/kg food was derived for the secondary poisoning scenario. The concentration of nonylphenol in fish and earthworms for predators has been estimated using the EUSES program. The resultant PEC/PNEC ratios are detailed in **Table 3.20** below.

Table 3.20 PEC/PNEC ratio for fish and earthworms

Life Cycle Stage	Concentration in fish for predators (mg/kg wet weight)	PEC <sub>fish</sub> /PNEC <sub>oral</sub>	Concentration in earthworms (mg/kg)	PEC <sub>earthworms</sub> /PNEC <sub>oral</sub>	
Direct release of nonylphenol					
Nonylphenol production					
Site A	0.795	0.08	n/a	0.18	
Site B	0.775	0.08	1.82		
Site C	n/a		n/a		
Site D	0.764	0.08	n/a		
Nonylphenol ethoxylate production					
Company B	2.34	0.23	n/a	8.47, 9.85	
Company C	134, 156		84.7, 98.5		
Company D	1.55, 1.48		1.34, 1.56		8.52, 7.95
Company E	n/a		0.16, 0.15		n/a
Company F	n/a				n/a
Company G	n/a				n/a
Company G	n/a				n/a
Phenol/formaldehyde resin production	2.14	0.21	2.55	0.25	
TNPP production	n/a		n/a		
Epoxy resin production	0.787	0.08	1.71	0.17	
Production of other plastic stabilisers	2.23	0.22	2.6	0.26	
Phenolic oximes	0.766	0.08	n/a		
Indirect releases of nonylphenol from the use of nonylphenol ethoxylates					
Formulation of nonylphenol ethoxylates	1.42, 2.4, 7.3	0.14, 0.24, 0.73	7.51, 16, 58.7	0.75, 1.6, 5.87	
Agriculture Pesticide application Veterinary medicine use	0.79	0.08	1.9 6.1	0.19 0.61	
Captive use by the chemical industry	0.774	0.08	24.9	2.49	
Electrical engineering industry	2.37	0.23	15.7	1.57	
Industrial and institutional cleaning	14.3	0.98	120	12.0	
Leather processing	9.59, 44.9	0.96, 4.5	78.6, 386	7.86, 38.6	
Metal extraction and processing	75.3	7.53	651	65.1	
Mineral fuel and oil industry	2.38	0.24	24.9	2.49	
Photographic industry	0.769, 1.57	0.08, 0.16	1.74, 8.75	0.17, 0.87	
Polymer industry	1.42	0.14	7.38	0.74	

Table 3.20 continued overleaf

Table 3.20 continued PEC/PNEC ratio for fish and earthworms

Life Cycle Stage	Concentration in fish for predators (mg/kg wet weight)	PEC <sub>fish</sub> /PNEC <sub>oral</sub>	Concentration in earthworms (mg/kg)	PEC <sub>earthworms</sub> /PNEC <sub>oral</sub>
Pulp, paper and board industry	8.93	0.89	72.9	7.29
Textile industry	184	18.4	1,600	160
Paint production and use	3.38 (Man) 0.769 (Dom) 0.77 (Ind)	0.21 0.08 0.08	24.5 (Man) 1.74 (Dom) 1.75 (Ind)	2.45 0.17 0.17
Civil engineering	17	1.7	143	14.3
Regional	0.764	0.08	1.69	0.17

In addition to these scenarios, a calculation was performed for indirect exposure through consumption of plants sprayed with pesticide containing NPEOs. This gave a PEC in food of 6 mg/kg. Compared to the PNEC, the PEC/PNEC ratio is 0.6. As this calculation includes several additive worst-case assumptions, this indicates there should not be any concern for this route.

### Conclusion to the risk assessment for secondary poisoning:

- (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those, which are being applied already.

This conclusion applies to the following life cycle stages (as well as to regional concentrations derived from all sources):

- Production of nonylphenol;
- Production of nonylphenol/formaldehyde resins;
- Production of epoxy resins;
- Production of TNPP;
- Production of other plastic stabilisers;
- Production of phenolic oximes;
- Use of nonylphenol ethoxylates in agriculture (pesticide formulations);
- Use of nonylphenol ethoxylates in agriculture (veterinary medicines);
- Use of paint containing nonylphenol ethoxylates;
- Use of nonylphenol ethoxylates in the photographic industry; and
- Use of nonylphenol ethoxylates in the polymer industry.

- iii) There is a need for limiting the risks; risk reduction measures that are already being applied shall be taken into account.

This applies to the following life cycle stages:

- Production of nonylphenol ethoxylates;
- Formulation of nonylphenol ethoxylates;
- Captive use of nonylphenol ethoxylates within the chemical industry;
- Use of nonylphenol ethoxylates in civil engineering;
- Use of nonylphenol ethoxylates in the electrical engineering industry;
- Use of nonylphenol ethoxylates in industrial and institutional cleaning;
- Use of nonylphenol ethoxylates in leather processing;



- Use of nonylphenol ethoxylates in metal extraction and processing;
- Use of nonylphenol ethoxylates in the mineral fuel and fuel industry;
- Production of paint containing nonylphenol ethoxylates;
- Use of nonylphenol ethoxylates in the pulp, paper and board industry; and
- Use of nonylphenol ethoxylates in the textile industry

### *Uncertainties*

There are a number of uncertainties in the risk characterisation section for secondary poisoning. Firstly, as already discussed, a number of emission scenarios are based upon default estimations. This may result in significant variations between predicted concentrations and actual environmental concentrations. Secondly, the aquatic and terrestrial PECs are subject to a number of uncertainties which will impact upon the PEC calculated for secondary poisoning.

## **4 HUMAN HEALTH**

### **4.1 HUMAN HEALTH (TOXICITY)**

#### **4.1.1 Exposure assessment**

##### **4.1.1.1 Occupational exposure**

###### **4.1.1.1.1 General introduction**

###### Definitions and sources

In this section, unless otherwise stated, the term exposure is used to denote personal exposure as measured or otherwise assessed without taking into account the attenuating effect of any respiratory protective equipment (RPE) which might have been worn. This definition permits the effects of controls, other than RPE, to be assessed and avoids the considerable uncertainty associated with attempting to precisely quantify the attenuation of exposure brought about by the proper use of RPE.

The section entitled general discussion summarises the more important issues arising from the exposure assessments and bring together measured exposure data with that predicted from the EASE (Estimation and Assessment of Substance Exposure) model. EASE is a general purpose predictive model for workplace exposure assessments. It is an electronic, knowledge based, expert system which is used where measured exposure data is limited or not available. The model is in widespread use across the European Union for the occupational exposure assessment of new and existing substances.

All models are based upon assumptions. Their outputs are at best approximate and may be wrong. EASE is only intended to give generalised exposure data and works best in an exposure assessment when the relevance of the modelled data can be compared with and evaluated against measured data. Dermal exposure is assessed by EASE as potential exposure rate predominantly to the hands and forearms (approximately 2000 cm<sup>2</sup>).

###### Overview of exposure

Nonylphenol is understood to be used as a chemical intermediate, for example, in the manufacture of nonylphenol ethoxylates. A further use in the manufacture of some speciality coatings has also been identified. The industry sectors where occupational exposure to nonylphenol may occur are:

- (a) manufacturer of nonylphenol;
- (b) users of nonylphenol as an intermediate;
- (c) manufacturers of speciality paints; and
- (d) users of speciality paints.

Some manufacturers of nonylphenol are also users. It was not possible to establish the number of workers exposed to nonylphenol, although it was estimated to be about 300 to 600.

Nonylphenol is manufactured and used in closed plant. The situations giving rise to occupational exposure are likely to be similar for both manufacturers and users (i.e. closed systems with some

breaching). Companies generally do not carry out air sampling for nonylphenol with control assumed from the nature of the process, and in many cases monitoring is carried out for materials deemed to be more hazardous, for example, ethylene oxide.

HSE's NEDB (National Exposure DataBase) has no occupational exposure data for nonylphenol and results were only received from two companies. These short-term and 8-hour TWA results were all less than the limits of quantification (LOQ) at one site; with the highest LOQ being less than 0.28 ppm for short-term measurements. The results of short-term measurements from the second site were up to 0.005 ppm, with one additional result of 21 ppm. This measurement of 21 ppm seems unlikely to be valid given the saturated vapour concentration (SVC) of 2.96 ppm at 25°C.

Considering the SVC and the industry exposure data, it was concluded that exposures are likely to be less than 1 ppm 8-hour TWA, and in most cases significantly less for manufacturers and chemical intermediate users. It seems reasonable to further assume that the most exposures will be less than 0.1 ppm 8-hour TWA since only one actual result exceeded this value; therefore this value represents the reasonable worst case scenario. The only other figures above this were up to 0.16 ppm 8-hour TWA, which is the limit of quantification. It is also likely that exposures during the manufacture of speciality paints containing nonylphenol are similarly low.

The potential for exposure during speciality paint spraying is higher, given the act of spraying generates aerosols. Considering that EASE is poor at predicting exposures to low volatility substances during spraying, data from analogous substances was used. De Pater et al., (1999 Draft), provides a model for predicting exposure to non-volatile compounds during spray painting of speciality paints. Using this analogous data and model, exposure during the spray application of speciality paints containing nonylphenol was predicted to be 1.7 mg/m<sup>3</sup> 8-hour TWA. It should be noted that this value is used with caution since there are many complicating factors that the model reported by De Pater does not address. In view of these uncertainties a value of 1 ppm (9.1 mg/m<sup>3</sup>) 8-hour TWA was taken forward for the risk characterisation.

#### Occupational exposure limits

There are thought to be no occupational exposure limits for nonylphenol in the EU.

##### **4.1.1.1.2 Occupational exposure to nonylphenol during its manufacture and use as a chemical intermediate**

The manufacture of nonylphenol and its use as a chemical intermediate are carried out in closed systems. It is estimated that about 300 to 600 workers are exposed during its production and use. Occupational exposure arises during tasks where the system is breached, for example, sampling, maintenance and product filling to drums or tankers. Occupational exposure to nonylphenol during its manufacture and use as a chemical intermediate will therefore be similar.

Exposure data for nonylphenol were received from two companies (see industry exposure data). Control of exposure is assessed and deemed adequate by industry on the basis that it is essentially an enclosed process and in many cases by monitoring for other substances, for example, ethylene oxide. It is likely that exposure to nonylphenol will be low during production and use.

The control regimes used by manufacturers and users of nonylphenol when breaching enclosed plants vary, consequently exposures are likely to be higher at some plants than others. These

control regimes may include, for example, the use of closed loop sampling points, dry break coupling points and sealed dedicated transfer lines.

Nonylphenol is manufactured and used at temperatures up to about 150°C. The potential for exposure may increase during tasks carried out at elevated temperatures. It is understood that it is processed at 50°C due to its viscosity.

### Industry data

Short-term exposure data were received from one EU company (CEFIC, 1996) manufacturing and using nonylphenol. Five results ranged from less than 0.001 ppm to 0.005 ppm and a further result of 21 ppm was reported. The operations monitored were sampling, pump repair, drum filling and road tanker filling.

Occupational exposure data was also received from a USA-based company using nonylphenol in the manufacture of surfactants. Personal air sampling was carried out using a method developed and validated by the company which utilised Tenax tubes to collect the nonylphenol and gas chromatography to carry out the analysis. These results are shown in **Table 4.1**.

**Table 4.1** Occupational exposure to nonylphenol during its use as a chemical intermediate

Work Activity	Year of Measurement	Sample Type	Number of Samples	Range of Results (ppm)
production operations (including unloading operations)	1994-95	4-hour TWA*	4	<0.16
production operations (including unloading operations)	1990-95	12-hour TWA*	23	<0.05 to <0.12
tank truck / car unloading	1996	12-hour TWA*	1	<0.05
painter	1995	8-hour TWA	1	<0.09
tank truck / car unloading	1994-96	short term	20	<0.15 to <0.28
sampling hot process stream	1994	short term	1	<0.08

All the results in **Table 4.1** are below the limits of quantification (LOQ) for the analytical method and measured sample volumes. The results are therefore all recorded as less than values, with the higher figures only representing the smaller sample volumes. The company did not report why the results are reported as 4-hour, 8-hour and 12-hour TWAs.

The work activity described as "production operations" monitored the workers as they carried out routine tasks such as sampling, charging reactors and unloading nonylphenol from rail cars. Short-term measurements covered tank truck/car unloading where the operator had to remove and replace caps on pipe outlets, connect and disconnect the unloading hose, open and close dome lid and control the delivery pump.

### Modelled dermal exposure data

Dermal exposure can occur during the production and use of nonylphenol, where operators come into contact with surfaces contaminated from splashing or condensed vapour, or as a result of direct contact onto the skin. As processing is in closed systems dermal exposure is only likely during activities such as sampling and the uncoupling of pipes.

The best EASE scenario for this exposure is direct handling with incidental contact, where incidental refers to one significant contact in a shift, for example spilling nonylphenol whilst sampling or touching a wet surface. This results in a prediction of 0 to 0.1 mg/cm<sup>2</sup>/day, although on most days no such accidental contacts will occur and exposure will be towards the bottom of this range. The higher end of the range, however, is likely to represent exposure during activities such as maintenance.

#### **4.1.1.1.3 Occupational exposure to residual nonylphenol during the use of its derivatives**

Occupational exposure to residual nonylphenol may also occur during the use of its derivatives. It is unlikely that this exposure will ever be significant. Chemical intermediate manufacturers appear not to monitor residual levels of nonylphenol. The reactivity of nonylphenol in ethoxylate manufacture is such that residual levels sufficient to generate significant occupational exposure for users is unlikely.

#### **4.1.1.1.4 Manufacture of nonylphenol containing speciality paints**

One UK company reported using 2 tonnes per annum of nonylphenol in a hardener for a two pack chemical- and abrasion- resistant protective coating for industrial applications. They receive the nonylphenol in 205 litre drums. It is added to a solvent by being lifted on a hoist and poured into the solvent-containing mixing tank. This activity is carried out under local exhaust ventilation. This activity takes place once a week and takes one person approximately 30 minutes to complete. The company reported that PPE including gauntlets, apron, overalls, full-face shield and RPE are worn during this activity.

Once the nonylphenol has been added to the solvent, the mixing process itself is enclosed. The only other activity identified by the company as having the potential for exposure to nonylphenol is during the filling of the product into tins. A hose is coupled between the mixing tank and the filling head. The filling head is served by LEV. The filling process itself (during which 1, 2.5 and 5 litre tins are filled) is semi-automated. The operator is required to place empty tins on the conveyor feeding the filling head and take sealed tins of hardener off the conveyor at the other end. The manufacture and filling of this product is run on a campaign basis and an operator may spend up to 8 hours at the filling machine, although that is dependent on the size of the orders.

The plant machinery is cleaned using one of two enclosed automatic circulating systems; a solvent cleaning system or a caustic soda cleaning system, so there is not thought to be the potential for exposure during cleaning.

There is reported by the company to be less than 5% nonylphenol in the finished product.

The company reported a potential increase in the use of nonylphenol. The company had no occupational exposure data available.

#### Modelled inhalation exposure data

There are two activities where potential exposure to nonylphenol can occur; during loading of the nonylphenol into the solvent for mixing of the hardener and during coupling and uncoupling of the pipework during filling of the product into tins.

The EASE parameters used to estimate the exposure range during loading of the nonylphenol into the tanks were non-dispersive use, with LEV. The estimated exposure range was 0 to 0.1 ppm. As this 30-minute exposure would be the only exposure during the working shift an 8-hour TWA can be calculated. The 8-hour TWA range would therefore be 0 to 0.006 ppm. This estimated exposure range takes no account of the effect of RPE reported to be worn during this activity.

The EASE parameters used to estimate exposure during coupling and uncoupling of pipework were; non-dispersive use with direct handling with dilution ventilation. The estimated exposure range taking into account that the hardener contains 10% nonylphenol was 0 to 0.01 ppm. Coupling and uncoupling of pipework would take place once each in a shift. Each process takes about three minutes to complete. It is possible that the rest of the shift would be spent operating the automatic filling machine. Using EASE the estimated exposure range for this activity is again 0 to 0.01 ppm. The combined 8-hour TWA range for the shift would therefore also be 0 to 0.01 ppm.

**The predicted low value only applies to the activities described above which involve short exposure times. Any alterations in the duration of these activities would result in the need for these predictions to be reviewed.**

#### Modelled dermal exposure data

There are two potential exposure scenarios for dermal exposure. These are during opening of the drums of nonylphenol prior to addition to the solvent, and during coupling and uncoupling of the pipework for filling of the product into tins.

The EASE parameters used for these scenarios were non-dispersive use, direct handling with the potential for incidental contact. Although the emptying of the drums into the solvent tanks takes approximately 30 minutes the period of time during which dermal exposure may occur is during the time it takes to open the drums prior to being hoisted up mechanically for pouring, which would take perhaps one or two minutes. The estimated dermal exposure range for opening the drums of nonylphenol is 0 to 0.1 mg/cm<sup>2</sup>/day.

During coupling and uncoupling of pipework, the potential would be for dermal contact with the hardener containing 10% nonylphenol. The dermal exposure range is therefore calculated to be 0 to 0.01mg/cm<sup>2</sup>/day. This activity is also short-lived, taking up to three minutes to complete. The potential for exposure is therefore very low and it is likely that actual dermal exposure is lower than the range estimated using EASE.

#### **4.1.1.1.5 Use of speciality paints containing nonylphenol**

It has been reported by the speciality paint manufacturers that their products are used to protect structural steelwork in industrial applications where chemical or abrasion resistance is required. It was reported by a company that the paints are applied by spraying, normally in the open air although smaller pieces may be sprayed in large buildings with natural dilution ventilation. There is no occupational exposure data available so EASE and analogous results have been used to estimate exposures. There are two potential exposure scenarios; mixing of the two pack system and during spraying of the speciality paint onto the structure.

Mixing of the speciality paint is carried out by pouring a small tin of hardener (containing 10% nonylphenol) into a larger tin of paint. The ratios are usually in the region of 1:4. The speciality paint and hardener are mixed either by hand using a palette knife or more usually, given the viscosity of the mixture, by an air driven mixer. As the mixture is so viscous, there is little likelihood of generating an aerosol, although there is a potential for some spillage. The amount of time spent mixing depends on the size of the team working and the way in which the work is organised. The final paint mixture is reported to contain a maximum of 5% nonylphenol. Often, there is one paint mixer mixing paint for a team of four or five paint sprayers. In other situations there may be a gang of two sprayers who take it in turns to mix paint.

#### Modelled inhalation exposure data

The EASE parameters used to estimate exposure during mixing of paint were non-dispersive use with direct handling and dilution ventilation. The paint mixer will handle both the hardener containing 10% nonylphenol and the final paint mixture containing a maximum of 5% nonylphenol, so the exposure range was predicted for this activity using the 10% figure to represent the worst-case scenario. The predicted exposure range for this activity was 0 to 0.01 ppm. It is not known whether RPE is used by paint mixers.

The EASE parameters used to estimate exposure during spraying were production of an aerosol, wide-dispersive use with dilution ventilation and direct handling. The exposure range estimated, taking into account that the speciality paint contains a maximum of 5% nonylphenol was 25 to 50 ppm 8-hour TWA. These exposures are significant overestimates by the EASE model since it is not particularly suited to predicting exposures to low volatility substances that are sprayed. The model will give a value that represents vapour more than aerosol. Since there is likely to be minimal vapour during the application of these paints the above predictions are clearly wrong.

De Pater et al., 1999 (Draft), provides a model for predicting exposure to non-volatile compounds during spray painting. Data is provided for polyisocyanates, HDI monomer and dusts, and from these reasonable worst case scenarios (RWS) of 10 mg/m<sup>3</sup>, 0.2 mg/m<sup>3</sup> and 50 mg/m<sup>3</sup> respectively are provided in the report. Using the polyisocyanate data for this scenario as a similar non-volatile liquid the report suggests the following formula to take account of the concentration of the substance in the formulation:

$$E = 10 \cdot C / 30$$

E = estimated exposure in mg/m<sup>3</sup>

C = the percentage of substance in the paint

10 = RWS exposure for polyisocyanates in mg/m<sup>3</sup>

30 = RWS concentration of polyisocyanate in the paint

Since the paint in this document contains 5% nonylphenol the equation becomes:

$$E = 10 \cdot 5 / 30$$

The predicted exposure is therefore 1.7 mg/m<sup>3</sup> 8-hour TWA.

There are many complicating factors that make it difficult to simply accept this result. The report does state that more work is needed to refine this method. The exact method of application will

influence exposure. For example, whether the spraying is inside or outside, the extent of any ventilation used, and the type of spray guns being used. The nonylphenol based paints are applied to surfaces outside, whereas the polyisocyanate paints were probably applied inside. The nature of the paint will also effect exposure. Some components maybe chemically or physically bound with the polymer matrix of the paint. Nonylphenol has been reported by industry to be strongly bonded to amines in coatings thus reducing the potential for exposure to the nonylphenol. The extent of this bonding within the paint appears to be unclear. The industry communication states that in UK systems bonding is lower, with the nonylphenol acting more as a plasticiser. It is therefore not possible to further refine the data, remaining with the assumption that whilst spraying these paints, 5% nonylphenol is available for exposure. However, it is likely that the figure of 1.7 mg/m<sup>3</sup> (0.2 ppm) 8-hour TWA is a more realistic value to use than that of 50 ppm (approx. 450 mg/m<sup>3</sup>) predicted using EASE. However, in view of these uncertainties a value of 1 ppm (9.1 mg/m<sup>3</sup>) was taken forward for the risk characterisation.

#### Modelled dermal exposure data

The EASE parameters used to estimate dermal exposure during paint mixing were non-dispersive use with direct handling and intermittent contact. The paint mixer will handle both the hardener containing 10% nonylphenol and the final paint mixture containing a maximum of 5% nonylphenol, so the exposure range was predicted for this activity using the 10% figure to represent the worst-case scenario. The dermal exposure range is predicted to be 0.01 to 0.1 mg/cm<sup>2</sup>/day.

The EASE parameters used to estimate dermal exposure during spraying were wide dispersive use, with direct handling and intermittent contact. Taking into account that the paint contains up to 5% nonylphenol, the exposure range is estimated to be 0.050 to 0.25 mg/cm<sup>2</sup>/day. Actual exposure should be lower if PPE is worn. Marquart et al., (1999 Draft); Lansink et al., 1998, measured dermal exposure during the spray painting (not nonylphenol based paints) of containers off-shore to be approximately 0.2 mg/cm<sup>2</sup>/day. This data for spraying of this similar paint agrees with the EASE prediction of 0.25 mg/cm<sup>2</sup>/day.

#### **4.1.1.1.6 General discussion**

Nonylphenol is understood to be used as a chemical intermediate, and in the manufacture and use of speciality paints. Apart from during the use of speciality paints, nonylphenol is always likely to be processed in closed plant. Since production is also in closed plant, occupational exposure to nonylphenol is always likely to be low and only occur when the plant is breached. It also has low volatility and is heated to above 50 °C to allow the viscous material to be handled. Companies generally do not measure exposure to nonylphenol due to the nature of its use and the low concern for occupational exposure. Control is, in some cases, demonstrated by measuring exposure to other more hazardous substances, for example, ethylene oxide and phenol.

HSE has no occupational exposure data on its NEDB and data were only received from two companies. The first company reported short-term measurements ranging from 0.001 to 0.005 ppm, with one further result of 21 ppm. The second company reported results for 4-hour, 8-hour and 12-hour TWAs, and short-term measurements. It was not reported why the results were reported as these three different TWAs. The results, however, were all less than the LOQ for the method. The LOQ were less than 0.05 ppm to less than 0.16 ppm for the long-term measurements. The short-term measurements were also all less than the LOQ (0.08 ppm to 0.28 ppm). The SVC was calculated to provide an indication of the maximum likely exposure. The



SVC for nonylphenol is 2.96 ppm (calculated) at 25°C. Occupational exposure to nonylphenol vapour will therefore not exceed 2.96 ppm and will actually be significantly below this in the work place. Nonylphenol is used at elevated temperatures, however, this is in closed systems therefore any releases of nonylphenol at higher temperatures are likely to be minimal. Releases of hot vapour are likely to cool and condense on to external plant surfaces. Therefore any increase in processing temperature is unlikely to result in a significant increase in airborne concentration in the work place. The reported measurement of 21 ppm therefore seems unlikely given the SVC of 2.96 ppm.

Considering the SVC and the industry exposure data, it was concluded that exposures are likely to be less than 1 ppm 8-hour TWA, and in most cases significantly less for manufacturers and chemical intermediate users. It seems reasonable to further assume that the most exposures will be less than 0.1 ppm 8-hour TWA since only one actual result exceeded this value; therefore this value represents the reasonable worst case scenario. The only other figures above this were up to 0.16 ppm 8-hour TWA, which is the limit of quantification. It is also likely that exposures during the manufacture of speciality paints containing nonylphenol are similarly low.

Occupational exposure to residual nonylphenol may also occur during the use of its derivatives. It is unlikely that this exposure will ever be significant. Chemical intermediate manufacturers appear not to monitor residual levels of nonylphenol. The reactivity of nonylphenol in ethoxylate manufacture is such that residual levels sufficient to generate significant occupational exposure for users is unlikely.

Exposure to nonylphenol during speciality paint manufacture is estimated to be controlled below 0.01 ppm 8-hour TWA. During charging of the mixing vessel with nonylphenol, exposure may reach 0.1 ppm for up to 30 minutes. These exposure estimates do not take into account the effects of respiratory protective equipment (RPE), which is reported to be worn.

Exposure to nonylphenol during on-site paint mixing is also estimated to be low (below 0.01 ppm). Exposure during spray application is estimated to be 25 to 50 ppm 8-hour TWA using the EASE model. However, these exposures are significant overestimates by the EASE model since it is not particularly suited to predicting exposures to low volatility substances that are sprayed. The model will give a value that represents the vapour more than the aerosol. Since there is likely to be minimal vapour during the application of these paints the above predictions are clearly wrong. De Pater et al., 1999 (Draft), provides a model for predicting exposure to non-volatile compounds during spray painting. Using this method an exposure of 1.7 mg/m<sup>3</sup> 8-hour TWA is predicted for the spray application of speciality paints containing nonylphenol.

There are many complicating factors that make it difficult to simply accept this result. The report does state that more work is needed to refine this method. The exact method of application will influence exposure. For example, whether the spraying is inside or outside, the extent of any ventilation used, and the type of spray guns being used. The nonylphenol based paints are applied to surfaces outside, whereas the polyisocyanate paints were probably applied inside. The nature of the paint will also effect exposure. Some components maybe chemically or physically bound with the polymer matrix of the paint. Nonylphenol has been reported by industry to be strongly bonded to amines in coatings thus reducing the potential for exposure to the nonylphenol. The extent of this bonding within the paint appears to be unclear. The industry communication states that in UK systems bonding is lower, with the nonylphenol acting more as a plasticiser. It is therefore not possible to further refine the data, remaining with the assumption that whilst spraying these paints, 5% nonylphenol is available for exposure. However, it is likely

that the figure of 1.7 mg/m<sup>3</sup> (0.2 ppm) 8-hour TWA is a more realistic value to use than that of 50 ppm (approx. 450 mg/m<sup>3</sup>) predicted using EASE. However, in view of these uncertainties a value of 1 ppm (9.1 mg/m<sup>3</sup>) was taken forward for the risk characterisation.

Dermal exposure was predicted using EASE to be in the range of 0 to 0.1 mg/cm<sup>2</sup>/day, for almost all activities, although on most days no such accidental contacts will occur and exposure will towards the bottom of this range. The higher end of the range, however, is likely to represent exposure during activities such as maintenance.

The potential for dermal exposure during paint spraying was estimated to be higher than that for other activities, at up to 0.25 mg/cm<sup>2</sup>/day. Again, this figure does not take into account the effects of any gloves worn. Marquart et al., 1999 (Draft); Lansink et al., 1998, measured dermal exposure during the spray painting (not nonylphenol) of containers off-shore to be approximately 0.2 mg/cm<sup>2</sup>/day. This data for spraying of a similar paint agrees with the EASE prediction of 0.25 mg/cm<sup>2</sup>/day.

Table 4.2 Summary of occupational exposure data taken forward to risk characterisation

Industry	Inhalation (8h TWA) ppm	Inhalation (8h TWA) mg/m <sup>3</sup>	Dermal (mg/cm <sup>2</sup> /day)
Manufacture of nonylphenol	0.1	0.91	0 to 0.1
The use of nonylphenol as a chemical intermediate	0.1	0.91	0 to 0.1
The manufacture of speciality paints containing nonylphenol	0.01	0.091	0 to 0.1
The use of speciality paints containing nonylphenol	1	9.1	0.01 to 0.25

#### 4.1.1.2 Consumer exposure

##### 4.1.1.2.1 Introduction

Nonylphenol is not used directly in products with which the consumer comes into contact. However, it is used to make other products which are sold to consumers. Consumer products may therefore contain very low levels of residual, unreacted nonylphenol and in certain products the derivative compound may break down to release small amounts of nonylphenol. These are the potential sources of consumer exposure to nonylphenol.

Most of the nonylphenol production is converted into alkyl phenol ethoxylates which are used as industrial detergents and emulsifiers. The industrial products are not sold directly to consumers although products containing the emulsifiers are.

Nonylphenol may also be used in the production of tris nonylphenol phosphite. This compound is used as a co-stabiliser and as an anti-oxidant in the synthesis of various polymers such as butadiene rubber, polystyrene, polyethylene and polyvinylchloride. It is also used in the production of food contact plastics.

In order to assess the exposure of consumers to nonylphenol it is necessary to address the exposure to residual nonylphenol and where appropriate breakdown to nonylphenol of derivative compounds. The major sources of potential exposure are detailed below.

#### 4.1.1.2.2 Potential exposure from nonylphenol ethoxylates

##### Pesticides

There are no measured data for this source of exposure. However, exposure may be modelled to predict an exposure per event. Although nonylphenol ethoxylates (NPEs) are used in agricultural pesticide formulations, there are no data on nonylphenol residue levels in the harvested crops.

Consumers can buy pesticide formulations containing nonylphenol ethoxylates in a range of products. These products contain nonylphenol ethoxylates at a concentration of up to 5% and do not require dilution. Residual levels of nonylphenol are likely to be low but very little real data on residue levels are available. The one available piece of data provided by industry showed a level of 0.04% (400 ppm) of nonylphenol in the nonylphenol ethoxylate. In the UK, the pesticide formulation available to consumers contains a maximum of 5% nonylphenol ethoxylate; thus, levels of free nonylphenol in the product are unlikely to be above 20 ppm. Inhalation is unlikely to be a significant route of exposure, despite the pesticide being applied as a mist, owing to the very low vapour pressure of nonylphenol at room temperature. There is a potential for dermal exposure during the spraying unless efficient hand protection is used. Both these exposure scenarios can be modelled. However, the most important exposure with this type of spray is due to the touching of contaminated surfaces (Thompson and Roff, 1996) following application. This exposure cannot be adequately modelled.

The exposure scenario models the use of an anti-mould spray, used indoors. The model is used to predict exposure arising from a single spraying event. It assumes that the spray contains 5% nonylphenol ethoxylate (the maximum figure seen in the UK), containing 400 ppm of free nonylphenol, an application rate of 250 ml/m<sup>3</sup> (the usual recommendation for this sort of spray), a surface area of 1 m<sup>2</sup>, an application period of 20 minutes and a room of 20 m<sup>3</sup> in a house of 292 m<sup>3</sup>. The US EPA's SCIES and DERMAL models can then be used to model the potential exposures.

##### *Modelled inhalation exposure*

Using the above information and the aerosol paint/clear coatings scenario of SCIES, an airborne concentration of about 60 µg/m<sup>3</sup> (0.007 ppm) would be predicted and the amount inhaled can be calculated to be 21 µg per event or 0.3 µg/kg per event for a 70 kg adult.

##### *Modelled dermal exposure*

Assuming that the hand's surface area exposed is 795 cm<sup>2</sup> over which there is a film thickness of  $2.14 \cdot 10^{-3}$  cm, the General Purpose Cleaner-dilute scenario of DERMAL may be used. The dermal exposure is calculated to be 3.2 µg per event assuming a dermal absorption of 10%. This is equivalent to 0.05 µg/kg per event for a 70 kg adult.

##### *Total exposure estimate*

The total systemic exposure from both inhalation and dermal routes combined is 0.35 µg/kg per event.

## Cosmetics

Nonoxynols are a group of ethoxylated alkyl phenols used as emulsifying agents in cosmetics. They vary in chain length from 1 to 40. They can be used in hair dyes and colours, hair bleaches, bath oils, eyeliners, personal cleanliness products, tonics, dressings, other hair grooming aids, shaving cream and hair conditioners (CTFA cosmetic ingredient handbook). It is thought that in Europe the uses are restricted to small-scale use as perfume solubilisers and as wetting agents in hair dyeing and bleaching preparations. American use is more widespread and includes bath products and mascaras.

There are no measured data on exposure from these products but it has been possible to construct one model for cosmetic consumer products.

The worst-case exposure scenario for consumer hair products is likely to be the use of dyes since they remain in contact with the skin for up to 30 minutes before being washed off. No complete set of exposure parameters has been provided by industry for this scenario, but use of information from various sources (industry and product information) allows the construction of a model.

Nonylphenol is present in these products as residues in nonoxynols at varying concentrations according to the chain length of the ethoxylate. Inspection of the contents of 10 different hair dyes (different types and different brands) showed only one product containing a nonoxynol, in that case nonoxynol-4. The exposure can be estimated as presented in **Table 4.3**.

Table 4.3 Consumer exposure to hair dyes

	Exposure calculation	Source of information
volume used 40 ml of solution	40 ml	product information
containing 10 % w/v nonoxynol ("representative of head-on exposures")	4 ml	industry data
of which 0.5 % will be nonylphenol residue (for nonoxynol-4)	0.02 ml	industry data
assume density = 1 g/ml	0.02 g (20 mg)	
assume 10 % of product is in contact with skin	2 mg	Kalopissis, 1985
10% dermal absorption	0.2 mg	
for 70 kg person	approximately 3 µg/kg per event	
Dye lasts for 24 washes: Assume hair washed 6 times a week; that means dye lasts 4 weeks; that means 1 event/4 weeks; 1/28th of an event every day: 1/28 of the exposure per event = total systemic exposure	0.1 µg/kg/day	product information

This estimate assumes that the exposure is constant during the month and that the whole amount applied has dispersed by the time of the next application.

### Spermicides and pharmaceutical preparations

Nonylphenol ethoxylates of chain length 9 and 11 are used as spermicides on condoms and in gels. Levels of exposure to residual nonylphenol are unknown. Nonylphenol ethoxylates are also used in pharmacological preparations. It is understood that these uses will be phased out by the year 2000.

### Textiles

Alkyl phenol ethoxylates (APEs) are used in the textile trade for wool scouring. This is an early stage of processing where the wool is washed and teased out. The wash waters are recycled and the wool is rinsed well afterwards. Because of the effectiveness of the washing, lanolin is often added to the wool later to replace some of the oils washed out. Although there are no data available it is believed that the level of residual APEs in the finished garments is minimal and therefore the level of nonylphenol present will be negligible.

Following concern about the potential environmental impact of these detergents the wool industry is rapidly reducing the use of APEs and replacing them with alternatives.

#### **4.1.1.2.3 Exposures from migration of residual nonylphenol from food contact materials**

##### **4.1.1.2.3.1 Introduction**

No estimates of dietary exposure to nonylphenol using EU data were available. However, estimates were made using the American Food and Drug Administration (FDA) model which uses consumption and food-type distribution factors and American data on residual levels of nonylphenol. Data on two potential sources were provided: trisnonylphenylphosphite<sup>4</sup> and nonylphenyl polyethoxylates<sup>5</sup>.

#### FDA method for calculating dietary exposure to migrants

The FDA method uses migration data derived from simulated food-contact use. Plaques or films of the polymer are subjected to various time and temperature regimes according to the intended use and food-type. The level of migrant at various time intervals (up to 10 days) is established in the food-simulating solvents. Four food stimulants are used: aqueous; acidic, alcoholic and fatty.

The estimated daily intake (EDI) for a substance in a given food-contact material is obtained by multiplying the migration value  $M$  of the substance obtained from the exposure of the food-contact material to a given food stimulant (under the most severe time and temperature of exposure) by the food type distribution factor  $f$ . The distribution factor is the fraction of food of each type that will contact the food-contact material.

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<sup>4</sup> Potential dietary exposure to nonylphenol from food contact use of trisnonylphenylphosphite (TNPP). Alkylphenol work group inter-industry group on bisphenol A and alkylphenols, The Society of the Plastics Industry Inc, Washington DC, USA, (1998)

<sup>5</sup> Potential dietary exposure to nonylphenol ethoxylates (NPE) from its use in food contact applications. Alkylphenol work group inter-industry group on bisphenol A and alkylphenols, The Society of the Plastics Industry Inc, Washington DC, USA, (1998)

The resulting migration values are summed to give an overall concentration of migrant  $\langle M \rangle$ .

$$\langle M \rangle = f_{aq} \cdot M_{aq} + f_{ac} \cdot M_{ac} + f_{al} \cdot M_{al} + f_f \cdot M_f$$

where the subscripts aq, ac, al and f refer to aqueous; acidic, alcoholic and fatty respectively.

The EDI is then determined by multiplying the total weight of food consumed by an individual per day (FDA default 3000 g/day) by the consumption factor CF (which represents the proportion of the diet in contact with the polymer) and  $\langle M \rangle$ .

$$EDI = \langle M \rangle \cdot CF \cdot 3000 \text{ g} \cdot \text{day}^{-1}$$

#### 4.1.1.2.3.2 Trisnonylphenylphosphite

Trisnonylphenylphosphite (TNPP) is used as an antioxidant to stabilise polymer coatings used as food contact materials against degradation by ultraviolet light. Nonylphenol is present in TNPP as a residual impurity and can be formed as a result of acid hydrolysis of TNPP. Various grades of TNPP are used by the American food industry and residual nonylphenol levels can vary.

Table 4.4 Residual levels of nonylphenol in TNPP

Grade	Nonylphenol content (%)
Production specifications	1-4
Typical	1-2
Low nonylphenol	0.1

#### TNPP use

TNPP is used in four types of food-contact polymers: polyolefins; rubber modified polystyrene; PVC films; and rubber. Its use in rubber is limited to repeat use articles such as rubber hoses used in the food-manufacturing industry. The report did not consider repeat use articles because over an article's working lifetime the total surface area of food which contacts the article is very high. Thus the concentration of any migrant in a food item from repeat use articles is extremely low. **Table 4.5** gives details of typical in-use concentrations of TNPP in various polymer types.

Table 4.5 Use of trisnonylphenylphosphite in food-packaging materials

Polymer type	TNPP in-use concentration (ppm)	
	Range	Typical
Polyolefins		
Linear low density polyethylenes (LLDPE) <sup>a</sup>	1000-2100	1100-1500
Ethylene vinyl acetate copolymers (EVA) <sup>b</sup>	not stated	500
Rubber modified polystyrene		
High impact polystyrene (HIPS)	50-2200	800
PVC film	6000-10000	

<sup>a</sup>Approximately 50% of LLDPE used in food contact materials contains TNPP

<sup>b</sup>Approximately 25% of EVA used in food contact materials contains TNPP

### Calculated exposure

The FDA allows the testing of low density polyethylene (LDPE) as a surrogate for other polymer types. Since TNPP is not significantly used in LDPE, LLDPE was tested in its place. Plasticized PVC film was also tested since its behaviour relative to LLDPE was uncertain. Nonylphenol content was determined before and after acid hydrolysis with concentrated hydrochloric acid which hydrolysed any TNPP or di- or mono-esters to free nonylphenol. During method validation, this method was found to be >90% efficient.

The contribution of nonylphenol from each packaging types was estimated to give an overall figure for dietary exposure.

### *LLDPE*

The contribution of LLDPE is shown below.

Table 4.6 Potential Nonylphenol exposure from LLDPE <sup>a</sup>

Application	CF <sup>b</sup>	Migration (ppm)	Exposure (ppb)
Film			
Produce	0.04	0.024	0.48
Frozen	0.001	0.024	0.012
Meat/Poultry	0.002	1.67	1.7
Dry	0.01	0.024	0.12
Bag-in box	0.006	0.024	0.072
Snack	0.002	1.67	1.7
Films/Coatings	0.0002	1.67	0.017
Lids/Tubs			
Aqueous	0.0027	0.016	0.22
Fatty	0.0013	4.09	2.7
total			7 ppb

<sup>a</sup>The calculated exposure values were halved since 50% of food contact LLDPE contains TNPP

<sup>b</sup>Consumption factor

### *EVA*

$$\begin{aligned}
 \text{The dietary concentration is given by:} &= 0.25 \cdot \text{CF} \cdot \langle M \rangle \\
 &= 0.25 \cdot \text{CF} \cdot [f_{\text{aq}} \cdot M_{\text{aq}} + f_{\text{f}} \cdot M_{\text{f}}] \\
 &= 0.25 \cdot 0.04 \cdot [(0.55 \cdot 0.01) + (0.45 \cdot 0.7)] \\
 &= \mathbf{3.2 \text{ ppb}}
 \end{aligned}$$

The factor of 0.25 accounts for the 25% of food contact EVA which contains TNPP.

*PVC film*

The dietary concentration is given by:  $= CF \cdot \langle M \rangle$   
 $= 0.05 \cdot [f_{aq} \cdot M_{aq} + f_f \cdot M_f]$   
 $= 0.05 \cdot [(0.51 \cdot 0.0278) + (0.49 \cdot 0.283)]$   
Dietary concentration  $= \mathbf{7.6 \text{ ppb}}$

*HIPS*

Table 4.7 Potential Nonylphenol exposure from HIPS

Application		CF <sup>a</sup>	Migration (ppm)	Exposure (ppb)	
Packaging					
	Yoghurt Cups	0.0036	0.11	0.36	
	Cheese/Cream	0.0036	0.11	0.36	
	Aseptic/Blow moulded	0.0009	0.11	0.099	
Disposable					
	Fatty	4°C	0.0001	0.12	0.012
		24 °C	0.0001	0.12	0.012
		54 °C	0.0003	1.21	0.36
	Aqueous	4°C	0.0108	0.017	0.18
		24 °C	0.0188	0.017	0.32
		54 °C	0.0016	0.035	0.056
	Alcoholic		0.0015	0.017	0.026
	total				1.8 ppb

<sup>a</sup>Consumption factorOverall exposure

The overall exposure from each of the packaging types is shown below:

Table 4.8 Overall exposures

Packaging type	Dietary concentration (ppb)
LLDPE	7
HIPS	1.8
EVA	3.2
PVC film	7.6
total	19.6

Using the FDA assumption that an individual's diet consists of 3000 g/day this corresponds to a nonylphenol exposure of approximately ~ 0.06 mg/day. The tests performed by the FDA produce data showing the total amount of nonylphenol potentially available for migration following the hydrolysis of TNPP. The value represents worst-case potential exposure to nonylphenol derived from TNPP in food-packaging polymers and papers.



### 4.1.1.2.3.3 Nonylphenyl polyethyloxylates

Nonylphenylpolyethyloxylates (NPE) are emulsifiers used in food-packaging polymers to prevent fogging through the condensation of water vapour. They are used for aesthetic reasons. The usual form of NPE used in food-packaging is made by ethoxylating 1 mole of nonylphenol with 4 mole of ethylene oxide and is known as NPE-4. Nonylphenol is present as a residual impurity at a typical level of 0.1% in NPE-4.

Antifogging agents can either be added during manufacture or externally applied to the polymer surface. When added during manufacture the antifog is chosen to have a controlled incompatibility with the packaging material so that it “blooms” to the surface where it exerts its effect. Internal incorporation also provides a reservoir of material which improves long-term performance and is the preferred method.

#### Patterns of use

The levels of NPE-4 used in various food packaging materials is shown in **Table 4.9**.

**Table 4.9** Levels of NPE-4 in food packaging materials

Polymer material	NPE-4 content
PVC <sup>a</sup>	2.7 %
Polyolefins <sup>b</sup>	0.9 %
Pigment coated paper	0.009 mg/cm <sup>2</sup>

<sup>a</sup>approximately 80% of PVC used in food-packaging contains NPE-4

<sup>b</sup>approximately 5% of polyolefins used in food-packaging contain NPE-4

#### Potential migration

##### *PVC and polyolefin films*

The potential migration of nonylphenol from PVC and polyolefin films was calculated using the following assumptions.

**Table 4.10** Assumptions for calculation of potential migration

Assumption	PVC	Polyolefin
all NPE-4 moves to the surface of the film		
all of the surface of the film is contact with the food		
film density (g/cm <sup>3</sup> )	1.25	0.92
film thickness (cm)	0.0016	0.0016
NPE-4 content (%)	2.7	0.9
nonylphenol content in NPE-4 (%)	0.1	0.1
3.1 g of food contacts cm <sup>2</sup> of packaging		
Calculated dietary concentrations of nonylphenol	17 ppb	4 ppb

*Paper and paperboard*

The calculated dietary concentration of nonylphenol was calculated using the following assumptions.

Table 4.11 Assumptions (paper and paperboard)

Assumption	Paper and paperboard
all NPE-4 moves to the surface of the paper	
all of the surface of the film is contact with the food	
NPE-4 content mg/cm <sup>2</sup>	0.009
nonylphenol content in NPE-4 (%)	0.1
food contact g/cm <sup>2</sup>	1.55
Calculated dietary concentrations	5.8 ppb

Results

Using the FDA calculation method with the assumption that an individual consumes 3000 g of food and drink per day the estimated dietary exposure to nonylphenol from NPE-4 is 0.08 mg/day.

Overall consumer exposure from food packaging materials

The overall exposure to nonylphenol from food packaging materials is the sum of the two sources:

$$= \text{nonylphenol derived from TNPP} + \text{nonylphenol derived from NPE}$$

$$= 0.06 \text{ mg/day} + 0.08 \text{ mg/day}$$

The overall exposure to nonylphenol from food packaging materials is 140 µg/day. These data are based on American residue data and patterns of consumption. However, the FDA is acknowledged to be conservative and predicts an upper limit of dietary exposure. In the absence of EU data, the estimate of 140 µg/day (equivalent to 2 µg/kg/day) nonylphenol from food-packaging materials will be used. Data from the EU on patterns of consumption and residue data would be useful.

**4.1.1.2.4 Potential exposure from phenolic resin coatings**

Nonylphenol is reacted with resins, organic solvents and formaldehyde at temperatures of between 80°C and 110°C to produce phenolic resin coatings. The theoretical residual nonylphenol levels may be up to 0.8% (Smith, 1996). These coatings may be used to line food contact cans. In this case the coatings are baked after application which should further reduce the amount of residual nonylphenol. At present, no specific migration limit has been set by the EC under 90/128/EEC and therefore nonylphenol is considered as part of the overall migration allowance of a maximum of 50 ppm into food (although 90/128/EEC does not yet apply to coatings but may influence any future coatings Directive). No quantitative data are available on nonylphenol migration into food from these coatings.

#### 4.1.1.2.5 Hardeners for 2-component adhesives

The Swedish Product Register indicates that nonylphenol is used in hardeners for 2-component adhesives. However, investigations to find out about these products have not been successful and there is no evidence that they are currently on the market. Consequently no consumer exposure estimate has been made.

#### 4.1.1.2.6 Summary

There are limited data on the potential exposure to nonylphenol from consumer products but estimates are available for the most likely sources of exposure. The potential systemic exposure arising from consumer use of pesticide products is calculated to be 21 µg via inhalation and 3.2 µg via dermal contact which, if used daily by a 70 kg adult, would be equivalent to 0.35 µg/kg/day. That for use of hair dyes is 3 µg/kg per event (equivalent to 0.1 µg/kg/day). Exposure from food contact materials is estimated to be 2 µg/kg/day. Systemic bioavailability by the oral route is 10%, thus systemic exposure from food contact materials is estimated to be 0.2 µg/kg/day. These values will be used in the risk characterisation. Other sources are considered to be minimal and most are being phased out in the near future.

For total daily exposure to nonylphenols it is assumed that a consumer uses pesticide products daily, uses hair dyes regularly and is exposed via food contact materials. The systemic exposure estimate is about 0.6 µg/kg/day.

#### 4.1.1.3 Indirect exposure via the environment

Nonylphenol has several uses that can result in release into surface water. Nonylphenol has been shown to bioconcentrate to some extent in aquatic organisms and so may enter the food chain, although biomagnification is not expected to occur. Low levels of nonylphenol are predicted to occur in air. The main source of exposure to humans via the environment is therefore likely to be via food and, to a lesser extent, drinking water.

The EUSES model has been used to estimate various concentrations in food, air and drinking water and from these a daily human intake figure is derived. The results are shown in **Table 4.12**. The local figures were derived from the default estimates of releases from production and use of nonylphenol (see Section 3.1.1.1), and are not based on measured data. These release estimates are used in the absence of reliable exposure information and may grossly overestimate the actual situation.

The highest daily human intake figure given in **Table 4.12** (4.42 mg/kg/day) is derived for the textile industry. Intake figures for other local sources were 4.32, 2.28 and 0.245 mg/kg/day for nonylphenol ethoxylate production sites,  $8.31 \cdot 10^{-3}$  mg/kg/day for use of nonylphenol as a monomer in polymer production, 0.015 mg/kg/day for use of nonylphenol as a stabiliser in polymer production and 1.66 mg/kg/day for use in metal extraction. At a regional level the estimated human intake is  $5.31 \cdot 10^{-3}$  mg/kg/day. The largest contributor to the figures is through the intake of fish. This accounts for around 70-80% of the daily dose. The other significant contributor to the figures is through intake of roots (1-29%).

There is considerable uncertainty in the estimated human daily intake figures, consequently the accuracy of the predictions is difficult to determine. The first cause of uncertainty results from the lack of reliable data on the quantities of nonylphenol released into the environment from the

various uses. Releases and hence concentrations from actual use sites are likely to be much lower than the figures used here.

The second cause of uncertainty concerns the assumptions made in the local calculations that all of the water, air and food comes from close to a point source of release. Concentrating on the most important contributors (fish and root crops), while it can reasonably be argued that it is extremely unlikely that all fish and roots would be supplied from local sources, it is equally reasonable to argue that (i) local sources may be significant for a small number of individuals and (ii) that the models demonstrate that these sources are a potential cause for concern.

The calculations may be overestimates but the degree of over estimation is uncertain. Whatever the degree of sourcing of food from the local area, the concern needs to be addressed. Further information is needed on emissions into the local environment from production and use plant.

#### **4.1.1.4 Combined exposure**

The highest exposure an individual is likely to experience would occur if they apply speciality paints (2 mg/kg/day), use a pesticide product (0.35 µg/kg/day), cosmetics (0.1 µg/kg/day) and are exposed via food packaging materials (0.2 µg/kg/day) while living in the locality of a textile factory (4.42 mg/kg/day). The total exposure would be approximately 6.4 mg/kg/day.

Table 4.12 Indirect exposure of man via the environment

Scenario	Concentration in air (mg/m <sup>3</sup> )	Concentration in drinking water (mg/l)	Concentration in fish (mg/kg)	Concentration in plant roots (mg/kg)	Concentration in plant leaves (mg/kg)	Concentration in meat (mg/kg)	Concentration in milk (mg/kg)	Daily human intake (mg/kg body weight/day)
Nonylphenol Production sites								
Site A	$5.73 \cdot 10^{-3}$	$3.24 \cdot 10^{-4}$	0.832	0.0283	0.317	0.0169	$5.33 \cdot 10^{-3}$	$8.31 \cdot 10^{-3}$
Site B	Background	$5.66 \cdot 10^{-4}$	0.766	0.146	$2.27 \cdot 10^{-4}$	$8.45 \cdot 10^{-5}$	$2.67 \cdot 10^{-5}$	$2.08 \cdot 10^{-3}$
Site C	Background	$3.04 \cdot 10^{-4}$	0.78	$3.97 \cdot 10^{-5}$	$1.75 \cdot 10^{-4}$	$2.2 \cdot 10^{-5}$	$6.95 \cdot 10^{-6}$	$1.29 \cdot 10^{-3}$
Site D	Background	$3.12 \cdot 10^{-4}$	0.8	$9.54 \cdot 10^{-4}$	0.0106	$5.74 \cdot 10^{-4}$	$1.82 \cdot 10^{-4}$	$1.55 \cdot 10^{-3}$
Nonylphenol/formaldehyde resin production	$1.5 \cdot 10^{-6}$	$1.41 \cdot 10^{-3}$	2.02	0.366	$1.03 \cdot 10^{-3}$	$2.36 \cdot 10^{-4}$	$7.47 \cdot 10^{-5}$	$5.38 \cdot 10^{-3}$
TNPP production	Background	$3.04 \cdot 10^{-4}$	0.78	$3.97 \cdot 10^{-5}$	$1.75 \cdot 10^{-4}$	$2.2 \cdot 10^{-5}$	$6.95 \cdot 10^{-6}$	$1.29 \cdot 10^{-3}$
Epoxy resin production	$3.22 \cdot 10^{-6}$	$3.0 \cdot 10^{-4}$	0.77	$6.38 \cdot 10^{-3}$	$1.78 \cdot 10^{-4}$	$2.41 \cdot 10^{-5}$	$7.61 \cdot 10^{-6}$	$1.31 \cdot 10^{-3}$
Use in other plastic stabilisers	$0.8 \cdot 10^{-6}$	$1.51 \cdot 10^{-3}$	0.878	0.39	$1.88 \cdot 10^{-4}$	$2.03 \cdot 10^{-4}$	$6.43 \cdot 10^{-5}$	$3.63 \cdot 10^{-3}$
Phenolic oxime production	Background	$3.05 \cdot 10^{-4}$	0.782	$5.11 \cdot 10^{-5}$	$3.04 \cdot 10^{-4}$	$2.89 \cdot 10^{-5}$	$9.13 \cdot 10^{-6}$	$1.3 \cdot 10^{-3}$
Nonylphenol ethoxylate production sites								
Company B	$3.7 \cdot 10^{-7}$	1.02	$2.61 \cdot 10^3$	$2.18 \cdot 10^{-4}$	$2.2 \cdot 10^{-3}$	0.0426	0.0135	4.32
Company C Sites 1 & 2	$3.5 \cdot 10^{-5}$	1.06	452	274	0.0248	0.137	0.0434	2.28
Company C Site 3	$4.2 \cdot 10^{-5}$	0.16	8.04	41.4	$3.29 \cdot 10^{-3}$	0.0207	$6.55 \cdot 10^{-3}$	0.245
Company D Site 1	$8.9 \cdot 10^{-6}$	0.0113	1.29	2.92	$7.27 \cdot 10^{-4}$	$1.49 \cdot 10^{-3}$	$4.71 \cdot 10^{-4}$	0.0185
Company D Site 2	$1.5 \cdot 10^{-6}$	$3.11 \cdot 10^{-3}$	1.19	0.804	$2.74 \cdot 10^{-4}$	$4.13 \cdot 10^{-4}$	$1.31 \cdot 10^{-4}$	$6.46 \cdot 10^{-3}$
Company E	$1.8 \cdot 10^{-6}$	$3.04 \cdot 10^{-4}$	0.78	$4.86 \cdot 10^{-5}$	$2.76 \cdot 10^{-4}$	$2.74 \cdot 10^{-5}$	$8.65 \cdot 10^{-6}$	$1.3 \cdot 10^{-3}$

Table 4.12 continued overleaf

Table 4.12 continued Indirect exposure of man via the environment

Scenario	Concentration in air (mg/m <sup>3</sup> )	Concentration in drinking water (mg/l)	Concentration in fish (mg/kg)	Concentration in plant roots (mg/kg)	Concentration in plant leaves (mg/kg)	Concentration in meat (mg/kg)	Concentration in milk (mg/kg)	Daily human intake (mg/kg body weight/day)
Company F	$1.22 \cdot 10^{-6}$	$3.04 \cdot 10^{-4}$	0.78	$9.9 \cdot 10^{-5}$	$8.49 \cdot 10^{-4}$	$5.78 \cdot 10^{-5}$	$1.83 \cdot 10^{-5}$	$1.31 \cdot 10^{-3}$
Company G	Background	$3.04 \cdot 10^{-4}$	0.78	$3.97 \cdot 10^{-5}$	$1.75 \cdot 10^{-4}$	$2.2 \cdot 10^{-5}$	$6.95 \cdot 10^{-6}$	$1.29 \cdot 10^{-3}$
Nonylphenol ethoxylate formulation								
Large		0.0945	13.8	24.4	0.606	0.0443	0.014	0.172
Medium		0.0238	4.05	6.15	0.606	0.0352	0.0111	0.054
Small		$9.63 \cdot 10^{-3}$	2.09	2.49	0.606	0.0334	0.0106	0.0303
Nonylphenol ethoxylate processing								
Captive use by the chemical industry		0.0385	0.77	9.94	$3.7 \cdot 10^{-4}$	$4.95 \cdot 10^{-3}$	$1.57 \cdot 10^{-3}$	0.0569
Electrical engineering industry		0.0232	3.8	5.99	$3.26 \cdot 10^{-3}$	$3.15 \cdot 10^{-3}$	$9.95 \cdot 10^{-4}$	0.0399
Industrial and institutional cleaning		0.195	18.8	50.44	$1.67 \cdot 10^{-3}$	0.0251	$7.94 \cdot 10^{-3}$	0.313
Leather processing								
Large		0.636	18.4	164	$3.58 \cdot 10^{-3}$	0.0817	0.0258	0.951
Average		0.127	18.4	32.9	$1.01 \cdot 10^{-3}$	0.0164	$5.17 \cdot 10^{-3}$	0.214
Metal extraction		1.07	65.8	278	$6.05 \cdot 10^{-3}$	0.138	0.0437	1.66
Photographic industry								
Large		0.0117	2.4	3.02	$2.35 \cdot 10^{-4}$	$1.51 \cdot 10^{-3}$	$4.78 \cdot 10^{-4}$	0.209
Small		$3.08 \cdot 10^{-4}$	0.79	0.195	$1.76 \cdot 10^{-4}$	$2.87 \cdot 10^{-5}$	$9.07 \cdot 10^{-6}$	$1.42 \cdot 10^{-3}$

Table 4.12 continued overleaf

Table 4.12 continued Indirect exposure of man via the environment

Scenario	Concentration in air (mg/m <sup>3</sup> )	Concentration in drinking water (mg/l)	Concentration in fish (mg/kg)	Concentration in plant roots (mg/kg)	Concentration in plant leaves (mg/kg)	Concentration in meat (mg/kg)	Concentration in milk (mg/kg)	Daily human intake (mg/kg body weight/day)
Polymer industry		$9.43 \cdot 10^{-3}$	0.985	2.44	$2.23 \cdot 10^{-4}$	$1.22 \cdot 10^{-3}$	$3.86 \cdot 10^{-4}$	0.0153
Pulp, Paper and Board industry		0.118	17.1	30.5	$7.71 \cdot 10^{-4}$	0.0151	$4.79 \cdot 10^{-3}$	0.199
Textile industry		2.64	367	682	0.0135	0.339	0.107	4.42
Paint manufacture		0.0377	3.39	9.75	$3.66 \cdot 10^{-4}$	$4.85 \cdot 10^{-3}$	$1.53 \cdot 10^{-3}$	0.0602
Paint domestic use		$3.08 \cdot 10^{-4}$	0.79	0.0195	$1.76 \cdot 10^{-4}$	$2.87 \cdot 10^{-5}$	$9.07 \cdot 10^{-6}$	$1.42 \cdot 10^{-3}$
Paint industrial use		$3.06 \cdot 10^{-4}$	0.784	0.0244	$1.76 \cdot 10^{-4}$	$3.02 \cdot 10^{-5}$	$9.56 \cdot 10^{-6}$	$1.44 \cdot 10^{-3}$
Civil engineering		0.0164	1.92	4.24	$1.84 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$	$6.96 \cdot 10^{-4}$	0.0269
Regional	$3.18 \cdot 10^{-9}$	$2.78 \cdot 10^{-3}$	0.78	0.719	$1.9 \cdot 10^{-4}$	$2.19 \cdot 10^{-4}$	$6.92 \cdot 10^{-5}$	$5.31 \cdot 10^{-3}$

#### **4.1.2 Effects assessment: Hazard identification and dose (concentration)-response (effect) assessment**

The test substance used in the toxicity studies were commercially produced nonylphenols which, as stated in section 1, consists of an isomeric mixture of variable composition. Few of the toxicity studies reported the composition of the substance tested and it is difficult to assess the extent (if any) to which this variability may influence the toxicological properties.

##### **4.1.2.1 Toxicokinetics, metabolism and distribution**

###### **4.1.2.1.1 Studies in animals**

The toxicokinetics of nonylphenol following oral administration has been investigated directly in two animal studies (Knaak et al., 1966, Fennell and MacNeela, 1997); both studies, which were briefly reported, involved the measurement of recovered radioactivity after administration of radiolabelled nonylphenol. Percutaneous absorption of nonyl phenol has been assessed using an *in vitro* system involving porcine and rat skin (Monteiro-Riviere et al., 1999). Additionally, the toxicokinetics following the oral administration of octylphenol (p-(1,1,3,3-tetramethylbutyl)-phenol), an alkyl phenol with a close structural relationship and similar physico-chemical and toxicological properties to nonylphenol, has been investigated in a series of detailed, well-reported studies, conducted in accordance with the principles of GLP (Hüls, 1995a,b 1996g,h, Certa et al., 1996). Octylphenol was selected as a model for alkyl phenol compounds because it has defined chemical structure whereas nonylphenol consists of a mixture of different isomers which, according to the authors, can cause analytical difficulties in toxicokinetic investigations.

In the Knaak et al. (1966) study, ring  $^{14}\text{C}$ -labelled nonylphenol was administered to groups of four male Wistar rats as a single dose of 6.6 mg/kg by either the oral or intraperitoneal routes. Urine, faeces and exhaled  $\text{CO}_2$  samples were collected for up to 7 days and analysed for radioactivity. It was found that for the oral route about 70% of the administered radioactivity had been excreted via the faeces and about 20% via the urine within 4 days. The presence of urinary radioactivity indicated that significant absorption had taken place. Little radioactivity was excreted after 4 days. No radioactivity was detected in exhaled  $\text{CO}_2$ . It was stated that identical results were obtained following intraperitoneal administration, although no data were presented, suggesting that a major route of excretion of absorbed nonylphenol is via the faeces, with the urinary route being of secondary importance. Ion exchange chromatography showed that the principal urinary metabolites of nonylphenol were glucuronic acid conjugates.

Fennell and MacNeela (1997), in a study reported as an abstract, administered a single gavage dose of ring  $^{14}\text{C}$ -labelled nonylphenol at 5 or 200 mg/kg to male and female Sprague-Dawley rats (number not stated). The rats were placed in glass metabolism cages and urine, faeces and expired air were collected for up to 7 days for measurement of radioactivity. After 7 days, blood, tissues, contents of the stomach, small and large intestine, and carcass were removed and analysed for radioactivity. For animals of both sexes and at both dose levels the majority of radioactivity was recovered in the faeces, with lesser amounts in the urine (the actual quantities were not reported). No radioactivity was exhaled as  $^{14}\text{CO}_2$ . Of the radioactivity administered to males of the 5 mg/kg group, about 0.4% was present in the tissues, 1.3% in the gastrointestinal tract, and a further 1.3% in the carcass. The levels detected in the tissues and carcasses of the other groups, as a percentage of the administered dose, were lower. These findings confirm that nonylphenol is systemically absorbed following oral exposure, and that excretion is via the faecal and urinary routes. The relatively low amounts of radioactivity in the tissues and carcass



suggest that although distribution appears to be widespread, the potential for bioaccumulation may be limited.

The *in vitro* percutaneous study involved an assessment of the penetration and absorption of  $^{14}\text{C}$  ring-labelled nonylphenol over an 8-hour period using pig and rat skin (Monteiro-Riviere et al., 1999). Human skin samples were also used; see 4.1.2.1.2. for a summary of this segment of the study. A 1% solution (10  $\mu\text{l}$ ) of labelled nonylphenol in PEG-400 was applied to a 0.32  $\text{cm}^2$  area of fresh skin mounted in a flow-through diffusion cell; the diffusion cell was not occluded. The dermal area dose was 0.3  $\text{mg}\cdot\text{cm}^{-2}$ . The skin samples were dermatomed to a standard thickness of 500  $\mu\text{m}$  prior to mounting. The amount of radioactivity in the perfusate was monitored over time and at the end of the exposure period the amount in the skin sample was measured. Percutaneous absorption was defined as the amount of radioactivity detected in the perfusate over the 8-hour perfusion period and expressed as a % of the applied dose. Percutaneous penetration was defined as the total amount of radioactivity in the perfusate, stratum corneum and dosed skin, and again expressed as a % of the applied dose. Absorption was less than 0.15% of the administered radioactivity for both pig and rat skin. Penetration was about 3% for porcine skin and 6% for rat skin; the % of administered dose in the stratum corneum was about 2% for the pig and 0.5% for the rat. Total recovery of radioactivity from the test system at the end of the study was in excess of 90% for both species. The results of this study suggest that nonylphenol is poorly absorbed across the skin, although some limited skin penetration, especially to the stratum corneum, can occur.

In the first of the octylphenol studies, the toxicokinetics following a single exposure by the oral and intravenous routes was determined in male Wistar rats (Hüls, 1995a). Groups of six rats received octylphenol dissolved in propyleneglycol as a single gavage dose of either 50 or 200  $\text{mg}/\text{kg}$  or a single intravenous injection of 5  $\text{mg}/\text{kg}$ . Repeat blood samples were taken (from three animals at each time point) up to 48 hours after administration for analysis for octylphenol using gas chromatography. Following the intravenous administration, the octylphenol concentration in the blood peaked at about 1970  $\text{ng}/\text{ml}$  and rapidly declined within 30 minutes. No octylphenol was detected in the blood 8 hours after administration. The elimination half-life was 310 minutes. Following the 50  $\text{mg}/\text{kg}$  oral dose, a peak blood concentration of 40  $\text{ng}/\text{ml}$  were seen at 20 minutes and within 6 hours octylphenol concentrations were close to the detection limit at about 5  $\text{ng}/\text{ml}$ . Blood samples collected after 6 hours were not analysed. There was considerable variation in the blood octylphenol concentrations in the 200  $\text{mg}/\text{kg}$  group, although two peak concentration of around 100  $\text{ng}/\text{ml}$  at about 1 - 2 hours and 4 - 8 hours could be distinguished. Octylphenol was still present in the blood of two animals, at between 5 - 10  $\text{ng}/\text{ml}$ , 48 hours after dosing. The oral bioavailability, calculated from the area under the blood concentration curves (AUCs), was found to be low at 2% and 10% of the administered dose for the 50 and 200  $\text{mg}/\text{kg}$  groups, respectively.

In the second octylphenol study, the toxicokinetic behaviour following repeated oral administration was investigated in male Wistar rats (Hüls, 1995b, 1996g). Groups of five rats received daily gavage doses of octylphenol in propyleneglycol at 50 or 200  $\text{mg}/\text{kg}/\text{day}$  for 14 consecutive days. Blood samples were taken on several occasions on day 1 and day 14 for analysis of octylphenol concentration. A further group of fifteen males received octylphenol via the drinking water at a concentration of 8  $\text{mg}/\text{l}$  (giving an intake of about 0.8  $\text{mg}/\text{kg}/\text{day}$ ) for up to 28 days, with blood samples being taken on several occasions throughout the exposure period. At the end of the exposure period the animals were killed (exact timing in relation to the last dose was not reported) and liver, kidney, brain, lung, skeletal muscle and abdominal fat were sampled for analysis of octylphenol concentration.

In the gavage groups octylphenol concentration in the blood peaked within one hour of the first dose, with maximum concentrations similar to those observed in the previous study. The concentration then declined steadily to a concentration of about 13 ng/ml at 24 hours in both groups. On day 14, the blood concentration-time profile was generally similar to that observed on day 1. In the group exposed via the drinking water, no octylphenol was detected in the blood (limit of detection 1 - 5 ng/ml) at any time. The organ and tissue analyses demonstrated the presence of octylphenol in fat and liver in several animals at 50 mg/kg/day; tissue levels were 16 - 32 and 10 - 14 ng/g, respectively. At 200 mg/kg/day octylphenol was found on all the tissues analysed. By far the highest concentration was in fat (mean 1285 ng/g), followed by the liver, kidney and muscle (mean 87, 71 and 43 ng/g, respectively). In the group exposed via drinking water, octylphenol was found only in the kidney and muscle of one animal.

The repeated dose gavage study indicates that octylphenol is distributed widely in the body, but with the highest concentrations in fat. The fact that the blood concentration-time profile was similar on day 1 and 14 suggests that bioaccumulation may be limited, but without information on the organ and tissue concentrations at more than one time point this study does not provide strong evidence with regard to bioaccumulation potential. The results from the drinking water group indicate that essentially no detectable amounts of octylphenol reach the blood and tissues following an intake of up to 0.8 mg/kg/day for 28 days.

In the final Hüls study, it was demonstrated that rat liver homogenate has the ability to metabolise octylphenol by glucuronide and sulphate conjugation, which are the principal metabolic pathways for many phenolic substances (Hüls 1996h).

By combining the information provided in the above animal studies it is possible to gain an understanding of some aspects of the toxicokinetic behaviour of nonylphenol in rats. The Knaak and Fennell and MacNeela studies, in which radioactivity was recovered from the urine, show that nonylphenol is absorbed following oral administration. The absorption of alkyl phenols from the gastrointestinal tract, which appears to be initially rapid, is confirmed in the octylphenol studies in which the substance was detected in the blood soon after oral administration. It is not possible to determine the extent of absorption on the basis of these studies, although the fact that in the Knaak study 20% of the administered radioactivity was recovered from urine suggests that extent of absorption must be at least this figure. The oral bioavailability for octylphenol was estimated to be 2-10%, but this cannot be considered to reflect the extent of absorption because the blood and tissue concentration of octylphenol metabolites were not measured in this study. The Fennell and MacNeela study, with support from the octylphenol studies, indicate that nonylphenol undergoes widespread distribution, with the highest concentrations in fat. Major metabolic pathways for nonylphenol, in common with other phenolic compounds, appear to be glucuronide and sulphate conjugation. The oral nonylphenol radiolabelled studies indicate that a single dose of up to 200 mg/kg is largely eliminated within several days, and the low amount of radioactivity retained in the tissues suggests that the potential for bioaccumulation may be limited, but no conclusion as to whether or not nonylphenol has the potential to bioaccumulate can be drawn because of limitations in the available data. The oral nonylphenol studies also show that the major routes of excretion are via the faeces and urine. Concerning the dermal route, the *in vitro* study suggests that nonylphenol is poorly absorbed across the skin, although some limited skin penetration, especially to the stratum corneum, can occur.

#### 4.1.2.1.2 Studies in humans

The toxicokinetic behaviour of radiolabelled nonylphenol was investigated in two male volunteers, aged 29 and 58 years (Müller, 1997). Ring  $^{14}\text{C}$ -labelled nonylphenol was administered to one volunteer as a single oral dose of 5 mg (66  $\mu\text{g}/\text{kg}$  bodyweight) and to the second volunteer as a single intravenous dose of 1 mg (14  $\mu\text{g}/\text{kg}$ ). Blood, urine and faeces were collected from the first volunteer at intervals for up to 56 hours after administration. Blood samples only were taken from the second volunteer, for up to 24 hours. The biological samples were analysed for nonylphenol and nonylphenol conjugates (glucuronide and sulphate) by gas chromatography/mass spectrometry (it is not clear why radiolabelled nonylphenol was used). Recovery experiments using spiked blood, urine, faeces and adipose tissue samples confirmed the efficiency of the analytical extraction technique.

Following oral administration, the concentration of nonylphenol and nonylphenol present as conjugates in the blood both peaked at about 1 hour; peak concentration of nonylphenol present as a conjugate was 86 ng/g blood, which was some 100-fold greater than that of unconjugated nonylphenol. For intravenous administration, the highest concentrations of nonylphenol, at 0.6 and 0.2 ng/g blood for unconjugated and conjugated compound, respectively, were seen at the first sampling point of 30 minutes; at all time points the concentrations of unconjugated and conjugated nonylphenol were of the same order of magnitude. For both the oral and intravenous routes, the time courses of blood concentration were indicative of an initial phase of distribution from the blood to a second compartment (presumably the lipid compartment) followed by a slower elimination phase. Comparison of the AUCs for the oral and intravenous routes suggested that oral bioavailability of unconjugated nonylphenol was about 20%. Analysis of the urine samples showed that about 10% of the oral dose was excreted in urine as unconjugated or conjugated nonylphenol, most of which was eliminated within eight hours. Only about 1.5% of the oral dose was excreted in the faeces during the 56-hour collection period.

Müller, (1997) also measured the nonylphenol content of 25 samples of adipose tissue taken at autopsies of persons thought to have had no occupational exposure to alkyl phenols. The measured tissue concentrations were all within the range of background contamination found in the analytical "blank" samples. The author indicated that all reasonable precautions were taken to minimise contamination during analysis.

Although the first part of the study has a major limitation in that it involved only two volunteers, it does provide evidence that nonylphenol is rapidly absorbed from the gastrointestinal tract in humans. Also, the fact that only a small proportion of the dose was recovered in faeces within 56 hours suggests that almost complete absorption of a dose had occurred. Following oral administration, most of the nonylphenol was present in the blood as glucuronide or sulphate conjugates, in contrast to the findings for intravenous administration where similar proportions of unconjugated and conjugated nonylphenol were detected; these findings are indicative of extensive first pass metabolism. Only 11.5% of the oral dose was recovered in the urine and faeces during the course of the study, which raises the question of the fate of the remainder of the dose. On the basis of the animal data, it is unlikely that excretion occurred via exhalation, so possibly a substantial proportion of the nonylphenol was taken up by the lipid compartment. However, this explanation does not appear to be consistent with the evidence from the animal studies which indicated that very little nonylphenol is retained in tissues and carcass 7 days after a single dose. The observation of negligible nonylphenol in the human autopsy samples is in concordance with the animal data which suggested that bioaccumulation may not occur. However, the supposition of low bioaccumulation is not supported by the excretion data from the

human volunteer receiving the oral dose. Overall, it is considered that there are insufficient appropriate data to allow a conclusion to be drawn as to whether or not nonylphenol has the potential to bioaccumulate in humans.

The percutaneous penetration and absorption of  $^{14}\text{C}$  ring-labelled nonylphenol was assessed using human skin in an *in vitro* study (Monteiro-Riviere et al., 1999). Pig and rat skin samples were also used in this study (see 4.1.2.1.1. for more information). A 1% solution (10  $\mu\text{l}$ ) of labelled nonylphenol in PEG-400 was applied to a 0.32  $\text{cm}^2$  area of 500  $\mu\text{m}$  thick fresh human skin, mounted in a flow-through diffusion cell; the diffusion cell was not occluded. The dermal area dose was 0.3  $\text{mg}\cdot\text{cm}^{-2}$ . The amount of radioactivity in the perfusate was monitored over an 8-hour perfusion period and at the end of the exposure period the amount in the skin sample was measured. The results for human skin were very similar to those for rat and pig skin. Absorption was 0.1% and penetration was about 4% of administered dose; 1.7% was recovered in the stratum corneum. Total recovery of radioactivity from the test system at the end of the study was 92% of administered radioactivity. The results of this study suggest that nonylphenol is poorly absorbed across human skin, although some limited skin penetration, especially to the stratum corneum, can occur.

There are no data on the toxicokinetics of nonylphenol following inhalation. However, on the basis that nonylphenol appears to be readily absorbed from the gastrointestinal tract and in view of its high partition coefficient, it would be prudent to assume that significant absorption via the inhalation route will occur. Furthermore, because first pass metabolism would not take place following exposure by this route, the inhalation systemic bioavailability is likely to be substantially greater than is associated with the oral route.

#### **4.1.2.1.3 Summary of toxicokinetics, metabolism and distribution**

Most of the information on the toxicokinetics of nonylphenol concerns oral exposure and is based on a small number of limited rat and human studies, supported by a read across from data relating to octylphenol, an alkyl phenol with a close structural relationship to nonylphenol. The available data, though sparse, do provide the basis for a general understanding of the main features of the toxicokinetic profile. Absorption from the gastrointestinal tract is initially rapid, and probably extensive. The major metabolic pathways are likely to involve glucuronide and sulphate conjugation, and there is evidence of extensive first pass metabolism of nonylphenol absorbed through the gastrointestinal tract. Because of first pass metabolism, the bioavailability of unconjugated nonylphenol is probably limited following oral exposure, at no more than 10-20% of the administered dose. Nonylphenol is distributed widely throughout the body, with the highest concentration in fat. Regarding bioaccumulation, considering the available information from both animals and humans, there are insufficient consistent data to allow a conclusion to be drawn on whether or not nonylphenol has this potential. The major routes of excretion are via the faeces and urine.

There are no data on the toxicokinetics of nonylphenol following inhalation exposure, but on the basis of the oral absorption data and high partition coefficient, it would be prudent to assume that significant absorption via the inhalation route can occur. Furthermore, because first pass metabolism will not take place following exposure by these routes, the systemic bioavailability is likely to be substantially greater than is associated with the oral route. Concerning the dermal route, *in vitro* data indicate that nonyl phenol is poorly absorbed across skin, although some limited skin penetration, especially to the stratum corneum, can occur.

#### **4.1.2.2 Acute toxicity**

Only data in animals are available

##### **4.1.2.2.1 Inhalation**

The only available study is inadequately reported and of little use. Smyth et al. (1969) exposed a group of six rats to an unquantified "concentrated vapour" of nonylphenol for 4 hours and found that there were no deaths. However, the corrosive nature of nonylphenol suggests that toxicity would be elicited following exposure by this route.

##### **4.1.2.2.2 Oral**

The acute oral toxicity of nonylphenol has been investigated in a number of animal studies. The three most recent studies were adequately reported, using methods equivalent to OECD test guideline 401; one was conducted according to GLP (Berol Kemi AB 1982, Hüls AG 1981, ICI 1984). Estimated LD<sub>50</sub> values ranged from about 1200 to 2400 mg/kg for males and 1600 to 1900 mg/kg for females. The 95% confidence intervals in these studies were generally relatively tight, suggesting that the dose-response curve is steep. Clinical signs of toxicity included excessive salivation, diarrhoea and lethargy. At necropsy, erosion of the mucosal surface of the stomach was seen in some of the animals which died. Similar LD<sub>50</sub> values were reported in earlier studies in the rat (Gaworski et al., 1979, Smyth et al., 1969).

Gaworski et al., (1979) also determined an oral LD<sub>50</sub> in male mice of 307 mg/kg in a briefly reported study.

##### **4.1.2.2.3 Dermal**

In a briefly reported study, a dermal LD<sub>50</sub> of 2031 mg/kg was determined in groups of four male New Zealand white rabbits (Smyth et al., 1969). The exposure period was 24 hours.

##### **4.1.2.2.4 Summary of acute toxicity**

No human data are available. In animals, nonylphenol is moderately toxic by the oral route, with LD<sub>50</sub> values for the rat in the ranges of about 1200 to 2400 mg/kg for males and 1600 to 1900 mg/kg for females. The dose-response curve for lethality appears to be steep. Erosion of the stomach mucosa is sometimes seen following the administration of a lethal dose. The acute toxicity of nonylphenol by the dermal route is similar, with an LD<sub>50</sub> of about 2000 mg/kg in rabbits. No data are available on the acute inhalation toxicity, although the corrosive nature of nonylphenol suggests that toxicity would be elicited following exposure by this route.

#### **4.1.2.3 Irritation**

Only animal data are available.

##### **4.1.2.3.1 Skin**

Skin irritation has been investigated in a number of well-reported studies which used methods equivalent to OECD test guideline 404. Union Carbide (1992 a, b) tested substances named "nonylphenol S" and "nonylphenol RNH" and found severe irritation including full-thickness

necrosis and ulceration within 24 hours of either a 1 or 4 hour application. Hüls (1986a) reported necrosis and maximum scores for erythema and eschar formation at 24, 48 and 72 hours following a 4-hour application of nonylphenol. In a GLP-compliant study sponsored by EniChem (1992), all rabbits showed skin reactions described as erythema grade 2 and oedema grade 3 at 24, 48 and 72 hours, progressing to eschar formation grade 4 at termination of the study on day 8. In contrast, Berol Kemi AB (1987), in a GLP-compliant study, reported less severe skin reactions, graded as 2 for erythema and 1-3 for oedema at the 24-, 48- and 72-hour observation times, with all animals appearing normal at 13 days.

Skin irritation has also been investigated in several studies which used non-standard methods. Gaworski et al., (1979), in contrast to the above studies, reported no signs of irritation following a 24-hour application of 0.5 ml nonylphenol to the skin of rabbits. ICI (1982) reported sensitivity to touch, severe erythema and thickening, wrinkling and hardening of the skin at the application site immediately after a 24-hour contact with 0.1 ml nonylphenol in a rat study. In an earlier ICI (1979) study a single applications of nonylphenol from two different sources caused slight erythema together with wrinkling and thickening of the skin at the application site in rats; the amount of test substance applied and contact time were not reported.

The results of these animal studies suggest that the irritant properties of nonylphenol may vary, depending on the source of the test sample. However, since full thickness destruction or skin necrosis were seen in two studies it is reasonable to consider nonylphenol to be corrosive on contact with skin.

#### **4.1.2.3.2 Eye**

Two well reported studies using methods equivalent to OECD guideline 405 are available. Hüls (1986b) described ocular lesions indicative of severe irritation. Maximum scores for conjunctival redness were reported for much of the 21-day observation period and two of the three rabbits tested had grade 3 or 4 corneal opacities at the end of the observation period.

In the other study nonylphenol from two different sources was tested in groups of three rabbits (ICI 1979). Nonylphenol from ICI 'Oil Works' caused grade 2 or 3 conjunctival redness, conjunctival chemosis grades 1 - 4, corneal opacity grades 1 or 2 and, in two rabbits, grade 1 lesions of the iris. At the end of the 7-day observation period eye lesions were still present in two rabbits. Nonylphenol from Rohm and Haas elicited less severe reactions, although lesions were still present at the end of the observation period.

In an earlier briefly-reported non-standard test the instillation 0.5 ml of a 1% solution of nonylphenol resulted in severe burns (Smyth et al., 1969).

These results indicate the nonylphenol is a severe eye irritant.

#### **4.1.2.3.3 Respiratory tract**

The sensory irritation potential of nonylphenol has been investigated (ICI, 1995). Atmospheres of saturated vapour concentration and one tenth saturated vapour concentration, nominally 3636 mg/m<sup>3</sup> (400 ppm) and 267 mg/m<sup>3</sup> (30 ppm), respectively, were tested. Groups of five female CD-1 mice were exposed, nose only, to each concentration and the respiration rate was monitored using pressure plethysmography. The duration of exposure to the nonylphenol vapour was not reported. The proportion of liquid particulate material in the test atmospheres was

determined, and found to be approximately 1% of the nominal concentration, an amount considered unlikely to have a significant influence on the results. At 3636 mg/m<sup>3</sup> a mean respiratory rate depression of about 25% was found during exposure. However, at 267 mg/m<sup>3</sup> there were no changes in the respiratory rate. These results suggest that nonylphenol can cause mild sensory irritation to the respiratory tract at high exposure levels.

#### **4.1.2.3.4 Summary of irritation**

No information is available from human studies. Animal data indicates that liquid nonylphenol can be corrosive to the skin, although its potency might vary according to source and exact composition. The liquid is also a severe eye irritant. Exposure to the saturated vapour elicited mild sensory irritation of the respiratory tract in mice.

#### **4.1.2.4 Corrosivity**

See irritation (4.1.2.3).

#### **4.1.2.5 Sensitisation**

Only animal data are available.

##### **4.1.2.5.1 Skin**

The skin sensitisation potential of nonylphenol has been investigated in several studies.

Hüls (1986c) conducted a fully-reported guinea pig maximisation study according to a method similar to the contemporary OECD guideline 406. Concentrations of 0.9 and 50% were used for the intradermal and topical induction phases, respectively, and 10, 30 and 45% for challenge. The 50% topical application was slightly irritating. No animals showed skin sensitisation reactions.

ICI (1980) also conducted a guinea pig maximisation using a method equivalent to the OECD guideline. Concentrations of 0.1 and 5% were chosen for the intradermal and topical induction phases. No skin reactions were seen 24 hours after a 1% challenge application but at 48 hours erythema was seen in both test and control animals. A rechallenge at 0.1% was conducted two weeks later and skin reactions occurred in seven out of fifteen test animals and one out of seven control animals. However, the authors reported difficulties in accurately assessing the frequency of response and consequently it is considered that no firm conclusions can be drawn from this study.

In another guinea pig maximisation study, for which only brief details of the methods and results are available, nonylphenol from two sources was tested (ICI 1979). For nonylphenol from ICI 'Oil Works' skin reactions were observed at challenge in two out of (probably) twenty test animals, whereas nonylphenol from Rohm and Haas elicited no reactions. This study is considered to be negative.

Gaworski et al., (1979) investigated the skin sensitisation potential using a non-standard method which did not apparently include the use of a control group. The skin reactions at challenge were reported in more than 50% of animals, but no conclusions can be drawn from this study in because of the lack of a control group.

#### **4.1.2.5.2 Respiratory tract**

No data are available, although it can be predicted from its low chemical reactivity that nonylphenol is unlikely to be a respiratory allergen.

#### **4.1.2.5.3 Summary of sensitisation**

No human data are available. The results of several guinea pig maximisation tests suggest that nonylphenol does not have significant skin sensitising potential. No information on respiratory tract sensitisation is available, although it can be predicted from its low chemical reactivity that nonylphenol is unlikely to be a respiratory allergen.

#### **4.1.2.6 Repeated dose toxicity**

##### **4.1.2.6.1 Animal data**

There are no data for the inhalation or dermal routes. Two high-quality oral repeated dose studies in rats, of 28 and 90 days duration, have been conducted. The studies followed OECD guidelines and were in compliance with GLP. Additionally, the influence of nonylphenol on growth and cell proliferation and of the mammary gland has been investigated in the rat in a non-standard study involving subcutaneous administration.

In the 28-day study, groups of five male and five female Sprague-Dawley rats were exposed to nonylphenol via incorporation in the diet at nominal dose levels of 0, 25, 100 or 400 mg/kg/day (Hüls 1989). Clinical signs of toxicity, bodyweights and food consumption were recorded and towards the end of the study routine haematology, blood clinical chemistry and urinalysis examinations were made. A full necropsy was performed on all animals at termination. Adrenals, liver, kidneys and testes with epididymides were weighed and a limited range of major organs was examined microscopically.

There were no mortalities or treatment related clinical signs of toxicity. At 400 mg/kg/day, bodyweight gain was significantly reduced throughout the study, and by week four mean bodyweights were 26% and 13% less than the controls for males and females, respectively. The amount of food consumed and food utilisation was also reduced at 400 mg/kg/day for both sexes. For males only at 400 mg/kg/day there were slight differences in comparison with the controls for certain clinical chemistry parameters; urea and cholesterol levels were increased and glucose levels were reduced. Also, there were increases in the group mean relative kidney, liver and testes weights (all by about 20% compared with controls). Histopathological examination revealed hyaline droplet accumulation in the renal proximal tubules (an effect considered to be of no relevance to human health) and a minor vacuolation in the periportal hepatocytes for males at 400 mg/kg/day. Among the females at this level, there were no treatment-related changes in the organs.

For males and females at 25 and 100 mg/kg/day, there were no differences in any of the parameters examined that could be conclusively related to treatment. It should be noted that minor increases in comparison with the concurrent control group were reported for kidney, adrenal and liver weights and for the incidence of minimal hyaline droplet formation in the kidney among males at 25 and 100 mg/kg/day. However, all values were within the laboratory's historical control range (personal communication with study sponsor) and confirmatory changes were not seen for adrenal and liver weight or hyaline droplet formation in the 90-day study (see



below). Consequently these marginal changes could not be reliably attributed to nonylphenol treatment. Overall, this study identifies a NOAEL of 100 mg/kg/day for 28-day exposure.

In the 90-day study, groups of fifteen male and fifteen female Sprague-Dawley rats were exposed to nonylphenol via incorporation in the diet at concentrations of 0 (control), 200, 650 or 2000 ppm (Chemical Manufacturers Association 1997a, Cunny et al., 1997). Calculated nonylphenol intakes were about 0, 15, 50 and 140 mg/kg/day, respectively. Additionally, control and high dose satellite groups of ten animals of each sex were included; these were given a 28 day recovery period at the end of the 90-day exposure. Clinical signs of toxicity, bodyweights and food consumption were recorded and towards the end of the study routine haematology, blood clinical chemistry and ophthalmoscopy examinations were made. A full necropsy was performed on all animals at termination. A number of organs were weighed and histopathological examinations were conducted on a comprehensive range of organs and tissues. Also, oestrous cycles were monitored during week 8 and sperm motility, sperm number (in epididymis) and sperm morphology were evaluated at necropsy.

There were no treatment-related mortalities or clinical signs of toxicity. At 140 mg/kg/day only, there were adverse effects on bodyweight gain, the amount of food consumed and food utilisation throughout the dosing period for both males and females. At 90 days, the mean bodyweights for both sexes at this exposure level were about 7% less than the controls. In the satellite group, some recovery of bodyweight and food consumption values was seen after exposure was discontinued. Haematology and ophthalmoscopy findings and oestrous cycle patterns were not affected by treatment. There was no evidence of effects on spermatogenesis. However, one interesting clinical chemistry change was seen among females from the 140 mg/kg/day group. Serum aspartate aminotransferase (AST) and alanine aminotransferase (ALT) levels were markedly elevated in two females, which correlated with some histopathological changes reported in the liver (see below).

At necropsy, no treatment-related macroscopic findings were reported. Among the males killed at 90 days, there was a dose-related increase in group mean absolute (by 6, 9 and 13%, relative to controls, at 15, 50 and 140 mg/kg/day respectively) and bodyweight-related (by 8, 11 and 24%, respectively) kidney weight. In the recovery group, the bodyweight-related kidney weight among males was also increased, although the effect was less marked. However, this organ weight increase could not be correlated with any clinical chemistry or histopathological change and consequently this finding was considered unlikely to be of toxicological significance, particularly at 15 and 50 mg/kg/day where magnitude of the change was small. Also, ovary weight was slightly decreased in females from the 140 mg/kg/day group, in comparison with the controls, at 90 days. In contrast, the weight of this organ was slightly increased in the recovery group. Again, this difference could not be correlated with any histopathological change which, together with the inconsistency between the findings for the main and satellite groups, makes the interpretation of this finding uncertain. Bodyweight-related liver weight was increased at 90 days only in males at 50 and 140 mg/kg/day and females at 140 mg/kg/day, by about 10% compared with controls. This was considered likely to be an adaptive rather than toxicological response.

The only noteworthy microscopic changes were seen in the kidneys and liver. Among males at 140 mg/kg/day in both the main and satellite groups there was a decrease in the occurrence of renal tubular hyaline droplets/globules in comparison with the control group. The biological significance of this change is uncertain. Also, a lack of correlation with the findings of the 28-day repeated dose study, in which an actual increase in the incidence of renal hyaline droplets occurred, casts doubt on whether these changes should be considered to be related to treatment. Slight or moderate individual hepatic cell necrosis was seen in three females at 140 mg/kg/day; two of the affected females also had raised serum ALT and AST. This provides evidence that the liver may be a target organ for nonylphenol toxicity, although this evidence is weak in view of the mild nature of response and small number of animals affected.

The renal histopathological findings have been reviewed by a pathologist not involved in the original investigation (Hard 1998), because of a lack of coherence between the results of this study and a multigeneration study summarised below (NTP 1997). An increased incidence of deposits of intratubular mineralisation in the P3 (straight) segment of the proximal tubule at the outer stripe of the outer medulla/inner stripe of outer medulla (OSOM/ISOM) junction was seen in males at 140 mg/kg/day; 11 out of 25 from this group were affected, compared with 1 out of 25 control males.

Overall, a NOAEL of about 50 mg/kg/day can be derived from this study. At 140 mg/kg/day there were reductions in bodyweight gain, food consumption and food utilisation together with evidence of morphological changes in the liver and possibly kidneys.

Further information on repeated dose toxicity can be derived from a good-quality multigeneration study (NTP 1997, see section 4.1.2.9.2 for full details of this study, including information on any findings in reproductive organs). Groups of thirty male and thirty female Sprague-Dawley rats were exposed to nonylphenol via incorporation in the diet at concentrations of 0 (control) 200, 650 or 2000 ppm over three generations. Calculated nonylphenol intakes were, respectively, about 0, 15, 50 and 160 mg/kg/day during non-reproductive phases. The F<sub>0</sub> generation were exposed for 15 weeks, the F<sub>1</sub> and F<sub>2</sub> generations from soon after birth to about 20 weeks of age and the F<sub>3</sub> generation from birth to about 8 weeks of age.

Evidence of general toxicity was seen in adults of all generations, although there were no treatment-related clinical signs, mortalities or adverse effects on food consumption. At 160 mg/kg/day, bodyweight gain was reduced in comparison with controls in adults across all generations, with the terminal bodyweights being about 10% lower than the controls. Similar reductions in bodyweight gain were also seen at 50 mg/kg/day in F<sub>1</sub> females, F<sub>2</sub> males and F<sub>3</sub> females. Relative kidney weights were increased at 50 and/or 160 mg/kg/day in adult males of the F<sub>0</sub>, F<sub>1</sub> and F<sub>2</sub> generations and also at 160 mg/kg/day in F<sub>1</sub> adult females. Histopathological examination revealed an increase, although often without a convincing dose-response relationship, in the incidence of renal tubular degeneration and/or dilatation in adult males from all generations and all nonylphenol treated groups; similar findings were reported for adult females at 160 mg/kg/day in the F<sub>1</sub>, F<sub>2</sub> and F<sub>3</sub> generations and at 15 and 50 mg/kg/day in the F<sub>3</sub> generation. These data are given in **Table 4.13**.

**Table 4.13** Number of animals with histopathological abnormalities in the kidney (n=10)**Males**

Generation	Finding	Dose level (mg/kg/day)			
		0	15	50	160
F <sub>0</sub>	Renal tubule degeneration	1	3	5	5
	Renal tubule dilatation	0	1	0	0
F <sub>1</sub>	Renal tubule degeneration	1	2	7	8
	Renal tubule dilatation	1	1	0	2
F <sub>2</sub>	Renal tubule degeneration	3	6	6	6
	Renal tubule dilatation	1	2	0	4
F <sub>3</sub>	Renal tubule degeneration	0	7	10	2
	Renal tubule dilatation	0	0	3	3

**Females**

Generation	Finding	Dose level (mg/kg/day)			
		0	15	50	160
F <sub>0</sub>	Renal tubule degeneration	3	3	0	0
	Renal tubule dilatation	0	0	1	0
F <sub>1</sub>	Renal tubule degeneration	0	1	1	6
	Renal tubule dilatation	0	0	0	3
F <sub>2</sub>	Renal tubule degeneration	1	2	0	4
	Renal tubule dilatation	0	0	0	1
F <sub>3</sub>	Renal tubule degeneration	0	8	9	7
	Renal tubule dilatation	0	0	1	1

It is difficult to decide for certain whether or not this increased incidence of renal tubular degeneration and/or dilatation is related to treatment because these changes were not seen to the same extent in the 90-day study, which was conducted using the same strain of rats, and because a dose-dependent trend was not apparent in all generations/sexes. The lack of concordance between the studies cannot be explained on the basis of a slightly longer exposure period in the multigeneration study because kidney effects were seen in the F<sub>3</sub> generation which was exposed for only 8 weeks, nor on the basis of *in utero* and neonatal exposure because the effect also occurred in the F<sub>0</sub> generation. Giving special emphasis to the fact that the increased incidence occurred consistently across all four generations in the multigeneration study, it is considered that this cannot be dismissed as background variation. Consequently, a conclusion has been drawn from this study that there is a LOAEL for repeated exposure of 15 mg/kg/day, based on histopathological changes in the kidneys; this value will be taken forward to the risk characterisation.

The renal histopathological findings have been reviewed by a pathologist not involved in the original investigation (Hard, 1998). The presence of renal lesions in all nonylphenol exposed groups was confirmed, as was the lack of a consistent dose-dependent trend in all generations. The

predominant renal lesions were described as tubular mineralisation at the OSOM/ISOM junction, cystic tubules surrounded by fibrosis, or granular cast formation at the OSOM/ISOM junction.

A briefly reported oral (gavage) study investigating the testicular toxicity of nonylphenol (de Jager et al., 1999a) is summarised in the toxicity to reproduction section. In this study, mortality was observed at 100 (the lowest dose level tested), 250 and 400 mg/kg/day; 3, 15 and 18, respectively, out of 20 animals in each group died during a 10-week dosing period. No further information on these mortalities is available. The presence of mortality at such dose levels contrasts with the findings of the dietary administration studies (Hüls, 1989; Chemical Manufacturers Association, 1997a; NTP, 1997). The differences can probably be accounted for by the method of administration; gavage dosing is likely to produce higher peak concentrations of nonylphenol in the blood than dietary administration.

The influence of nonylphenol on growth and cell proliferation and of the mammary gland has been investigated in rats of the Nobel strain in two studies using non-standard methods. The Nobel strain of rat is particularly sensitive to oestrogenic activity. In the original study, groups of six female juvenile rats were exposed to nonylphenol by the subcutaneous route for 11 days, administered via osmotic minipumps implanted in the dorsal cervical region (Colerangle and Roy, 1996). The dose levels were 0 (DMSO vehicle control), 0.01 and 7.12 mg/day (0.05 and 35.6 mg/kg/day, assuming a bodyweight of 200 g). An additional group received diethylstilbestrol (DES) at 0.01 mg/day (0.05 mg/kg/day) for 11 days by an unspecified route. At the end of the exposure period the rats were killed and the abdominal mammary glands removed for evaluation. Mammary gland growth was assessed by counting the number of mammary structures (terminal ducts, terminal end buds or lobules) and cells in 16 mm<sup>2</sup> areas of the mammary gland. Cell proliferation and cell-cycle kinetics were evaluated using immunohistochemical techniques (reaction with antiproliferating cell nuclear antigen (PCNA)) which allowed cells in S, G1 and G0 phases to be identified. The labelling index (LI, proportion of cells in S phase) growth fraction (GF, proportion of cells in the G1 or S phase) were calculated.

In the group receiving the highest dose of nonylphenol there was a 1.5-fold increase in the number of mammary structures and a 4-fold increase in the number cells/16 mm<sup>2</sup> area, compared with the vehicle control group. At the lowest level the number of structures was similar to the controls, but there was a 2-fold increase in the number of cells. DES caused a 6-fold increase in the number of cells. The LI was increased by 1.3 and 1.8 fold and GF by 1.2 and 2 fold in the nonylphenol low and high dose groups, respectively, in comparison with the vehicle control. DES had a much greater influence on the indices, with increases of 4 and 5 fold for the LI and GF. Cell cycle time was unchanged in the low dose group, slightly decreased (by about 10%) in the high dose group and markedly decreased (by more than half) in the DES group. This study shows that nonylphenol at dose levels of 0.05 and 35.6 mg/kg/day increases growth and proliferation activity in a dose-related manner in the mammary gland of the Nobel rat, although the effects at 0.05 mg/kg/day are marginal. The significance for human health of such a finding is unknown. Furthermore, the use of the subcutaneous route of administration and selection of the oestrogen-sensitive Nobel rat as the model casts doubts about the relevance of these findings to humans. Ashby and Odum (1998) draw attention to the fact that same positive control (DES) data reported for this study also appear in two other reports by Colerangle and Roy (1995 and 1997), and that the vehicle control data of the nonylphenol study is duplicated in the 1997 study. This raises some uncertainties as whether the control data were generated concurrently with the nonylphenol data and questions the validity of this study.

The Colerangle and Roy (1996) study was duplicated by Odum et al. (1999). Groups of ten female OVR<sup>+</sup> Noble rats were exposed to nonylphenol at dose levels of 0 (DMSO vehicle control), 0.073 or 53.2 mg/kg/day or DES at 0.076 mg/kg/day by the subcutaneous route for 11 days, administered via osmotic minipumps implanted in the dorsal cervical region. Mammary gland differentiation and mammary gland cell proliferation were assessed following similar methodology to Colerangle and Roy (1996), except that BRDU as well as PNCA staining was used (BRDU incorporation was considered to be a more sensitive and robust technique) and a more objective method was used to quantitate mammary gland changes. The quantitative determination of the numbers and areas of mammary gland structures showed no differences between the vehicle control and nonylphenol exposed groups, in contrast to the findings of the original study. DES, however, had a marked influence of the differentiation of mammary structures. Terminal ducts were completely absent and terminal end buds were present only in peripheral regions. Also, the numbers and areas of lobules were markedly increased in peripheral and central areas. The mammary gland cell proliferation assessment revealed, in comparison with the vehicle control group, no changes in the nonylphenol exposed groups, and a marked increase (about 4 fold in the lobules) in the DES group. This study shows the DES can induce growth and proliferation activity in the mammary gland of the Nobel rat, but failed to confirm the observation in the Colerangle and Roy (1996) study of such activity following nonylphenol exposure at similar dose levels.

#### **4.1.2.6.2 Human data**

The effects of nonylphenol exposure have not been evaluated in humans. There are two isolated case reports of leucoderma on the hands and forearms, with subsequent spreading to other areas, among Japanese workers exposed to alkaline detergents containing polyethylene alkyphenylether (Ikeda et al., 1970). The authors speculated that this might be caused by free octylphenol or nonylphenol, which were found to be present in the detergents. However, in the absence of corroborative reports from elsewhere, no firm conclusions regarding causality can be made.

#### **4.1.2.6.3 Summary of repeated dose toxicity**

No useful human data are available. In a multigeneration study in the rat involving oral exposure via the diet for up to 20 weeks, a LOAEL for repeated dose toxicity of 15 mg/kg/day was identified, based on histopathological changes in the kidneys (tubular degeneration or dilatation), although such changes were not apparent at this dose level in a 90-day dietary exposure rat study. At higher dose levels the liver may also be a target organ; minor histopathological changes in the liver (vacuolation in the periportal hepatocytes or occasional individual cell necrosis) were seen at doses of 140 mg/kg/day and above in some dietary studies. The oral toxicity of nonylphenol appears to be enhanced when dosed by gavage, with mortalities being reported at dose levels of 100 mg/kg/day and above. No studies involving dermal or inhalation exposure have been conducted. Nonylphenol has been reported to induce cell proliferation in the mammary gland of the Nobel rat following subcutaneous exposure at levels down to 0.05 mg/kg/day, but this finding could not be reproduced in a duplicate study; furthermore, there are doubts about the relevance of this finding to humans and regarding the validity of the original study.

#### **4.1.2.7 Mutagenicity**

Only data from *in vitro* test systems and animals are available.

#### 4.1.2.7.1 Studies in vitro

Two pre-incubation bacterial mutagenicity (Ames) tests have been conducted. Both were negative. The first cannot be fully appraised because only a summary report is available (Hüls 1984). *Salmonella typhimurium* strains TA1537, TA 1538, TA 98 and TA 100 were exposed to nonylphenol at concentrations to 5000 µg/plate, both in the presence and absence of metabolic activation (Aroclor induced rat liver S9). The same *Salmonella* strains were used in the second study, together with *Escherichia coli* strain WP2urvA (Shimizu et al., 1985). Concentrations up to 100 µg/plate were tested, both in the presence and absence of metabolic activation (polychlorinated biphenyl induced rat liver S9), and toxicity was reported at the highest concentrations tested. A limitation of both studies is that the results of neither appeared to have been confirmed by a second independent experiment.

In a well-conducted *in vitro* mammalian cell gene mutation test, following OECD guideline 476 and in compliance with GLP, the potential for nonylphenol to induce mutations at the HPRT-locus was investigated in Chinese hamster V79 cells (Hüls, 1990). The exposure period was 5 hours, and a range of concentrations up to 2.5 µg/ml (without metabolic activation) or 1.25 µg/ml (with metabolic activation) were tested. At higher concentrations there was no cell survival. The results were confirmed by independent experiment. The test was negative.

#### 4.1.2.7.2 Studies in vivo

Two micronucleus studies are available.

In the most recent study, conducted according to OECD guideline 474, groups of 5 male and 5 female NMRI strain mice received a single intraperitoneal dose of 50, 150 or 300 mg/kg (Hüls, 1999b). Appropriate positive (cyclophosphamide) and negative (vehicle) control groups were included. The highest treatment level was chosen as the maximum tolerated dose, based on the results of a preliminary study. Bone marrow was sampled 24 hours after treatment. There was a second sampling time of 48 hours for additional groups receiving either nonylphenol at 300 mg/kg or only the vehicle. Toxicity was elicited at 150 and 300 mg/kg, seen as clinical signs such as sedation, squatting posture, abnormal gait and piloerection. There was no consistent effect on the polychromatic to normochromatic erythrocyte (PCE/NCE) ratio. No increases in the frequency of micronucleated PCEs were seen in the nonylphenol exposed groups; thus the tests is considered to be negative. The anticipated response was seen in the positive control group. Although the PCE/NCE ratio was not affected, the fact that the study was conducted at the maximum tolerated dose and using the intraperitoneal route of administration, it can be presumed that exposure of the bone marrow to nonyl phenol was maximised. Accordingly, a high level of confidence can be given to this negative result.

An earlier micronucleus test was conducted using the oral route of administration (Hüls, 1988). In accordance with the OECD guideline, groups of five male and five female mice of the NMRI strain received a single oral dose of nonylphenol at 500 mg/kg. The dose level was chosen as the maximum tolerated dose. No evidence was presented to support this choice, but it is noted that it is greater than a reported oral LD<sub>50</sub> of 307 mg/kg/day for mice. Appropriate positive and negative controls were included. Bone marrow was sampled at 18, 48 and 72 hours. There were no increases in the frequency of micronuclei at any of the sampling times and the test was declared negative. The PCE/NCE ratio was not affected by nonylphenol, which raises concerns about adequacy of exposure of the bone marrow to the test substance. The toxicokinetic information suggests that the systemic bioavailability of nonylphenol following oral administration is

restricted, which adds to this concern. Overall, because of doubts regarding the extent of exposure of the target tissue, only limited significance can be given to this negative result.

#### **4.1.2.7.3 Summary of mutagenicity**

No human data are available. Nonylphenol tested negative in two bacterial assays and an *in vitro* mammalian cell gene mutation assay. An *in vivo* micronucleus test, conducted using the intraperitoneal route, was negative. A second *in vivo* micronucleus test, which used the oral route, was also negative, although there were methodological weaknesses in this study. These results show that nonylphenol is not mutagenic.

#### **4.1.2.8 Carcinogenicity**

Carcinogenicity has not been studied directly in humans or animals. However, some information on the carcinogenic potential can be derived from other data. On the basis of the information currently available it is considered unlikely that that nonylphenol is mutagenic, so concerns for cancer caused by a genotoxic mechanism are low. Considering the potential for carcinogenicity by a non-genotoxic mechanism, no evidence of sustained cell proliferation or hyperplasia was seen in the standard repeated exposure toxicity studies. Nonylphenol has been reported to induce cell proliferation in the mammary gland of the Nobel rat following subcutaneous exposure at levels down to 0.05 mg/kg/day, but this finding could not be reproduced in a duplicated study; furthermore there are doubts about the relevance of this model to humans because of the route of exposure and sensitivity of the strain selected. Overall, there are low concerns for carcinogenicity by a non-genotoxic mechanism.

#### **4.1.2.9 Toxicity to reproduction**

Only data from animals or *in vitro* test systems are available.

##### **4.1.2.9.1 Studies investigating oestrogenic activity**

The oestrogenic activity of nonylphenol has been investigated in a number of studies using either recombinant yeast, oestrogen sensitive MCF-7 cells or a rodent uterotrophic assay response. None of these assays have been validated as an internationally accepted toxicity test method, although the MCF-7 and uterotrophic assays have been established for a number of years as standard assays for oestrogenic activity. It should be noted that the significance to human health of oestrogenic activity detected in these assays has yet to be established.

##### In vitro systems

4-Nonylphenol was one of a number of alkyl phenols tested in a yeast assay in a study which looked at the structural features important for oestrogenic activity in this chemical group (Routledge and Sumpter, 1997). The assay uses a recombinant strain of yeast (*Saccharomyces cerevisiae*) which contains an oestrogen-inducible expression system. In the presence of oestrogens a reporter gene (Lac-Z) encoding for the enzyme  $\beta$ -galactosidase is expressed, which can be monitored by measuring a colour change reaction in the culture medium. The oestrogenic activity of the test substances was expressed as a potency relative to 17 $\beta$ -oestradiol by comparing the molar concentrations required to produce the same response. 17 $\beta$ -oestradiol was found to be about 30 000 times more potent than nonylphenol. Tamoxifen, an oestrogen antagonist known to act via the oestrogen receptor, was shown to inhibit the activity of the alkyl

phenols, demonstrating that the assay response was due to interaction with the oestrogen receptor.

The oestrogenic activity of nonylphenol has also been assessed in an *in vitro* assay involving oestrogen sensitive human breast tumour MCF-7 cells (Soto et al., 1991). The cells are cultured in the presence of charcoal-stripped (to remove endogenous oestrogens) human serum which inhibits cell proliferation. Substances with oestrogenic activity can then overcome this inhibition. The MCF-7 cells were cultured with 17 $\beta$ -oestradiol and nonylphenol at several concentrations were each cultured in triplicate in multiwell plates and cell proliferation was assessed after a six-day exposure period by counting nuclei from lysed cells. Nonylphenol at a concentration of 10  $\mu$ M elicited a similar proliferative response to oestradiol at a concentration of 30 pM; thus, on a molar basis the oestrogenic potency of oestradiol, as measured in this assay, is 3 000 000 times greater than that of nonylphenol. At concentrations of 1 and 0.1  $\mu$ M the proliferative response produced by nonylphenol was similar to that observed in negative control cultures.

In another similar *in vitro* assay, MCF-7 and ZR-75 human breast cancer cell lines were used (White et al., 1994). Cells were cultured in quadruplicate in the presence of nonylphenol at concentrations ranging from 0.1 nM to 10  $\mu$ M or 17 $\beta$ -oestradiol at 10 nM. No oestrogenic activity was detected at nonylphenol concentration of 100 nM and less. At 1 and 10  $\mu$ M nonylphenol elicited a proliferative response which at the higher concentration was similar to that produced by oestradiol. Thus, 17 $\beta$ -oestradiol was 1000 times more potent than nonylphenol in this assay. In a further investigation, the ability of nonylphenol to stimulate transcriptional activity was determined in MCF-7 and chicken cell fibroblasts (CEFs) transfected with reporter gene pERE<sub>B</sub>LCAT and a mouse oestrogen receptor. Nonylphenol stimulated transcription at culture concentrations of 1 and 10  $\mu$ M.

To summarise the *in vitro* oestrogenic data, there is evidence that nonylphenol has oestrogenic activity, of 3-6 orders of magnitude less potent than oestradiol.

### In vivo systems

The oestrogenic activity of nonylphenol has been assessed in several studies using an assay based upon the uterotrophic response in the rat.

In the first study, five groups of immature (aged 20 - 22 days) female rats (six in each group) of a Wistar derived strain received single oral gavage doses of nonylphenol in corn oil on each of three consecutive days (ICI, 1996). The dose levels ranged from 9.5 to 285 mg/kg/day. Vehicle and positive (oestradiol benzoate 8  $\mu$ g/kg, by subcutaneous route) groups were included. One day after the final dose the females were killed and the uterus was removed from each animal and weighed. Absolute uterus weight and bodyweight related uterus weight were statistically significantly increased, in a dose-dependent manner, at levels of 47.5 mg/kg/day and above. The NOAEL was 9.5 mg/kg/day. The uterine response seen in the positive control group was much greater than that of the nonylphenol groups, although a direct comparison of potency is not possible given the differing exposure routes. Similar data from the same laboratory have also been presented in peer-review literature (Odum et al., 1997). This latter report also included oral positive control groups (17 $\beta$ -oestradiol, 10-400  $\mu$ g/kg), which indicated that oestradiol was about 1000 times more potent in this assay than nonylphenol.

In a similar assay, groups of ten ovariectomised female Sprague-Dawley rats were dosed once daily for three consecutive days by the oral route with ethanol/oil suspensions of nonylphenol at



levels of 0 (vehicle control), 30, 100 and 300 mg/kg/day (Chemical Manufacturers Association 1997b). Positive control groups received ethynloestradiol in ethanol at levels of 10, 30 and 80 µg/kg/day according to the same dosing regimen. One day after the final dose the females were killed and the uterus was removed from each animal and weighed. Uterus weights at 300 mg/kg/day were significantly increased (1.5-fold) in comparison with the vehicle control group. A slightly greater response (a 2-fold increase) was seen in the 30 and 80 µg/kg/day positive control groups.

In another uterotrophic assay, groups of three immature (aged 20 - 21 days) Sprague-Dawley rats each received a single intraperitoneal injection of nonylphenol at dose levels of 0, 1, 2 or 4 mg/animal (approximately 25, 50 or 100 mg/kg) (Lee and Lee, 1996). Oestradiol, administered by the same route, served as a positive control. The animals were killed 24 hours later and each uterus was removed, weighed and analysed for protein and DNA content and peroxidase (thought to be a uterotrophic marker enzyme) activity. There was a dose-dependent and statistically significant increase in uterine weight at all levels, with associated increases in uterine protein and DNA content and uterine peroxidase activity. In further experiments, the uterotrophic activity of nonylphenol was found to be blocked by the co-administration ICI 182,780, an oestrogen antagonist, providing evidence that the effect of nonylphenol is mediated through the oestrogen receptor. Also, the potency was compared with oestradiol; in this assay oestradiol was found to be about 1000 - 2000 times more potent than nonylphenol.

Overall, these *in vitro* and *in vivo* studies show that nonylphenol has oestrogenic activity of a potency that is between 3 to 6 orders of magnitude less than that of oestradiol.

#### **4.1.2.9.2 Effects on fertility**

The effects of nonylphenol on fertility and reproductive performance have been investigated in a multigeneration study, and additionally, the testicular toxicity of nonylphenol has been studied in a repeated exposure study.

The multigeneration study was comprehensive, of good quality, and was conducted in compliance with GLP (NTP 1997). The overall study design was based on the OECD two-generation reproduction toxicity study guideline, with an extension to include the production of an F<sub>3</sub> generation. Groups of thirty male and thirty female Sprague-Dawley rats were exposed to nonylphenol via incorporation in the diet at concentrations of 0 (control) 200, 650 or 2000 ppm over three generations. Calculated nonylphenol intakes were, respectively, about 0, 15, 50 and 160 mg/kg/day during non-reproductive phases and rising to around 0, 30, 100 and 300 mg/kg/day during lactation.

Nonylphenol exposure commenced for the F<sub>0</sub> generation at about 7 weeks of age and continued until study termination when the F<sub>3</sub> generation were about 8 weeks old. F<sub>0</sub> animals were mated (one male with one female) within each dose group to produce the F<sub>1</sub> generation, selected F<sub>1</sub> animals were similarly mated to produce the F<sub>2</sub> generation and selected F<sub>2</sub> animals were mated to produce the F<sub>3</sub> generation. For the F<sub>0</sub> generation and retained F<sub>1</sub>, F<sub>2</sub> and F<sub>3</sub> animals, clinical signs of toxicity, bodyweights and food consumption were reported. Oestrous cycles were monitored prior to mating. At the necropsy of adult animals, sperm samples were taken (but not from the F<sub>3</sub> generation) for analysis of density, motility (using a computer assisted sperm motion analysis system, only conducted on control and high dose group males) and morphology, a number of organs were weighed and selected organs were sampled for histopathology. Additionally, testicular spermatid counts were made. Parameters assessed in the young offspring included litter

size, bodyweights, survival, gross appearance, ano-genital distance, sexual development and, for animals killed at weaning, gross appearance of organs at necropsy and reproductive organ weights.

There was evidence of general toxicity in adults of all generations, seen as a reduction in bodyweight gain at 50 and 160 mg/kg/day and histopathological changes in the kidneys at all dose levels. These aspects are described in greater detail in section 4.1.2.6.1.

Considering the reproduction-related parameters, there were no adverse effects on fertility or mating performance. However, several other parameters were affected. Oestrous cycle length was increased by about 15% in the F<sub>1</sub> and F<sub>2</sub> females at 160 mg/kg/day, in comparison with controls. The timing of vaginal opening was accelerated by 1.5-7 days at 50 mg/kg/day and by 3-6 days at 160 mg/kg/day in females of the F<sub>1</sub>, F<sub>2</sub> and F<sub>3</sub> generations. Also, absolute ovarian weights were decreased at 50 mg/kg/day in the F<sub>2</sub> generation and at 160 mg/kg/day in the F<sub>1</sub>, F<sub>2</sub> and F<sub>3</sub> generations; however, no effect on ovarian weight was apparent in the F<sub>1</sub> and F<sub>3</sub> generations when analysed as an organ-to-bodyweight ratio. In males, changes in sperm endpoints were seen only in the F<sub>2</sub> generation; epididymal sperm density was decreased by about 10% at 50 and 160 mg/kg/day and spermatid count was decreased by a similar amount at 160 mg/kg/day. However, there may have been methodological problems with the epididymal sperm density measurements, because the density in all F<sub>2</sub> generation groups, including controls, was considerably greater (by about 25-40%) than reported for the F<sub>0</sub> and F<sub>1</sub> generation males; the age of each generation was similar at necropsy, so major differences in the sperm density would not be expected.

To summarise the reproductive aspects of this study, fertility and mating performance were not adversely affected by nonylphenol treatment. However, there were changes, albeit relatively slight, in the oestrous cycle length, timing of vaginal opening, ovarian weight and sperm/spermatid count. The effects on the oestrous cycle were seen in both the F<sub>1</sub> and F<sub>2</sub> generations (not assessed in F<sub>3</sub> females) and the timing of vaginal opening was influenced in all three generations; this consistency provides firm evidence of a relationship with treatment. These effects were possibly related to the oestrogenicity of nonylphenol. There is some uncertainty about the relationship to nonylphenol treatment with respect to the ovarian weight reduction because this effect was apparent after adjusting for bodyweight in only one generation and did not correlate with any histopathological changes; nevertheless, it is compatible with the anticipated direct effects of exogenous oestrogenic activity. Also, there is uncertainty regarding the cause of the apparent reduced sperm/spermatid numbers in the F<sub>2</sub> generation. It has been hypothesised that such changes could result from foetal or neonatal exposure to exogenous oestrogenic activity (Sharpe and Skakkebaek, 1993), but if the hypothesised mechanism were operating, semen/testicular changes should also have occurred in the F<sub>1</sub> generation. Furthermore, the possibility of methodological problems adds to the difficulty in interpreting the sperm/spermatid count data. However, the observation of impaired male reproductive tract development in an intraperitoneal study summarised in section 4.1.2.9.3 provides supporting evidence in favour of the sperm/spermatid count changes being causally related to nonylphenol treatment. Furthermore, the intraperitoneal study indicates that a critical window of exposure for this effect is likely to be the neonatal period. Overall, this study provided evidence that nonylphenol exposure over several generations can cause minor perturbations in the reproductive system of offspring, which are compatible with the predictable or hypothesised effects of exogenous oestrogenic activity, although these perturbations do not cause functional changes in reproduction of the rat at the dose levels tested. A clear NOAEL for these changes of 15 mg/kg/day was identified.

The testicular toxicity of nonylphenol was investigated in Sprague Dawley rats in a briefly reported repeated dose study (de Jager et al., 1999a). Groups of 20 male rats were dosed once daily by the oral (gavage) route at doses levels of 0 (vehicle control, cotton seed oil), 100, 250 or 400 mg/kg/day for a period of 10 weeks, from the age of 12 weeks. The animals were killed at the end of the dosing period and a detailed evaluation of the reproductive organs was conducted. Testes and epididymal weight were recorded. The total cauda epididymal sperm numbers were determined. The testes were stored in Bouin's fixative and processed for histological examination, which included the identification of the stages of spermatogenesis present and the measurement of the seminiferous tubule diameter, lumen diameter and epithelial thickness.

Three, 15 and 18 animals from the 100, 250 and 400 mg/kg/day groups, respectively, died during the dosing period; no further information on these deaths was presented. Clinical signs of toxicity were not reported. The bodyweight gain of surviving animals was not affected by treatment, although bodyweight gain was reduced among the decedents. In comparison with the control group, lower testicular and epididymal weight, tubule and lumen diameter and seminiferous epithelial diameter were seen in surviving animals at 250 and 400 mg/kg/day and the sperm count was reduced at 400 mg/kg/day, but because of the very small groups sizes due to mortality, little toxicological significance can be accorded to these findings. At 100 mg/kg/day, testes and epididymal weight were not affected, but tubule and lumen diameter and seminiferous epithelial diameter were statistically significantly lower than found in the control group; the mean tubule diameter was reduced by 10%, but data for the other two parameters were not presented. Testicular abnormalities were identified by histopathology at both 250 and 400 mg/kg/day. In one animal at 250 mg/kg/day vacuolization and cell necrosis with sloughing of the epithelium was seen in about 40% of tubules. Both surviving animals at 400 mg/kg/day had tubular vacuolization, cell necrosis and derangement, with very few secondary spermatocytes and sperm being present.

This study provides evidence of nonylphenol-related testicular toxicity at exposure levels which also cause mortality. A LOAEL for testicular toxicity of 100 mg/kg/day can be designated. The observation of mortality at 100, 250 and 400 mg/kg/day in this gavage study contrasts with the findings of studies involving dietary administration summarised in the Repeated Dose Toxicity section (Hüls, 1989; Chemical Manufacturers Association, 1997a; NTP, 1997). This difference can probably be accounted for by the method of administration; gavage dosing is likely to produce higher peak concentrations of nonylphenol in the blood than dietary administration.

#### **4.1.2.9.3 Developmental toxicity**

A good quality standard oral rat developmental toxicity study and two studies, one using the intraperitoneal route and one using the oral route, looking specifically at the potential effects on the developing male reproductive tract are available.

The standard rat developmental toxicity study is well-reported, conducted according to OECD guideline 414 and in compliance with GLP (Initiative Umweltrelevante Altstoffe, 1992). Groups of timed-mated females of the Wistar strain were administered by oral gavage corn oil solutions of nonylphenol from days 6 to 15 of pregnancy at dose levels of 0, 75, 150 and 300 mg/kg/day. A further group receiving 600 mg/kg/day was terminated prematurely because many females died during the first few days of treatment. Sufficient females were allocated to the study to produce at least 21 pregnant females in each group. Surviving females were killed on day 20 of pregnancy and the fetuses were subjected to routine external, visceral and skeletal examinations.

There was clear evidence of maternal toxicity at 300 mg/kg/day, manifested as a reduction in bodyweight gain and food consumption, mortality of two females and the macroscopic organ changes in the kidney (pale or irregular shape in seven mothers) or spleen (reduced size in two mothers). Similar macroscopic changes were seen occasionally at 150 mg/kg/day and at a high incidence in females from the prematurely terminated 600 mg/kg/day group. No maternal toxicity was seen at 75 mg/kg/day. Post-implantation loss, litter size, foetal weights and incidence of both major and minor foetal abnormalities were not affected by treatment. To conclude, this study provides no evidence of developmental toxicity in the rat at exposure levels which are toxic to the mother; thus the maternal NOAEL was 75 mg/kg/day and the foetal NOAEL was 300 mg/kg/day.

In the intraperitoneal study, which was briefly reported, the effects of nonylphenol on male reproductive tract development were investigated in neonatal Sprague-Dawley rats (Lee, 1998; additional information was obtained by personal communication with the author). Age-matched male pups were randomly allocated to either the control or treated groups. Daily doses of nonylphenol were administered by the intraperitoneal route at a dose volume of 5-10 µg/injection, for varying schedules between the day of birth (day 0) and 30 days of age. Control animals received the vehicle (dimethylsulfoxide) only, by the same route. The pups were killed at 31 days of age; terminal observations included external appearance of genital area, ano-genital distance, the presence of undescended testes, and reproductive organ weights (which were reported as bodyweight-related values).

In the initial experiment, groups of at least three pups were dosed at 0, 0.08, 0.8 and 8 mg/kg/day, from birth to 15 days of age. At 0.8 and 8 mg/kg/day there was a statistically significant, dose-dependent, reduction in testes, epididymis, seminal vesicle and prostate weight; typically weights were about 15 to 25% less than found in the control group. Additionally, ano-genital distance was reduced at 8 mg/kg/day, only. Reproductive organ weights were not affected at 0.08 mg/kg/day. Next, groups of three or four pups received nonylphenol at 0 or 8 mg/kg/day, either from days 1 to 18 of age, days 6 to 24 or days 13 to 30, to see if there is a vulnerable phase of development. Reproductive organ weights were significantly reduced in the groups for which dosing commenced on day 1 or 6, but not in the group dosed from day 13. In a third experiment, the influence of the oestrogen receptor antagonist ICI 182,780 on nonylphenol-impaired reproductive organ weight development was investigated in groups of six or seven pups dosed with nonylphenol at 8 mg/kg/day from days 1 to 5 of age. The antagonist was administered by the intraperitoneal route at a dose of 0.5 mg/kg and dose volume of 5-10 µg/injection, 10 minutes after the nonylphenol dose. It was found that ICI 182,780 blocked the effects of nonylphenol on organ weights. Administration of ICI 182,780 alone had no effect on reproductive organ weight. The incidence of undescended testes was reported in groups of between 6 and 34 pups dosed with nonylphenol at 8 mg/kg/day, days 1 to 5, days 1 to 10 or days 1 to 18; this was 33%, 55% and 62%, respectively. Undescended testes were not observed in vehicle control pups, in pups receiving a single dose of nonylphenol on day 1, or when ICI 182,780 was administered concurrently with nonylphenol.

In a final experiment, eight male pups, selected from two litters, were dosed by the intraperitoneal route from days 1 to 15 of age with nonylphenol at 8 mg/kg/day and then reared to sexual maturity. Their fertility was assessed by serial pairing with either six or twenty untreated female rats and recording the number of females which became pregnant. Vehicle control male pups, selected from the same two litters, were used for comparison. Among the controls, pregnancies resulted from almost all pairings. In contrast, in the nonylphenol treated group, two males were completely infertile, failing to impregnate any females; three were

initially fertile, but failed to impregnate females in later pairings; two showed comparable fertility to the controls; the remaining male died near the start of the fertility trial. Necropsy findings were reported for five of the nonylphenol-treated males; all were observed with undescended testes and/or either slight or marked testicular atrophy.

There are a number of design weaknesses to this study: the group sizes were generally very small; the pups were apparently not weight-matched at the start of treatment; and the intraperitoneal route of administration, which could result in unrealistically high exposure of the reproductive organs, is of questionable relevance to the human risk assessment involving the inhalation, dermal and oral routes. Nevertheless, the consistent observation throughout the series of experiments of reduced reproductive organ weight or undescended testes, supported by observations of reduced ano-genital distance and, in animals reared to sexual maturity, reduced fertility, provide evidence that nonylphenol exposure during the neonatal period impairs male reproductive tract development in the rat. The period of maximum vulnerability to this effect appears to be prior to the age of 13 days. The blocking influence of the oestrogen receptor antagonist ICI 182,780 suggests that the effect of nonylphenol on the male reproductive tract may be mediated through action on the oestrogen receptor. However, in view of corrosive properties of nonylphenol and use of the intraperitoneal route of administration, it is possible that non-specific irritation of the undescended testes may have contributed to the observed effects. The author has stated that about 50% of the nonylphenol treated pups had peritoneal cavity adhesions, while none were seen in control animals, which supports this hypothesis. Although adhesions were seen, there were no treatment-related clinical signs of toxicity or increased mortality. The blocking influence of ICI 182,780 may possibly have resulted from dilution of the injected nonylphenol (this alternative explanation was not tested as the study did not include a control group receiving nonylphenol followed by a vehicle only injection). It should be noted that precise information on clinical signs, mortality and general macroscopic necropsy findings were not available from the author. No effects were seen in pups dosed at 0.08 mg/kg/day but, because of the very small numbers of animals receiving doses other than 8 mg/kg/day, information on the NOAEL and dose-response relationship can be gained from this study. Overall, because of the design weaknesses and the possibility that non-specific irritation may have contributed to the observed effects on the male reproductive tract, it is not possible to draw any firm conclusions from this study with respect to specific reproductive toxicity of relevance to humans. Consequently, this study carries little weight in the overall assessment of the available reproductive toxicity data base.

In the third study, which was briefly reported, the effects of nonylphenol exposure from the *in utero* period to sexual maturity of nonylphenol exposure were investigated in an oral (gavage) study (de Jager et al., 1999b). Groups of 10 mated females were dosed once daily with nonylphenol at levels of 0 (vehicle control, cotton seed oil), 100, 250 and 400 mg/kg/day from day 7 of pregnancy to weaning of their litters. Twenty F<sub>1</sub> generation males were randomly selected from each group for dosing as for the mother until 10 weeks of age. The selected F<sub>1</sub> males were then killed. Testes and epididymal weight were recorded. The total cauda epididymal sperm numbers were determined. The testes were stored in Bouin's fixative and processed for histological examination, which included the identification of the stages of spermatogenesis present and the measurement of the seminiferous tubule diameter, lumen diameter and epithelial thickness.

Concerning maternal toxicity, no information was presented on maternal bodyweights, but it was stated that no females showed any physical or behavioural abnormalities. No offspring were born from the mothers receiving 400 mg/kg/day; it is not clear from the report if this was because of maternal deaths or embryonic/foetal resorption.

There were no malformations or still births among the F<sub>1</sub> offspring. No physical or behavioural abnormalities were seen among the selected F<sub>1</sub> males, although possibly two animals at 250 mg/kg/day died since the group size at termination of the study was reduced to 18; this contrasts with the de Jager (1999a) study conducted in adult males in which 15 out of 20 animals died at 250 mg/kg/day (see section on Effects on Fertility). F<sub>1</sub> bodyweight gain over the course of the study was significantly reduced at both 100 and 250 mg/kg/day (by 11 and 20%, respectively), relative to the control group. F<sub>1</sub> absolute testicular and epididymal weights were less than the controls at both 100 and 250 mg/kg/day, but this effect was not evident when organ weights were expressed relative to bodyweight; the differences in absolute organ weight are thought likely to be related to the intergroup bodyweight differences. Total cauda epididymal sperm count was reduced at 250 mg/kg/day (by 36%, relative to controls), but at 100 mg/kg/day sperm counts were similar to those of the control group. Seminiferous tubule diameter was slightly lower in both nonylphenol treated groups (by about 10%); surprisingly, these slight differences were declared to be highly statistically significantly different from the control group. The authors also stated that the tubule lumen diameter and seminiferous epithelium thickness were highly statistically significantly less than the control group in both nonylphenol groups, but the data were not presented. Although these quantitative tubular changes were consistent with those of the de Jager (1999a) study, in the present study these may be related to the fact that testicular weight was lower in these groups. Histopathology revealed pathological changes in the testes of one F<sub>1</sub> male from the 100 mg/kg/day group; in the tubules, cell necrosis, vacuolation and sloughing of the germinal epithelium were described. However, no such histopathological abnormalities were seen at 250 mg/kg/day, so the changes outlined above cannot be attributed to nonylphenol treatment.

This study provides evidence of a reduction in sperm count at 250 mg/kg/day, a dose level which may have caused mortality, although it is not possible to state whether this is a developmental effect or as a result of direct exposure to the males after weaning. It is not clear if the changes in the tubular measurements represent specific reproductive toxicity or non-specific secondary consequences of the reduction in bodyweight gain.

#### 4.1.2.9.4 Summary of toxicity to reproduction

No human data are available. Nonylphenol has been shown to have oestrogenic activity in a number of *in vitro* and *in vivo* assays. The potency of this oestrogenic activity in these assays ranged from 3 to 6 orders of magnitude less than that of oestradiol. The effects of nonylphenol on fertility and reproductive performance have been investigated in a good quality oral (dietary administration) multigeneration study in the rat. This study provided evidence that nonylphenol exposure over several generations can cause minor perturbations in the reproductive system of offspring, namely slight changes in the oestrous cycle length, the timing of vaginal opening and possibly also in ovarian weight and sperm/spermatid count, although functional changes in reproduction were not induced at the dose levels tested. The NOAEL for these changes was 15 mg/kg/day. The observed perturbations in offspring are compatible with the predictable or hypothesised effects of exogenous oestrogenic activity. Evidence of testicular toxicity, seen as seminiferous tubule vacuolation, cell necrosis and a reduction in tubule diameter, was reported at exposure levels which also cause mortality in a repeated dose gavage study in rats. The LOAEL for testicular toxicity was 100 mg/kg/day. The toxicity of nonylphenol appears to be enhanced by gavage administration in comparison to dietary administration, presumably because higher peak blood concentrations of nonylphenol are achieved by gavage.

No evidence that nonylphenol is a developmental toxicant was seen in a standard oral developmental toxicity study in the rat; maternal and foetal NOAELs were 75 and

300 mg/kg/day, respectively. In contrast, in a gavage study involving *in utero*, lactational and direct post-weaning exposure, there was a reduction in sperm count at 250 mg/kg/day, although it is not possible to state whether this is a developmental effect or as a result of direct exposure after weaning. In an intraperitoneal study designed to investigate the effects of nonylphenol on male reproductive tract development of neonatal rats, evidence of impaired development was observed. However, this study was difficult to interpret, such that these results carry little weight in the overall assessment of the available data.

Overall, the observations of oestrogenic activity in the *in vitro* and *in vivo* assays, minor perturbations in the reproductive system of offspring in the multigeneration study, and testicular changes in gavage studies collectively raise concerns for reproductive toxicity, possibly mediated through action on the oestrogen receptor. These concerns for reproductive toxicity are addressed in the risk characterisation, although there are uncertainties. The oestrogenic activity assays are merely screening tests. The effects on reproduction-related parameters in the multigeneration study were marginal and there was no evidence of functional changes in reproduction; furthermore any changes that were seen occurred at exposure levels in excess of the LOAEL for repeated dose toxicity (LOAEL for renal toxicity is 15 mg/kg/day, NOAEL for reproductive changes is 15 mg/kg/day). Evidence of testicular toxicity was reported in two repeated exposure studies designed specifically to investigate the effects on this organ, but only at doses which also caused mortality. No evidence of testicular toxicity was seen in standard repeated dose studies involving dietary administration. Development was not affected in a standard rat oral developmental toxicity study.

### **4.1.3 Risk characterisation**

The risk characterisation below is divided into two parts. The first provides an overview of the toxicological assessment, pointing out the effects of nonylphenol (and the concentrations at which they occur) and making clear where there are critical gaps in the data. The second part contrasts the effects data with measured and modelled exposures. From the effects and exposure information available it is clear that not all of the possible effects will be expressed. The risk characterisation therefore concentrates on the key effects and the circumstances under which they are likely to occur.

#### **4.1.3.1 General aspects**

Few significant human data are available so this assessment of the hazardous properties of nonylphenol is based mainly on animal data.

Most of the information on the toxicokinetics of nonylphenol concerns oral exposure and is based on a small number of limited rat and human studies, supported by a read across from data relating to octylphenol, an alkyl phenol with a close structural relationship to nonylphenol. The available data, though sparse, do provide the basis for a general understanding of the main features of the toxicokinetic profile. Absorption from the gastrointestinal tract is initially rapid, and probably extensive. The major metabolic pathways are likely to involve glucuronide and sulphate conjugation, and there is evidence of extensive first pass metabolism of nonylphenol absorbed through the gastrointestinal tract. Because of first pass metabolism, the bioavailability of unconjugated nonylphenol is probably limited following oral exposure, at no more than 10-20% of the administered dose. Nonylphenol is distributed widely throughout the body, with the highest concentration in fat. The major routes of excretion are via the faeces and urine.

Regarding bioaccumulation, there are insufficient data to allow a conclusion to be drawn on whether or not nonylphenol has this potential.

There are no data on the toxicokinetics of nonylphenol following inhalation exposure, but on the basis of the oral absorption data and high partition coefficient, it would be prudent to assume that significant absorption via this route can occur. Furthermore, because first pass metabolism will not take place following exposure by the inhalation route, the systemic bioavailability is likely to be substantially greater than is associated with the oral route. Concerning the dermal route, *in vitro* data indicate that nonylphenol is poorly absorbed across skin, although some limited skin penetration, especially to the stratum corneum, can occur. For the risk characterisation, it is assumed that absorption by the oral and inhalation routes is 100%, but for the oral route systemic bioavailability is 10%. For the dermal route, it is assumed that 10% of a dose will be absorbed and systemically bioavailable. Using these values the risk assessment will err on the side of caution.

Nonylphenol is moderately toxic by the oral route, with LD<sub>50</sub> values for the rat in the range of about 1200 to 2400 mg/kg. The dose-response curve for lethality appears to be steep. Erosion of the stomach mucosa is sometimes seen following the administration of a lethal dose. The acute toxicity of nonylphenol by the dermal route is similar, with an LD<sub>50</sub> of about 2000 mg/kg in rabbits. No data are available on the acute inhalation toxicity, although the corrosive nature of nonylphenol suggests that acute toxicity could be elicited following exposure by this route. Liquid nonylphenol can be corrosive to the skin, although its potency might vary according to source and exact composition. The liquid is also a severe eye irritant. Exposure to the saturated vapour (400 ppm) elicited mild sensory irritation of the respiratory tract in mice, but no reaction was elicited at 30 ppm. The results of several guinea pig maximisation tests suggest that nonylphenol does not have significant skin sensitising potential. No information on respiratory tract sensitisation is available, although it can be predicted from its low chemical reactivity that nonylphenol is unlikely to be a respiratory allergen.

In a multigeneration study in the rat involving oral exposure for up to 20 weeks, a LOAEL for repeated dose of 15 mg/kg/day was identified, based on histopathological changes in the kidneys (tubular degeneration or dilatation), although such changes were not apparent at this dose level in a 90-day rat study. At higher dose levels the liver may also be a target organ; minor histopathological changes in the liver (vacuolation in the periportal hepatocytes or occasional individual cell necrosis) were seen at doses of 140 mg/kg/day and above in some studies. No repeated-dose studies involving dermal or inhalation exposure have been conducted.

Concerning mutagenicity, nonylphenol tested negative in two bacterial assays and an *in vitro* mammalian cell gene mutation assay. An *in vivo* micronucleus test, conducted using the intraperitoneal route, was negative. A second *in vivo* micronucleus test, which used the oral route, was also negative, although there were methodological weaknesses in this study. These results show that nonylphenol is not mutagenic.

Carcinogenicity has not been directly studied. However, some information on the carcinogenic potential can be derived from other data. On the basis of the information currently available it is unlikely that nonylphenol is mutagenic, so concerns for cancer caused by a genotoxic mechanism are low. Considering the potential for carcinogenicity by a non-genotoxic mechanism, no evidence of sustained cell proliferation or hyperplasia was seen in the standard repeated exposure toxicity studies. Nonylphenol has been reported to induce cell proliferation in the mammary gland of the Nobel rat following subcutaneous exposure at levels down to 0.05 mg/kg/day, but this finding could not be reproduced in a duplicated study; furthermore there



are doubts about the relevance of this model to humans because of the route of exposure and sensitivity of the strain selected. Overall, there are low concerns for carcinogenicity by a non-genotoxic mechanism.

Nonylphenol has been shown to have oestrogenic activity in a number of *in vitro* and *in vivo* assays. The potency of this oestrogenic activity in these assays ranged from 3 to 6 orders of magnitude less than that of oestradiol. The effects of nonylphenol on fertility and reproductive performance have been investigated in a good quality oral multigeneration study in the rat. This study provided evidence that nonylphenol exposure over several generations can cause minor perturbations in the reproductive system of offspring, namely slight changes in the oestrous cycle length, the timing of vaginal opening and possibly also in ovarian weight and sperm/spermatid count, although functional changes in reproduction were not induced at the dose levels tested. The NOAEL for these changes was 15 mg/kg/day. The observed perturbations in offspring are compatible with the predictable or hypothesised effects of exogenous oestrogenic activity. Evidence of testicular toxicity, seen as seminiferous tubule vacuolation, cell necrosis and a reduction in tubule diameter, was reported at exposure levels which also cause mortality in a repeated dose gavage study in rats. The LOAEL for testicular toxicity was 100 mg/kg/day. The toxicity of nonylphenol appears to be enhanced by gavage administration in comparison to dietary administration, presumably because higher peak blood concentrations of nonylphenol are achieved by gavage. No evidence that nonylphenol is a developmental toxicant was seen in a standard oral developmental toxicity study in the rat. In contrast, in a gavage study involving *in utero*, lactational and direct post-weaning exposure, there was evidence of a reduction in sperm count at 250 mg/kg/day, although it is not possible to state whether this is a developmental effect or as a result of direct exposure after weaning. In an intraperitoneal study designed to investigate the effects of nonylphenol on male reproductive tract development of neonatal rats, evidence of impaired development was observed. However, this study was difficult to interpret, such that these results carry little weight in the overall assessment of the available data. Overall, the observations of oestrogenic activity in the *in vitro* and *in vivo* assays, minor perturbations in the reproductive system of offspring in the multigeneration study, and testicular changes in gavage studies collectively raise concerns for reproductive toxicity, possibly mediated through action on the oestrogen receptor. These concerns are addressed in the risk characterisation, although there are uncertainties.

Overall, the hazardous properties of nonylphenol have been evaluated in animals to the extent that the minimum data requirements according to Article 9(2) of Regulation 793/93 have been met. The key health effects of acute toxicity, corrosivity, repeated dose toxicity and reproductive effects have been identified. For acute toxicity, the oral LD<sub>50</sub> is in the range 1200 - 2400 mg/kg and the dermal LD<sub>50</sub> is around 2000 mg/kg. The inhalation LC<sub>50</sub> is not known but the corrosive nature of nonylphenol suggests that nonylphenol may cause acute toxicity by this route. No dose response information is available on corrosivity. Mild sensory irritation of the respiratory tract is elicited at 400 ppm, but not at 30 ppm. A LOAEL for repeated dose toxicity is 15 mg/kg/day. Concerns for mutagenicity and carcinogenicity are low. Regarding the effects on the reproductive system, a NOAEL of 15 mg/kg/day has been established in a multigeneration study; this value is used in the risk characterisation. A LOAEL of 100 mg/kg/day was derived for a testicular toxicity in a gavage study. However, the above NOAEL for reproductive changes is used in preference because this value is substantially lower and it is derived from a study involving dietary administration which is more applicable to the human exposure scenarios.

To conduct the risk characterisation for workers and consumers, it is necessary to compare human exposure for the inhalation/dermal route with oral N(L)OAELs from repeated-dose

animal studies, because of the absence of significant inhalation/dermal toxicity data. A direct comparison between exposure and effects is not valid because first pass liver metabolism is likely to limit systemic bioavailability by the oral route. To compensate for this limited oral bioavailability (assumed to be 10% of administered dose), the animal N(L)OAELs have been reduced by a factor of 10 for the comparison of inhalation or dermal exposure and effects. Thus, the "systemic" values used for comparison in the risk characterisation are a LOAEL of **1.5 mg/kg/day** for repeated dose toxicity, and a NOAEL of **1.5 mg/kg/day** for reproductive effects. It is assumed that the acute oral toxicity of nonylphenol is mainly the result of a local effect in the gastrointestinal tract, related to corrosivity. Therefore, compensation for limited systemic bioavailability is not applicable for this endpoint.

#### **4.1.3.2 Workers**

##### **4.1.3.2.1 Introduction**

Nonylphenol is understood to be used only as a chemical intermediate, for example, in the manufacture of nonylphenol ethoxylates. There are therefore two industry sectors where occupational exposure to nonylphenol may occur. These are:

- (a) manufacture of nonylphenol;
- (b) use of nonylphenol as an intermediate;
- (c) manufacturer of speciality paints; and
- (d) use of speciality paints.

Some manufacturers of nonylphenol are also users. It was not possible to establish the number of workers exposed to nonylphenol, although it was estimated to be about 300 to 600.

Nonylphenol is manufactured and used in closed plant. The situations giving rise to occupational exposure are likely to be similar for both manufacturers and users (i.e. closed systems with some breaching). Companies generally do not carry out air sampling for nonylphenol with control assumed from the nature of the process, and in many cases monitoring for materials deemed to be more hazardous, for example ethylene oxide.

##### **4.1.3.2.2 Comparison of exposure and effects**

Inhalation exposures to nonylphenol during manufacture and use as an intermediate are likely to be less than 0.1 ppm (8-hour TWA). The dose of nonylphenol resulting from an 8-hour exposure to an airborne concentration of 0.1 ppm is estimated to be about 0.13 mg/kg (assuming 10 m<sup>3</sup> air is breathed in, a body weight of 70 kg and 100% absorption).

During the manufacture of speciality paints, inhalation exposures to nonylphenol are estimated to be less than 0.01 ppm (8-hour TWA). The dose of nonylphenol resulting from an 8-hour exposure to an airborne concentration of 0.01 ppm is estimated to be about 0.013 mg/kg, using the above assumptions.

Routine dermal exposure during nonylphenol manufacture, use as an intermediate and manufacture of speciality paints is negligible and consequently this route of exposure is considered unlikely to contribute significantly to the overall systemic body burden. Infrequent accidental dermal contact with contaminated surfaces may occur, but because of the corrosive nature of the substance, the duration of contact will be brief and significant systemic exposure is unlikely.

The potential inhalation exposure during paint spray application is estimated to be up to 1 ppm (8-hour TWA). The dose of nonylphenol resulting from an 8-hour exposure to an airborne concentration of 1 ppm is estimated to be about 1.3 mg/kg, using the above assumptions. Dermal exposure during this activity is estimated to be 0.25 mg/cm<sup>2</sup>/day which, assuming an area of 2000 cm<sup>2</sup> of skin on the hand and forearms are exposed, absorption is 10% and a bodyweight of 70 kg, could result in a dose of 0.7 mg/kg/day. Thus, the dose received during paint spray application from inhalation and dermal exposure combined could potentially be up to 2 mg/kg/day.

#### Manufacture of nonylphenol and use as an intermediate

##### *Acute toxicity*

The acute oral LD<sub>50</sub> is in the range 1200 - 2400 mg/kg. The estimated human daily dose from inhalation exposure of 0.13 mg/kg/day is about 10 000-fold less than the LD<sub>50</sub> values. A margin of this magnitude provides reassurance that health effects will not occur, particularly in view of the steep dose-response curve. There are no concerns for acute dermal toxicity because exposure by this route is low.

##### *Irritation and corrosivity*

The corrosivity of the substance in relation to the skin and eye is unlikely to be expressed during normal use because exposure is negligible, providing good occupational hygiene practices are in operation. However, if there is contact with the skin or eye, which could occur accidentally, then local damage is possible.

Concerns for respiratory tract irritation are low because the estimated highest possible exposure of 0.1 ppm is considerably less than the concentration of 400 ppm which elicited only mild sensory irritation in mice and a factor of 300 below the study NOAEL of 30 ppm.

##### *Repeated dose toxicity and effects on the reproductive system*

For repeated dose toxicity, the MOS is close to 10, based on the animal systemic LOAEL of 1.5 mg/kg/day and human exposure estimate of 0.13 mg/kg/day; this MOS gives rise to concerns for human health, bearing in mind that the MOS calculation is based on a LOAEL. For effects on the reproductive system the MOS is also close to 10, based on the animal systemic NOAEL of 1.5 mg/kg/day; considering the potential seriousness of this hazardous property, this MOS gives rise to concerns for human health (**conclusion iii**).

**Table 4.14** Summary of the risk characterisation for workers during nonylphenol manufacture and use as an intermediate

Key health effect	Human exposure	Quantitative animal toxicity data	MOS	Concern for risks to human health	Conclusion
Acute toxicity	0.13 mg/kg/day	LD <sub>50</sub> 1200-2400 mg/kg	-	Low	ii
Corrosivity skin/ eye	Negligible	No quantitative data	-	Low, providing hygiene good	ii
Resp. tract	0.1 ppm	Sensory irrit. LOAEL 400 ppm Sensory irrit. NOAEL 30 ppm	4000 300	Low Low	ii
Repeat dose toxicity	0.13 mg/kg/day	Systemic LOAEL 1.5 mg/kg/day	~10	High	iii
Reproductive system effects	0.13 mg/kg/day	Systemic NOAEL 1.5 mg/kg/day	~10	High	iii

### Manufacture of speciality paints

#### *Acute toxicity*

The systemic acute oral LD<sub>50</sub> is in the range 1200 - 2400 mg/kg. The estimated human daily dose from inhalation exposure is 0.013 mg/kg/day, which is 5 orders of magnitude less than the LD<sub>50</sub> value. Hence, there are no concerns for human health. There are no concerns for acute dermal toxicity because exposure by this route is low.

#### *Irritation and corrosivity*

The corrosivity of the substance in relation to the skin and eye is unlikely to be expressed during normal use because exposure is negligible, providing good occupational hygiene practices are in operation. However, if there is contact with the skin or eye, which could occur accidentally, then local damage is possible.

Concerns for respiratory tract irritation are low because the estimated highest possible short-term exposure of 0.1 ppm (for 30 minutes) is considerably less than the concentration of 400 ppm which elicited only mild sensory irritation in mice, and a factor of 300 below the study NOAEL of 30 ppm.

#### *Repeated dose toxicity and effects on the reproductive system*

For repeated dose toxicity, the MOS is 115, based on the animal systemic LOAEL of 1.5 mg/kg/day and human exposure estimate of 0.013 mg/kg/day. For reproductive effects the MOS is also 115, based on the animal systemic NOAEL of 1.5 mg/kg/day. These MOS values provide reassurance that health effects will not occur.

Table 4.15 Summary of the risk characterisation for workers during the manufacture of speciality paints

Key health effect	Human exposure	Quantitative animal toxicity data	MOS	Concern for risks to human health	Conclusion
Acute toxicity	0.013 mg/kg/day	Systemic LD <sub>50</sub> 1200-2400 mg/kg	-	Low	ii
Corrosivity skin/ eye	Negligible	No quantitative data	-	Low, providing hygiene good	ii
Resp. tract	0.1 ppm	Sensory irrit. NOAEL 30 ppm	300	Low	ii
Repeat dose toxicity	0.013 mg/kg/day	Systemic LOAEL 1.5 mg/kg/day	115	Low	ii
Reproductive system effects	0.013 mg/kg/day	Systemic NOAEL 1.5 mg/kg/day	115	Low	ii

### Speciality paint spray applications

#### *Acute toxicity*

The systemic acute oral LD<sub>50</sub> is in the range 1200 - 2400 mg/kg and the acute dermal LD<sub>50</sub> about 2000 mg/kg. The estimated maximum dose from inhalation and dermal exposure combined is 2 mg/kg/day, which is about 1000-fold less than the LD<sub>50</sub> values. A margin of this magnitude provides reassurance that adverse health effects will not occur, particularly in view of the steep dose-response curve.

#### *Irritation and corrosivity*

The corrosivity of the substance in relation to the skin and eye is unlikely to be expressed when good occupational hygiene practices are in operation. However, if there is contact with the skin or eye, which could occur accidentally, then local damage is possible. Because of the variation in hygiene practice for the spraying of paints, it is considered prudent to reach **conclusion (iii)**.

Concerns for respiratory tract irritation are low because the estimated highest possible exposure of 1 ppm is considerably less than the concentration which of 400 ppm which elicited only mild sensory irritation in mice. The more frequently predicted exposure of 0.1 ppm is a factor of 300 below the study NOAEL of 30 ppm.

#### *Repeated dose toxicity and effects on the reproductive system*

The estimated maximum human exposure is about 2 mg/kg/day, which is similar to the animal LOAEL of 1.5 mg/kg/day for repeated dose toxicity and the animal NOAEL of 1.5 mg/kg/day for reproductive effects. Hence, there are concerns for human health (**conclusion iii**).

Table 4.16 Summary of the risk characterisation for workers during speciality paint spray applications

Key health effect	Human exposure	Quantitative animal toxicity data	MOS	Concern for risks to human health	Conclusion
Acute toxicity	2 mg/kg/day	LD <sub>50</sub> 1200-2400 mg/kg	-	Low	ii
Corrosivity skin/ eye	Variable, depending on hygiene practice	No quantitative data	-	Low-high, depending on hygiene practice	iii
Resp. tract	1 ppm	Sensory irrit. LOAEL 400 ppm Sensory irrit. NOAEL 30 ppm	400 30	Low Low	ii ii
Repeat dose toxicity	2 mg/kg/day	Systemic LOAEL 1.5 mg/kg/day	-1	High	iii
Reproductive system effects	2 mg/kg/day	Systemic NOAEL 1.5 mg/kg/day	-1	High	iii

#### 4.1.3.2.3 Summary of risk characterisation for workers

The key health effects are acute toxicity, corrosivity, repeated dose toxicity and effects on the reproductive system. Sensitisation, mutagenicity and carcinogenicity are of low concern.

With respect to the industry sectors involving the manufacture of nonylphenol and its use as an intermediate, the margins between actual exposure and the N(L)OEALs for repeated dose toxicity and reproductive effects are low, giving rise to concerns for risks to human health **conclusion (iii)**. The corrosivity of the substance in relation to the skin and eye is unlikely to be expressed when good occupational hygiene practices are in operation. However, if there is contact with the skin or eye, which could occur accidentally, then local damage is possible. For acute toxicity the margin between exposure and the lethal dose is large and hence there are no concerns.

In the manufacture of speciality paints, the margins between exposure and the LD<sub>50</sub> or N(L)OAEL values are of sufficient magnitude to provide reassurance that health effects will not occur. Regarding the spray application of speciality paint, the margin between exposure and a lethal dose is of sufficient magnitude to provide reassurance that health effects will not occur. Because of the variation in hygiene practice for the spraying of paints, **conclusion (iii)** is considered appropriate for corrosivity. The N(L)OAELs for repeat dose toxicity and reproductive effects are similar to the exposure estimate, and hence there are concerns for human health (**conclusion iii**).

#### 4.1.3.3 Consumers

##### 4.1.3.3.1 Introduction

Nonylphenol is not used directly in products with which the consumer comes into contact. However it is used to make other substances which are in products sold to consumers. Consumer products may therefore contain very low levels of residual, unreacted nonylphenol. These may be present at very low levels in pesticides, cosmetics, spermicides and pharmaceutical preparations.

Certain plastic products contain the derivative compound TNPP, which may break down to release small amounts of nonylphenol.

### 4.1.3.3.2 Comparison of exposure and effects

Quantitative data are available for three of the consumer exposure scenarios, the first of these being from pesticide formulations containing alkyl phenol ethoxylates. Inhalation and dermal exposure are estimated to result in a systemic dose of 21 and 3.2 µg/event, respectively, assuming 100% absorption by the inhalation route and 10% absorption by the dermal route. For an adult with a bodyweight of 70 kg and daily use, the systemic dose resulting from the combined routes is approximately 0.35 µg/kg/day. These exposures are several orders of magnitude below the levels at which acute and corrosive effects can reasonably be expected to occur and also several orders of magnitude below the LOAEL for repeated dose toxicity and NOAEL for reproductive effects. Accordingly there are no concerns for effects on human health from this use.

A risk characterisation for the use of hair dyes (cosmetics) containing a residual amount of nonylphenol can be carried out using modelled exposure data. Systemic exposure per event is 3 µg/kg and if the product is used regularly, daily systemic exposure would be equivalent to 0.1 µg/kg/day. There is a large difference between the exposure for humans per event and the doses at which acute toxicity, repeat dose toxicity and reproductive effects are observed in animals. No quantitative data are available for skin corrosivity but the exposures are so low it is concluded that there is no cause for concern.

Exposure from food contact materials is estimated at 2 µg/kg/day. Assuming a bioavailability of 10% via the oral route, this equates to a systemic dose of 0.2 µg/kg/day. This is several orders of magnitude below the NOAEL and LOAELs from repeat dose and reproductive toxicity studies. It is therefore concluded that there is no cause for concern for consumers from these materials.

The risk characterisations are summarised in the following tables (**Tables 4.17-4.21**).

**Table 4.17** Risk characterisation for consumers for acute toxicity

Exposure scenario	Exposure (µg/kg)	MOS (in comparison to an LD <sub>50</sub> of 1200-2400 mg/kg)	Concern for risks to human health	Conclusion
Pesticide	0.35	>3 · 10 <sup>6</sup>	very low	ii
Hair dye	3	>4 · 10 <sup>5</sup>	very low	ii
Food contact materials	Not acute exposure	-	-	n/a
Total	3.35	>3 · 10 <sup>5</sup>	very low	ii

**Table 4.18** Risk characterisation for consumers for corrosivity (skin/eye)

Exposure scenario	Concern for risks to human health	Conclusion
Pesticide	Low because exposure is	ii
Hair dye	very low	ii

**Table 4.19** Risk characterisation for consumers for corrosivity (respiratory tract)

Exposure scenario	Exposure (ppm)	MOS (LOAEL 400 ppm; NOAEL 30 ppm)	Concern for risks to human health	Conclusion
Pesticide	0.007	>50 000 (LOAEL) >4000 (NOAEL)	low	ii
Hair dye	no data	-	-	ii

**Table 4.20** Risk characterisation for consumers for repeated dose toxicity

Exposure scenario	Exposure ( $\mu\text{g}/\text{kg}/\text{day}$ )	MOS (Systemic LOAEL 1.5 mg/kg/day)	Concern for risks to human health	Conclusion
Pesticide	0.35	4300	low	ii
Hair dye	0.1	15000	low	ii
Food contact materials	0.2	7500	low	ii
Total	0.6	2500	low	ii

**Table 4.21** Risk characterisation for consumers for reproductive effects

Exposure scenario	Exposure ( $\mu\text{g}/\text{kg}/\text{day}$ )	MOS (Systemic NOAEL 1.5 mg/kg/day)	Concern for risks to human health	Conclusion
Pesticide	0.35	4300	low	ii
Hair dye	0.1	15000	low	ii
Food contact materials	0.2	7500	low	ii
Total	0.6	2500	low	ii

When the consumer scenarios are combined into what might reasonably be a total consumer exposure, the total exposure is about 0.6  $\mu\text{g}/\text{kg}/\text{day}$ . All MOS are more than adequate. The most sensitive risk assessment is that for total consumer exposure on the basis of reproductive toxicity where the MOS is about 2500. This MOS is considered more than adequate even taking into consideration the sensitivity of the endpoint.

#### 4.1.3.3 Summary of risk characterisation for consumers

The key health effects are acute toxicity, corrosivity, repeated dose toxicity and reproductive effects. Sensitisation, mutagenicity and carcinogenicity are of low concern (**conclusion ii**).

There may be other product types for which risk characterisations have not been provided; this has occurred where insufficient data are available. The product types for which risk characterisations are presented probably represent the worst-case exposures given that pesticide use is a spray application, the hair product involves direct application to the body and the food contact materials result in potential oral exposure. However, even considering these exposures together on a daily basis, there is no concern for human health. There is also sufficient confidence in the MOS derived that if similar low exposures were to occur from one or two other products there would still be no cause for concern for human health.

#### 4.1.3.4 Indirect exposure via the environment

##### 4.1.3.4.1 Introduction

There is considerable uncertainty in the estimated human daily intake figures, consequently the accuracy of the predictions is difficult to determine. The first cause of uncertainty results from the lack of reliable data on the quantities of nonylphenol released into the environment from actual production and various uses. Releases and hence concentrations from actual production and use sites are likely to be much lower than the figures used here. The second cause of uncertainty concerns the assumptions made in the local calculations that all of the water, air and food comes from close to a point source of release.



#### 4.1.3.4.2 Comparison of exposure and effects

The calculations of human intake from air, water and food assume absorptions of 75% by inhalation and 100% from the oral route. Exposure via the air makes little contribution to the overall dose. The oral uptake may be an overestimate but the amount taken up is compared directly with the rat oral LOAEL for repeat dose effects and NOAEL for reproductive toxicity effects (both of 15 mg/kg/day) which represents the dose given rather than the amount taken up. Consequently, absorption efficiency does not affect the comparison between human exposure and the N(L)OAEL, assuming this is similar for humans and the animal models.

The highest estimate for exposure to man via the environment not in the vicinity of a nonylphenol plant is provided by the regional model at  $5.31 \cdot 10^{-3}$  mg/kg/day. The MOS for both repeated dose toxicity and reproductive effects is  $>2500$ , which provides reassurance that adverse health effects will not occur. For this scenario, acute toxicity is not a relevant endpoint of concern. Corrosivity is considered to be an endpoint of no concern, since concentrations will be low as exposure to the material is dispersed across the environment. Therefore **conclusion (ii)** is reached.

The maximum combined local intake, taking account of exposure via air, drinking water and food is 4.42 mg/kg/day (from the textile industry). The MOS for both repeated dose toxicity and reproductive effects is about 3, which is of insufficient magnitude to provide reassurance that adverse effects will not occur. Accordingly there are concerns for risks to human health. However, as indicated, there are considerable uncertainties in the estimated intake figures, and these estimates may considerably overestimate exposure from local sources. Therefore further information is required to refine the risk characterisation, and **conclusion (i)** is reached.

#### 4.1.3.4.3 Summary of risk characterisation for exposure via the environment

The key health effects are acute toxicity, corrosivity, repeated dose toxicity and effects on the reproductive system. Acute toxicity and corrosivity are of low concern where exposure is dissipated throughout the environment.

As shown in **Table 4.22** there are concerns for human health with respect to local exposure, based on MOSs of about 3 for repeated dose toxicity and reproductive effects. In order to refine the exposure estimate, further information is needed on emissions into the local environment from production and use plant.

Table 4.22 Summary of risk characterisation for humans exposed via the environment

	Local scenario	Regional scenario
Exposure (mg/kg/day)	4.42	$5.31 \cdot 10^{-3}$
MOS: repeated dose toxicity LOAEL (15 mg/kg/day)	3.4	$>2800$
MOS: reproductive toxicity NOAEL (15 mg/kg/day)	3.4	$>2800$
Conclusion: repeated dose toxicity	i	ii
Conclusion: reproductive effects	i	ii

### 4.1.3.5 Combined exposure

As described in section 4.1.1.4, the maximum combined daily exposure for an individual is approximately 6.4 mg/kg/day from the estimates provided in this report. **Table 2.23** summarises the risk characterisation for combined exposure with respect to repeated dose toxicity and reproductive effects. Acute toxicity and corrosivity are of low concern.

**Table 4.23** Risk characterisation for combined exposure

Exposure (mg/kg/day)	Repeated dose toxicity		Reproductive effects	
	MOS based on LOAEL (1.5 mg/kg/day)	Conclusion	MOS based on NOAEL (1.5 mg/kg/day)	Conclusion
6.4	0.2	i	0.2	i

The risk characterisation is influenced by both the exposure to workers and to those exposed in the locality of a textile plant. The MOS values indicate a cause for concern. However, **conclusion (i)** is proposed because the risk characterisation can be refined when risk reduction measures have been considered for workers and further information on local environmental exposure has been obtained as described in the relevant sections.

## 4.2 HUMAN HEALTH (PHYSICOCHEMICAL PROPERTIES)

The physicochemical properties of nonylphenol (as defined in this risk assessment document) are not easily available in the literature but can be established by contacting manufacturers and via safety data sheets. There is some evidence that the physicochemical properties vary slightly depending on the particular manufacturing process. Nonylphenol is a complex mixture of isomers, so this is not unexpected.

The substance is of high viscosity, low vapour pressure and flammability and does not have any explosive potential that would be a cause for concern either from the substance directly or in solution in water. There are no specific major hazard regulations associated with this material and controls on storage and use should be addressed at a local level.

During the manufacture, storage and use of this substance the control measures that are used ensure that risks arising from the physicochemical properties are of no concern to workers. No risk from physico chemical properties is considered to arise from consumer plastics and phenolic coatings or other consumer goods; no cause for concern is identified for consumers from any of these exposures. There is also considered to be no cause for concern to humans from indirect exposure via the environment. Therefore **conclusion (ii)** is reached.

## **5 RESULTS**

### **5.1 INTRODUCTION**

Four companies produce nonylphenol within the European Union. In 1997 the total EU production of nonylphenol was 73,500 tonnes, exports were 3,500 tonnes and imports were 8,500 tonnes. The total EU consumption of nonylphenol was estimated to be 78,500 tonnes. Nonylphenol is used as a chemical intermediate in the production of nonylphenol ethoxylates, plastics/resins, polymer stabilisers and phenolic oximes. The use level appears to have been fairly constant over the period 1994-1997.

### **5.2 ENVIRONMENT**

**Table 5.1** summarises the environmental risk characterisation for nonylphenol for all life cycle stages.

Table 5.1 Summary of risk characterisation for the environment

Life cycle stage	Risk characterisation					
	Waste water treatment plant micro-organisms	Aquatic compartment (Surface water)	Aquatic compartment (Sediment) <sup>a</sup>	Terrestrial compartment	Atmosphere	Secondary poisoning
Nonylphenol production	(ii)	(iii)	(i)	(ii)	(ii)	(ii)
Nonylphenol ethoxylate production	(ii)	(iii)	(i)	(iii)	(ii)	(iii)
Production of phenol/formaldehyde resins	(ii)	(iii)	(i)	(ii)	(ii)	(ii)
Production of TNPP	(ii)b	(ii)b	(ii)b	(ii)	(ii)	(ii)
Production of epoxy resins	(ii)	(iii)	(i)	(ii)	(ii)	(ii)
Production of other plastic stabilisers	(ii)	(iii)	(i)	(ii)	(ii)	(ii)
Production of phenolic oximes	(ii)	(iii)	(i)	(ii)	(ii)	(ii)
Formulation of nonylphenol ethoxylate	(ii)	(iii)	(i)	(iii)	(ii)	(iii)
Use of nonylphenol ethoxylates						
Agriculture (pesticides)	(ii)	(iii)	(i)	(ii)	(ii)	(ii)
Agriculture (veterinary medicines)	(ii) b	(ii)b	(ii)b	(iii)	(ii)	(ii)
Captive use by the chemical industry	(ii)	(iii)	(i)	(iii)	(ii)	(iii)
Electrical engineering industry	(ii)	(iii)	(i)	(iii)	(ii)	(iii)
Industrial and institutional cleaning	(ii)	(iii)	(i)	(iii)	(ii)	(iii)
Leather processing	(ii)	(iii)	(i)	(iii)	(ii)	(iii)
Metal extraction and processing	(ii)	(iii)	(i)	(iii)	(ii)	(iii)
Mineral fuel and oil industry	(ii)	(iii)	(i)	(iii)	(ii)	(iii)
Photographic industry	(ii)	(iii)	(i)	(iii)	(ii)	(ii)
Polymer industry	(ii)	(iii)	(i)	(iii)	(ii)	(ii)
Pulp, paper and board industry	(ii)	(iii)	(i)	(iii)	(ii)	(iii)
Textile industry	(ii)	(iii)	(i)	(iii)	(ii)	(iii)
Paint production	(ii)	(iii)	(i)	(iii)	(ii)	(iii)
Domestic paint use	(ii)	(iii)	(i)	(ii)	(ii)	(iii)
Industrial paint use	(ii)	(iii)	(i)	(ii)	(ii)	(iii)
Civil engineering	(ii)	(iii)	(i)	(iii)	(ii)	(iii)

a)No further work is recommended as the sediment risk characterisation is dependant upon the aquatic risk characterisation for which a conclusion (iii) is reached.

b)A conclusion (ii) is reached because there are no emissions to the aquatic compartment from these uses.

Local releases of nonylphenol to the environment may occur during production, use as a chemical intermediate and from the breakdown of nonylphenol ethoxylates in wastewater treatment plants. Site-specific data and generic data have been used with default values from the TGD to generate PECs for the various environmental compartments. There is a large ecotoxicity database from which to derive a PNEC for aquatic and terrestrial organisms.

The estimated regional PEC for surface water (0.6 µg/l) exceeds the aquatic PNEC (0.33 µg/l), and consequently all uses of nonylphenol that give rise to emissions to the aquatic environment automatically cause a risk at the local scale (since the regional PEC is added to local concentrations to derive the local PEC). If the regional PEC were lowered, the following uses might not give rise to concern (to the aquatic environment):

- Production of nonylphenol (certain sites only);
- Production of epoxy resins;
- Production of phenolic oximes;
- Use of nonylphenol ethoxylates in agriculture (pesticide formulations);
- Captive use of nonylphenol ethoxylates by the chemical industry;
- Use of photographic materials containing nonylphenol ethoxylates by small scale photographic processors; and
- Use of domestic and industrial emulsion paints containing nonylphenol ethoxylates.

Risks to the sediment and terrestrial compartments and to top predators by secondary poisoning arise principally from emissions to the aquatic compartment. The risk to sediment organisms could be refined with further sediment toxicity data, but the need for these data should await the outcome of the risk reduction strategy for the aquatic compartment.

### 5.3 HUMAN HEALTH

The hazardous properties of nonylphenol have been evaluated in animals to the extent that the minimum data requirements according to Article 9(2) of Regulation 793/93 have been met. The key health effects of acute toxicity, corrosivity, repeated dose toxicity and reproductive effects have been identified. For acute toxicity, the oral LD<sub>50</sub> is in the range 1200-2400 mg/kg and the dermal LD<sub>50</sub> is around 2,000 mg/kg. The inhalation LC<sub>50</sub> is not known but the corrosive nature of nonylphenol suggests that nonylphenol may cause acute toxicity by this route. No dose response information is available on corrosivity. Mild sensory irritation of the respiratory tract is elicited at 400 ppm, but not at 30 ppm. An oral LOAEL for repeated dose toxicity is 15 mg/kg/day. Concerns for mutagenicity and carcinogenicity are low. Regarding the effects on the reproductive system, the observations of oestrogenic activity in *in vitro* and *in vivo* assays, minor perturbations in the reproductive system of offspring in a multigeneration study, and testicular changes in gavage studies collectively raise concerns. The oral NOAEL for reproductive effects is 15 mg/kg/day.

Thus, the result of the hazard assessment is that **conclusion (ii)** is reached because the minimum data requirements according to Article 9(2) of Regulation 793/93 have been met and no further data are required:

**Conclusion (ii):** There is at present no need for further information and/or testing or for risk reduction measures beyond those that are being applied already.

### Occupational assessment

Inhalation exposures to nonylphenol during manufacture and use as an intermediate are likely to be less than 0.1 ppm (8-hour TWA). During the manufacture of speciality paints, inhalation exposures to nonylphenol are estimated to be less than 0.01 ppm (8-hour TWA). Routine dermal exposure during nonylphenol manufacture, use as an intermediate and manufacture of speciality paints is negligible and consequently this route of exposure is considered unlikely to contribute significantly to the overall systemic body burden. Infrequent accidental dermal contact with contaminated surfaces may occur, but because of the corrosive nature of the substance, the duration of contact will be brief and significant systemic exposure is unlikely. The potential inhalation exposure during speciality paint spray application is estimated to be up to 1 ppm (8-hour TWA), not taking account of the effects of RPE or the dilution afforded by working outdoors. Dermal exposure during this activity is estimated to be 0.25 mg/cm<sup>2</sup>/day.

With respect to manufacture of nonylphenol and its use as an intermediate, the margins between actual exposure values and N(L)OAELs for repeated dose toxicity and reproductive effects are low, giving rise to concerns for risks to human health. For acute toxicity the margin between exposure and the lethal dose is large and hence there are no concerns. In the manufacture of speciality paints, the margins between exposure and the LD<sub>50</sub> or N(L)OAEL values are of sufficient magnitude to provide reassurance that health effects will not occur. Regarding the spray application of paint, the margins between exposure and the N(L)OAELs for repeat dose toxicity and reproductive effects are low, hence there are concerns for human health. For acute toxicity the margin between exposure and the lethal dose is large and hence there are no concerns. Although there are risks to the skin in relation to corrosivity in all these industry sectors, it is considered that these are suitably mitigated by adherence to good occupational hygiene practices; however there are concerns for corrosivity in the spray application of speciality paint because hygiene practice can be variable.

Thus, **conclusion (iii)** applies for workers in the industry sectors of: manufacture of nonylphenol, use of nonylphenol as an intermediate and use of speciality paints:

**Conclusion (iii):** There is a need for limiting the risks; risk reduction measures that are already being applied should be taken into account.

For the remaining scenario, the manufacture of speciality paint, **conclusion (ii)** is reached:

**Conclusion (ii):** There is at present no need for further information and/or testing or for risk reduction measures beyond those that are being applied already.

### Consumer assessment

Consumer exposure is so low from the quantifiable estimates that there are no concerns for risks to human health from the hazardous properties of acute toxicity, corrosivity, repeated dose toxicity and reproductive effects and **conclusion (ii)** applies for all these endpoints. Concerns for mutagenicity and carcinogenicity are low.

**Conclusion (ii):** There is at present no need for further information and/or testing or for risk reduction measures beyond those that are being applied already.

### Indirect exposure via the environment

There is considerable uncertainty in the estimated human daily intake figures, consequently the accuracy of the predictions is difficult to determine. However, modelled data have been used to construct risk characterisations. Acute toxicity and corrosivity are of low concern and lead to a **conclusion (ii)** for both regional and local scenarios.

#### *Regional exposure*

The best estimate for exposure to man via the environment not in the vicinity of a nonylphenol plant is  $5.13 \cdot 10^{-3}$  mg/kg/day. The MOS for both repeated dose toxicity and reproductive effects are high and provide reassurance that adverse health effects will not occur. Therefore **conclusion (ii)** is reached for these endpoints. Acute toxicity is not a relevant endpoint of concern, and corrosivity is of no concern.

**Conclusion (ii):** There is at present no need for further information and/or testing or for risk reduction measures beyond those that are being applied already.

#### *Local exposure*

The available modelled data suggest that there are concerns for human health with respect to local exposure, based on a low margins between modelled exposures and the N(L)OAELs for repeated dose and reproductive toxicity. Acknowledging that the model exposures may overestimate real exposures from local sources, **conclusion (i)** applies.

**Conclusion (i)** There is need for further information and/or testing:

In order to refine the estimates of exposure from local sources, further information is needed on emissions into the local environment from production and use plant.

**Conclusion (ii)** is reached for acute toxicity and corrosivity, which are of low concern for this scenario where exposure is dissipated throughout the environment.

**Conclusion (ii):** There is at present no need for further information and/or testing or for risk reduction measures beyond those that are being applied already.

### Combined exposure

The MOS values for repeated toxicity and reproductive effects indicate a cause for concern. However, **conclusion (i)** is proposed because the risk characterisation can be refined when risk reduction measures have been considered for workers and further information on local environmental exposure has been obtained as described in the relevant sections.

**Conclusion (i):** There is need for further information and/or testing:

**Conclusion (ii)** is reached for acute toxicity and corrosivity, which are of low concern for this scenario.

**Conclusion (ii):** There is at present no need for further information and/or testing or for risk reduction measures beyond those that are being applied already.

#### **5.4 RISKS FROM PHYSICOCHEMICAL PROPERTIES**

There are no significant risks to humans from the physico-chemical properties of nonylphenol and 4-nonylphenol (branched). Therefore **conclusion (ii)** is reached.

**Conclusion (ii):** There is at present no need for further information and/or testing or for risk reduction measures beyond those that are being applied already.



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## GLOSSARY

<b>Standard term / Abbreviation</b>	<b>Explanation/Remarks and Alternative Abbreviation(s)</b>
<i>Ann.</i>	Annex
AF	assessment factor
BCF	bioconcentration factor
bw	body weight / <i>Bw, b.w.</i>
°C	degrees Celsius (centigrade)
CAS	Chemical Abstract System
CEC	Commission of the European Communities
CEN	European Committee for Normalisation
CEPE	European Council of the Paint, Printing Ink and Artists' Colours Industry
d	day(s)
d.wt	dry weight / dw
DG	Directorate General
DT <sub>50</sub>	period required for 50 percent dissipation (define method of estimation)
DT <sub>50lab</sub>	period required for 50 percent dissipation under laboratory conditions (define method of estimation)
DT <sub>90</sub>	period required for 90 percent dissipation (define method of estimation)
DT <sub>90field</sub>	period required for 90 percent dissipation under field conditions (define method of estimation)
EC	European Communities
EC	European Commission
EC <sub>50</sub>	median effective concentration
EEC	European Economic Community
EINECS	European Inventory of Existing Commercial Chemical Substances
EU	European Union
EUSES	European Union System for the Evaluation of Substances
f <sub>oc</sub>	Fraction of organic carbon
G	gram(s)
PNEC(s)	Predicted No Effect Concentration(s)
PNEC <sub>water</sub>	Predicted No Effect Concentration in Water

(Q)SAR	Quantitative Structure Activity Relationship
STP	Sewage Treatment Plant
TGD	Technical Guidance Document <sup>6</sup>
UV	Ultraviolet Region of Spectrum
UVCB	Unknown or Variable composition, Complex reaction products or Biological material
v/v	volume per volume ratio
w/w	weight per weight ratio
w	gram weight
GLP	Good Laboratory Practice
h	hour(s)
ha	Hectares / <i>h</i>
HPLC	High Pressure Liquid Chromatography
IARC	International Agency for Research on Cancer
C <sub>50</sub>	median immobilisation concentration or median inhibitory concentration 1 / <i>explained by a footnote if necessary</i>
ISO	International Standards Organisation
IUPAC	International Union for Pure Applied Chemistry
kg	kilogram(s)
kPa	kilo Pascals
K <sub>oc</sub>	organic carbon adsorption coefficient
K <sub>ow</sub>	octanol-water partition coefficient
K <sub>p</sub>	Solids water partition coefficient
l	litre(s)
log	logarithm to the basis 10
L(E)C <sub>50</sub>	lethal concentration, median
m	meter
µg	microgram(s)
mg	milligram(s)
MOS	Margins Of Safety

<sup>6</sup> Commission of the European Communities, 1996. Technical Guidance Documents in Support of the Commission Directive 93/67/EEC on risk assessment for new substances and the Commission Regulation (EC) No 1488/94 on risk assessment for existing substances. Commission of the European Communities, Brussels, Belgium. ISBN 92-827-801[1234]

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NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration
NOEL	No Observed Effect Level
OECD	Organisation for Economic Co-operation and Development
OJ	Official Journal
pH	potential hydrogen <i>-logarithm</i> (to the base 10) of the hydrogen ion concentration {H <sup>+</sup> }
pKa	<i>-logarithm</i> (to the base 10) of the acid dissociation constant
pKb	<i>-logarithm</i> (to the base 10) of the base dissociation constant
Pa	Pascal unit(s)
PEC	Predicted Environmental Concentration

## **Appendix 1 Formation of Nonylphenol during the Biodegradation of Nonylphenol Ethoxylates**

### Introduction

This appendix discusses the formation of nonylphenol during the biodegradation of nonylphenol ethoxylates. No methods for doing this are currently incorporated in the Technical Guidance Document and so an attempt has been made to try and assess the available data on the biodegradation of nonylphenol ethoxylates in terms of the amount of nonylphenol formed under various conditions.

There is a large body of work concerning the degradation of nonylphenol ethoxylates to various products. Much of this work has been directed towards identification of the various intermediate degradation products. This appendix is concerned with the formation of nonylphenol during the biodegradation and so the other products are not considered further. Throughout this appendix the following convention will be used as abbreviations for the various products.

NPnEO - nonylphenol ethoxylate with n ethoxylate groups - for commercial products that are mixtures of several oligomers n refers to the range of ethoxylate groups/molecule or the average number of ethoxylate groups/molecule present. Typically for many of the products studied the average value for n is 9 or 10, with the range for n from 1-20.

NP1EO - refers specifically to nonylphenol monoethoxylate.

NP2EO - refers specifically to nonylphenol diethoxylate.

NP1EC - refers to the carboxylic acid of NP1EO formed by oxidation of the terminal hydroxyl group.

NP2EO - refers to the carboxylic acid of NP2EO formed by oxidation of the terminal hydroxyl group.

{OPnEO etc. refer to the octylphenol derivatives}

Most of the data refers to branched chain p-nonylphenol groups.

Much of the earlier work on biodegradation of nonylphenol ethoxylates has been reviewed previously (e.g. Swisher, 1970) and is consistent with the information given in this appendix.

### Biodegradation tests

#### *Standard tests*

Standard biodegradation tests have been developed specifically for surfactants, for example the OECD Screening Test and the OECD Confirmatory Test.

In the OECD Screening Test the surfactant is added to a flask as sole carbon source in a mineral nutrient solution. The flask is then inoculated with a mixed bacterial population, usually from sewage treatment plant effluent. The test is carried out for 19 days. For nonylphenol ethoxylates, the primary degradation of the surfactant is usually monitored by using an analytical method

based on bismuth active substance (BiAS). In this method, the polyethoxylate chain forms a complex with the barium ion of the added barium iodo bismuthate. The complex is poorly soluble and is filtered off, redissolved in ammonium tartrate solution and titrated potentiometrically with carbamate solution to determine the concentration of the nonylphenol ethoxylate. The pass mark for the test is 80% BiAS removal in the 19-day period (Gerike, 1987).

The OECD Confirmatory Test is used to model the behaviour of a surfactant in a domestic wastewater treatment plant. In this test, the surfactant (concentration 10 mg BiAS/l) is added to synthetic sewage which is then fed into a vessel containing activated sludge. The average residence time of the vessel is 3 hours. The effluent is fed to a settling vessel, where the sludge is removed and the final effluent is then collected and analysed for BiAS.

The BiAS method of analysis detects molecules with five or more consecutive alkoxide units, thus degradation results based on BiAS removal only indicate that the nonylphenol ethoxylate has been degraded to compounds with <5 ethoxylate groups. Therefore only information on the primary biodegradability of a surfactant can be obtained from methods that use BiAS removal as the end point.

Nonylphenol ethoxylates have also been tested in standard biodegradation tests (e.g. OECD) that measure the ultimate biodegradation (mineralisation). The reported results from standard biodegradation tests are shown in **Table A**.

**Table A** Results from standard biodegradation tests (Gerike, 1987).

Substance	OECD Screening test	OECD Confirmatory Test	Closed Bottle Test	Modified OECD Screening Test	Coupled Units Test
i-Nonylphenol ethoxylate (9 EO)	6-78% BiAS removal	97% BiAS removal	5-10% of ThOD	8-17% DOC removal	48±6% DOC removal
n-C <sub>8-10</sub> Alkylphenol ethoxylate	84% BiAS removal	96% BiAS removal	29% of ThOD	-	68±3% DOC removal

These results indicate that some primary biodegradation is occurring in the tests. When the test looking at ultimate degradation is considered, it is clear that a less degradable intermediate is building up in the test. The Coupled Units test is a simulation test and it is not possible to distinguish between removal due to mineralisation and removal due to adsorption onto sludge from the data given. Recently, it has been reported that NPnEO (n=9) showed 53-58% degradation (measured as % CO<sub>2</sub> generation in 28 days) in a OECD 301B ready biodegradation test, although no details of the test are currently available (Varineau and Williams, 1997).

Narkis and Schneider-Rotel (1980) found that ozonation of the NPnEO (average n=13, range of n=10-15) prior to carrying out a modified OECD screening test increased markedly the total organic carbon removal (up to 62.5% TOC removal was observed overall compared to 22.9% TOC removal with no ozonation). Ozonation was thought to cause changes to the aromatic ring that facilitated biodegradation.

Rudling and Solyom (1974) studied the degradation of several NPnEO (n=8, 10 and 14) using the OECD Screening Test (temperature was 15 or 20°C rather than the usual 25°C). All three compounds were found to degrade >90% within 12 days (primary degradation). Gas chromatographic analysis of the test media after 4 days at 20°C indicated that NP2EO was the

major degradation product and around 50% of this had itself degraded after 28 days. In contrast to this, when incubated at 15°C, no further degradation of NP2EO was seen.

#### *Other laboratory biodegradation tests*

The biodegradation of  $^{14}\text{C}$  ring-labelled NPnEO (average  $n=9$ ) has been studied in a semi-continuous activated sludge treatment system. The activated sludge was derived from the mixed liquors from the aeration basin of a wastewater treatment plant. The water used in the test was the primary effluent from the settling basin at the wastewater treatment plant, supplemented with nutrient broth. The background concentration of nonylphenol and NPnEO (range  $n=1-17$ ) were 43.6  $\mu\text{g/l}$  and 978  $\mu\text{g/l}$  respectively. Before the test was started, the activated sludge was acclimated for 14 days by exposure to the primary effluent. After 14 days 300 ml of the activated sludge was placed into the degradation reactor and primary effluent containing 2 mg/l of the  $^{14}\text{C}$ -labelled NPnEO was fed into the reactor. A semi-continuous fill and draw procedure was used such that around 200 ml of the liquid in the reactor was drawn off and replaced by the primary effluent containing the  $^{14}\text{C}$ -labelled substance every 2.3 days. This gave a sludge retention time and hydraulic retention time of 52 and 3.45 days respectively in the system. The total sampling time was 30 days. Based on radioactivity measurements, 20.8% of the influent radioactivity was removed as  $\text{CO}_2$ , 55.9% was found in effluent as nonylphenol/NPnEO (6.9%), NPnEC (26%) and highly degraded metabolites (23.1%), 6% remained in the test system adsorbed to sludge (3.5% as nonylphenol/NPnEO and 2.5% as biomass), 8.35% remained in the aqueous part of the system (1.03% as nonylphenol/NPnEO, 2.88% as NPnEC, and 3.45% as highly degraded metabolites), 0.72% of the radioactivity was removed from the system in sludge (0.09% as nonylphenol/NPnEO, 0.34% as NPnEC and 0.3% as highly degraded metabolites) and 8.23% of the radioactivity was unaccounted for. Overall, there was a 93% removal of the NPnEO from the influent. Specific analysis for nonylphenol showed that from the total influent concentration of nonylphenol/NPnEO compounds (total 204  $\mu\text{g}$ , of which around 8  $\mu\text{g}$  was nonylphenol), around 4  $\mu\text{g}$  of nonylphenol was discharged in effluent, 5  $\mu\text{g}$  was adsorbed on sludge and 8  $\mu\text{g}$  was retained in the system. Thus there appears to have been a net generation of nonylphenol in the system (i.e. 8  $\mu\text{g}$  was added to the system, 17  $\mu\text{g}$  present in the system - if it is assumed that no degradation of nonylphenol occurred then around 4.6% of the NPnEO was converted to nonylphenol) (Varineau et al., 1996a).

Kravetz et al. (1982) looked at the biodegradation of radiolabelled NPnEO ( $n=9$ ) during wastewater treatment. The radiolabelled compound had  $^{14}\text{C}$ -labelling on the ethoxylate chain and  $^3\text{H}$ -labelling on the phenolic ring. The system used was a closed bench-scale bioreactor that was seeded with mixed liquor from the aeration basin of a domestic activated sludge wastewater treatment plant in Texas. The bioreactor was installed on-site at the wastewater treatment plant and used water from the aeration tank (shown to contain nonylphenol and NPnEO), spiked with labelled or unlabelled NPnEO (concentration 5 mg/l), as continuous influent. Mild mechanical mixing and aeration with  $\text{CO}_2$ -free air was used in the bioreactor, and the hydraulic retention time in the system was around 8 hours. The test was divided into 3 phases: an acclimation period of 14 days, where the reactor was fed unlabelled NPnEO; a 14 day biodegradation test phase with the radiolabelled NPnEO; and finally a 12 day period to monitor the die-away of the radiolabelled components (unlabelled NPnEO was fed into the reactor during this period). During the 14-day acclimation period, >98% removal of NPnEO based on cobalt thiocyanate active substance (CTAS) analysis and >95% removal based on foam height measurements and surface tension data was seen, indicating substantial primary biodegradation of the nonylphenol ethoxylate. When the radiolabelled NPnEO was used, about 40-60% of the  $^{14}\text{C}$  was converted to  $^{14}\text{CO}_2$  and around 10-40% of the  $^3\text{H}$  was converted to  $^3\text{H}_2\text{O}$ , indicating that some mineralisation of



both the ethoxylate chain and phenolic ring was occurring. It was estimated that around 35-50% of the hydrophobe of NPnEO was discharged in the effluent from the system, probably as NPnEO or NPnEC with low values for n (the EO to hydrophobe ratio in the effluent was estimated to be 2.4). Yoshimura (1986) studied the degradation of a NPnEO (average n=9) in sediment and river water. Sediment was collected from the Yahagi River in Kawasaki City and 20 mg/l of the nonylphenol ethoxylate was incubated with 3,000 mg/l of the sediment both with and without stirring. The primary degradation of the nonylphenol ethoxylate was determined by monitoring the disappearance of the parent NPnEO either by HPLC or by a colourimetric method (cobalt-thiocyanate method). Around 98% primary degradation of the NPnEO was seen within 5 days with stirring and within 10 days without stirring. New peaks were observed to be formed in the HPLC trace which still remained 30 days after inoculation, indicating the formation of less biodegradable metabolites. Nonylphenol ethoxylates with 1-3 ethoxy groups/molecule were seen to be formed only in small amounts after 5-10 days incubation. The concentration of NPnEO on sediment also decreased after 10 days, indicating that primary biodegradation was also occurring in the sediment bound fraction. The major intermediates identified in the study were NP1EC and NP2EC. In a river die-away test using brackish water (chloride ion concentration 6,500 mg/l, hardness 3,400 mg/l as CaCO<sub>3</sub>), primary degradation of the NPnEO of 39%, 90%, 92% and 94% was seen after 4,5,8, and 10-16 days incubation respectively.

The degradation of a NPnEO (average n=10, range 1-18) has been studied in brackish and saline water using a static die-away method. The water was collected from Šibenik Harbour which receives a significant amount of municipal wastewater (the input of nonylphenol ethoxylates to the harbour was estimated at 5 tonnes/year). The water in the harbour is highly stratified with a brackish layer overlaying the saline layer, and both water types were collected in March, September, October and November. The die-away tests were carried out at the temperature at the time of sampling, which ranged from 13°C in March to 22.5°C in September. The test NPnEO was added to the water samples (0.1 or 1 mg/l) and incubated in the dark. The disappearance of the total nonylphenol ethoxylates present in the sample was monitored, and this was found to occur faster in the brackish water than the saline water. This was thought to be due to an increased amount of pre-exposure of the brackish water to NPnEO compared to the saline layer. The half-life for disappearance of the NPnEO was found to be longer in the winter months (half-life >1 month at 13°C) than in the Summer (half-life of 2.5-4 and 14-35 days in brackish and saline water respectively). The changes in oligomer distribution of the parent NPnEO was also investigated. The added NPnEO was found to be relatively unchanged during the first 3 days incubation. After around 8 days incubation, there was a shift from the higher oligomers (all NPnEO with n>5 had disappeared) to lower oligomers (an increase in the amounts of NPnEO with n<4, with the biggest increase in NP2EO), which then degraded at a slower rate than seen for the higher oligomers, with residual amounts of NP2EO being seen after 30 days. No trace of nonylphenol was found in any of the cultures (Kveštak and Ahel, 1995).

The degradation of <sup>14</sup>C ring-labelled NPnEO (average n=9) has been studied in river die-away tests. The river water for the tests was from the Missouri River, several miles downstream from a wastewater treatment plant. The water was spiked with 1% (w/w) of secondary effluent from a publicly owned wastewater treatment plant to ensure that the bacteria present in the water had been previously exposed to NPnEO (the total number of bacterial colony forming units (cfu) in the test was around 1 · 10<sup>4</sup> cfu/ml, which is similar to the number typically found in the Missouri River (1 · 10<sup>3</sup>-1 · 10<sup>4</sup> cfu/ml)). For the die-away tests, samples of the water were spiked with 200 µg/l of the <sup>14</sup>C-labelled NPnEO and were incubated at 20°C with slow stirring and a gentle airflow over the surface. Primary degradation (defined as degradation into species not identifiable as nonylphenol and NPnEO) was monitored and 89% primary degradation occurred

after 28 days and 96% after 128 days. At the end of the experiment (128 days) <5% of the original NPnEC existed as NPnEC. Ultimate biodegradation (conversion to  $^{14}\text{CO}_2$ ) measurements indicated that approximately 50% of the  $^{14}\text{C}$ -labelled nonylphenol was converted to  $^{14}\text{CO}_2$  in the first 60 days of the test, with an additional 10% of the nonylphenol being to  $^{14}\text{CO}_2$  over days 60-128. The apparently reduced rate of mineralisation during the second half of the experiment may have been due to a loss of biomass viability (Varineau et al., 1996b and CMA, 1997).

Three bacterial strains (*Pseudomonas putida* strain Fus1B1; *Pseudomonas* sp. strain SscB2; *Xanthomonas* sp. strain SscB3) that were capable of utilising a NPnEO (average n=9) as sole energy and carbon source have been identified (Frassinetti et al., 1996). The bacteria were all isolated from activated sludge from a tannery wastewater treatment plant and all species were found to effect primary biodegradation of the nonylphenol ethoxylate.

Maki et al. (1994) isolated a Pseudomonad bacterium from activated sludge that was capable of using NPnEO as sole carbon source. The bacterium was shown to degrade the ethylene oxide chain of a NPnEO (average n=9.5). NP2EO was identified as a major metabolic product.

The aerobic biodegradation of a NPnEO (a commercial product (Imbetin N/7A) with the following composition: 75% NP1EO, 20% NP2EO and 5% NP3EO) was determined using a shake culture test. In the test, two types of growth media were used, synthetic sewage and a mineral medium. Three bacterial cultures were derived from the wastewater of a detergent manufacturing plant, chronically polluted river water and a pristine forest soil. The bacterial cultures were enriched by growth in synthetic sewage medium containing NPnEO (average n=9) over 5 weeks. For the degradation experiments, 200 ml of either synthetic sewage or mineral medium was spiked with the test NPnEO (Imbetin N/7A), inoculated with one of the enriched bacterial cultures and incubated at 23.5°C with shaking. In the tests the removal of NP1EO and NP2EO was monitored (primary biodegradation). Similar rates of removal for both compounds were observed in all media. The degradation was slightly faster in synthetic sewage media than mineral media. In synthetic sewage media the first order reaction rate constants for both compounds were  $k=0.23-0.33\text{ d}^{-1}$  for inocula derived from wastewater and polluted river water, and  $k=0.18-0.21\text{ d}^{-1}$  for inocula derived from the pristine soil. The corresponding rate constants for degradation in mineral media were  $0.16-0.20\text{ d}^{-1}$  for inocula from wastewater and polluted river water and  $0.06-0.12\text{ d}^{-1}$  for inocula from pristine soil. In addition to these test, river water die-away tests were also carried out using river water from the Sava River spiked with Imbetin N/7A at a concentration of 1.1 mg/l and using secondary sewage effluent from a wastewater treatment plant (concentrations of NP1EO and NP2EO were 90 and 64  $\mu\text{g/l}$  respectively). The experiments were carried out a 20°C with river water and 4 and 20°C with the sewage effluent. In the river die-away test the first order rate constant for primary degradation of NP1EO and NP2EO was  $k=0.35-0.37\text{ d}^{-1}$  with continuous stirring and  $k=0.23\text{ d}^{-1}$  under static conditions. The rate of primary degradation of the two compounds was slightly lower in the sewage effluent, with rate constants of  $k=0.09\text{ d}^{-1}$  at 20°C and  $k=0.01\text{ d}^{-1}$  at 4°C. The degradation products formed during the shake culture experiments after 8-10 days incubation were identified mainly as NP1EC and NP2EC which accounted for >90% of the amount of NPnEO originally added. No traces of any other metabolites were detected (Ahel et al., 1994a).

A lab-scale activated sludge system has been used to study the behaviour of several NPnEO (n=8, 10, 14, 16 and 30). Pre-settled sewage was used as the influent to the system. This was found to have a “background” concentration of around 0.5 mg/l of total nonionic surfactants. Activated sludge from a municipal wastewater treatment plant was used as seed for the system and after 1 week of operation, 5 mg/l of NPnEO (n=8) was added to the influent. The other NPnEOs were

added to the influent over the next 7-24 days depending on the degradation seen. Degradation of the original NPnEO was determined by monitoring the effluent using methods that detected NPnEO with  $n > 2$  and removals of 82-91%, >91%, >90%, 95-96% and 88-93% were determined for NPnEO with  $n = 8, 10, 14, 16$  and 30 ethoxylate groups/molecule respectively. In order to establish if removal was due to adsorption or biodegradation to NP2EO, activated sludge and effluent from experiments with NPnEO ( $n = 10$  and 14) were analysed by gas chromatography. Neither the original surfactant or NP2EO could be detected (Rudling and Solyom, 1974).

The degradation of NPnEO (average  $n = 10$ ) has been studied using a method for determining recalcitrant metabolites. The test is based on a coupled units version of the OECD Confirmatory test. The test was run like a coupled units test except that test material and nutrient solution was added every day to the effluent from the system and this served as influent for the following day. Around 93.6% dissolved organic carbon (DOC) removal was obtained during the test, but it is not known what fraction of this is adsorbed onto sludge. Between 3.7-9.1% of the material (as DOC) left the unit in effluent. In a standard coupled units test with a retention time of 3 hours, 59% DOC removal was seen (Gerike and Jasiak, 1986).

The biodegradation of nonylphenol ethoxylate and a commercial spray adjuvant product containing 76% nonylphenol ethoxylate has been studied in soil in lab-scale tests. The system used consisted of flasks containing 50 g of dry soil, to which 10 mg (as carbon) of test substance in solution was added. The flasks were incubated in the dark at  $22 \pm 3^\circ\text{C}$  for 64 days and biodegradation (mineralisation) was measured by  $\text{CO}_2$  evolution from the system compared with controls. In some instances, parent compound analysis was also carried out. By day 64 of the experiment, 57% of the nonylphenol ethoxylate and 64% of the adjuvant had degraded to  $\text{CO}_2$ . The pass mark for complete mineralisation in the test is usually 50% (based on the fact the microorganisms generally assimilate a significant amount of the available carbon) but for the nonylphenol ethoxylate tested, a third of the carbon in the was associated with the alkylphenol chain, and so the  $\text{CO}_2$  evolution seen was not sufficient to confirm that the entire parent compound had degraded. However samples analysed on day 63 showed that no compound containing an aromatic ring or ethoxylate chain was present in the soil, indicating that complete mineralisation had occurred (Hughes et al., 1996).

### *Field data*

Several detailed studies of the behaviour of nonylphenol ethoxylates and their degradation products have been reported. Many of these refer to wastewater treatment plants in Switzerland and were carried out before controls were introduced to limit the use of nonylphenol ethoxylates in domestic products. Thus, although the data is still useful when looking at the overall behaviour of nonylphenol ethoxylates during wastewater treatment, the actual concentrations measured may not reflect the current situation in Europe.

Evidence for formation of nonylphenol from nonylphenol ethoxylates during anaerobic digestion of sewage sludge in Switzerland has been reported by Giger et al. (1984). Concentrations of nonylphenol in 30 anaerobically digested sewage sludges were found to be in the range 0.45-2.53 g/kg dry weight (mean 1.01 g/kg dry weight) compared with the much lower levels found in aerobically stabilised sewage sludges (range 0.08-0.5 g/kg dry weight; mean 0.28 g/kg dry weight). Primary and secondary sewage sludges also showed much lower levels of nonylphenol (0.09-0.15 g/kg dry weight and 0.04-0.14 g/kg dry weight respectively) than was found in the anaerobically digested sludge. Further, when raw and anaerobically stabilised sludges were

mixed in equal parts and anaerobically digested for up to 40 days, a 4-8·increase in the nonylphenol content of the sludge was seen.

Wahlberg et al. (1990) also found that the concentration of nonylphenol in anaerobically digested sludge was higher than that in secondary sludge. At one plant where sludge was sampled before and after anaerobic digestion, the nonylphenol concentration was found to be increased by around 4 times after digestion.

Recent measurements of nonylphenol concentrations in sewage sludge from the United States also show a similar increase in the nonylphenol concentration during anaerobic digestion (Williams and Varineau, 1996). Levels of nonylphenol were measured in sludges fed into the anaerobic digester and at the outlet of the anaerobic digester at 4 treatment works. The levels measured in the sludge before anaerobic digestion were 21-64, 3, 180 and 960 mg/kg and the levels measured after digestion were 380, 1,030, 940 and 540 mg/kg at the four plants respectively. In contrast, the levels of nonylphenol measured in aerobic sludges at 5 other treatment plants were in the range 1-175 mg/kg.

Brenner et al. (1987) studied the fluxes of nonylphenol, NP1EO and NP2EO through sewage treatment plants in Switzerland, focusing on the digestion/stabilisation of the sewage sludge at the plants. High levels of nonylphenol (mean 1.27 g/kg dry weight; range 0.64-2.2 g/kg dry weight) were found in samples of anaerobically digested sewage sludge from 24 plants. Significantly lower levels of nonylphenol were found in samples of aerobically stabilised sludge from 5 plants (mean 0.30 g/kg dry weight; range 0.12-0.65 g/kg dry weight). The data showed that nonylphenol accumulated in sewage sludge during anaerobic treatment of sludge. Both NP1EO and NP2EO were present in the sewage treatment works and were thought to be precursors to the formation of nonylphenol. Based on detailed measurements at one plant with anaerobic digestion of sludge it was estimated that 50% on a molar basis or 17% on a weight/weight basis of the NPnEO entering into the plant was converted to nonylphenol in the final sewage sludge.

Ahel et al. (1994b) reported results from surveys of 11 mechanical-biological wastewater treatment plants in the Glatt Valley, Switzerland. The wastewater treatment plants typically consisted of a primary clarifier for mechanical treatment, and aeration tank and secondary clarifier for biological treatment and an anaerobic digester for sewage sludge treatment. Samples were analysed for the presence of nonylphenol, NPnEO (n=1 to 20), NP1EC and NP2EC. In untreated sewage and primary effluent the main components found were generally NPnEO (n=3-20) which accounted for 82.4% of the total nonylphenol derivatives present, followed by NP1EO + NP2EO (11.5% of the total), nonylphenol (3% of the total) and NP1EC + NP2EC (3.1% of the total). In secondary effluent the composition of the nonylphenol based compounds had changed markedly, with NPnEO (n=3-20) only present in trace amounts. NP1EC and NP2EC were now the most abundant substances found (46.1% of the total), followed by NP1EO + NP2EO (21.8% of the total) and nonylphenol (3.9% of the total). Based on analysis of the various effluents and sludges in the plants, an overall budget for the nonylphenolic compounds (mainly NPnEO) entering the plant was given as:

- 19% released to the environment as NPnEC
- 11% released as NP1EO and NP2EO
- 25% released as nonylphenol (>90% of which is adsorbed onto digested sewage sludge)
- 8% released as untransformed NPnEO

Thus the overall removal of NPnEO ( $n > 2$ ) is around 92%. The majority of NPnEO, NPnEC, NP1EO and NP2EO released to the environment is via secondary effluents. Most of the nonylphenol is thought to be formed during anaerobic sludge digestion.

In another report of the behaviour of NPnEO in wastewater treatment plants in Switzerland, effluents from the various stages of treatment at 4 plants were studied in detail. When comparing the concentrations of various species seen in primary effluent as compared with secondary effluent it was seen that NPnEO ( $n = 3-20$ ) was eliminated to varying degrees in all plants (approximately 81.3%, 99.4%, 95% and 95.3% at the four plants). The concentrations of NP1EO and NP2EO were only slightly lower in secondary effluent as compared to primary effluent, and at one plant their concentration was higher in secondary effluent. The concentration of nonylphenol was always found to be lowered by activated sludge (secondary treatment), while the concentration of NP1EC and NP2EC increased in the effluent after secondary treatment. Tertiary treatment (anaerobic sludge digestion) was shown to further reduce the concentration of nonylphenol, NP1EO and NP2EO in the effluent, but had little or no effect on the concentration of NP1EC and NP2EC. Sludge samples taken during sludge digestion indicated that accumulation of nonylphenol was occurring (concentration in sludge increased by a factor of 15), while the concentration of NP1EC and NP2EC in sludge reduced slightly (Giger et al., 1987).

Very similar degradative behaviour of NPnEO has been observed in the Glatt River, Switzerland (Ahel et al., 1994c). The main input of nonylphenol based compounds into the river was thought to be from secondary effluents from municipal wastewater treatment plants. The study was undertaken in 1983-1986 using sampling campaigns that simultaneously collected 1-day composite samples from several parts of the river and secondary effluent samples from wastewater treatment plants along the river. This was carried out in such a way that the same "package" of water was sampled at each point. The most abundant nonylphenol based compounds detected were NP1EC and NP2EC, followed by NP1EO and NP2EO, then nonylphenol and finally NPnEO ( $n > 3$ ), which made up only a very small fraction of the total. The hydraulic residence time of the river was 10-15 hours and it was estimated that 85% of the NPnEO ( $n > 3$ ), 70% of the NP1EO and NP2EO and 62% of the nonylphenol were eliminated in the river (by biodegradation and/or adsorption to sediment), but there was around of 27% increase in NP1EC and NP2EC in the river. Nonylphenol was found to be a major component in sediment.

The behaviour of nonylphenol ethoxylates in sewage treatment plants in the United States has been studied (Naylor, 1992; Naylor et al., 1992). The results are shown in **Table B**. Removal of the nonylphenol ethoxylate in the plants was generally  $> 92\%$ . At the Midwest wastewater treatment plant anaerobically digested sludge was sampled for nonylphenol and it was found to be present at concentrations of 1,800-2,800  $\mu\text{g}/\text{kg}$ , which was reported to represent 0.1% of the nonylphenol (it is not clear from the paper on what this percentage is based). Lower levels of nonylphenol (19-43 and 740  $\mu\text{g}/\text{kg}$ ) were found in sludge from the two wastewater treatment plants sampled in the Northwest, but it is not clear from the report if this is secondary sludge or digested sludge.

**Table B** Removal of NPnEO in wastewater treatment in the United States

Location	Influent type	Sampling date	Nonylphenol ethoxylate		
			Influent conc.	Effluent conc.	% removal
South-eastern United States	Textile and furniture industries	May 1988	1,780 µg/l	103 µg/l	94.1
	Domestic	May 1988	2,400 µg/l	71 µg/l	97.0
Midwest United States	Cleaning product manufacturing and domestic	August 1990	1,540 µg/l	43 µg/l	97.2
		March 1991	1,130 µg/l	85 µg/l	92.5
Northwest United States	Wood pulp mill 1	June 1990	4,700-12,200 µg/l	170-250 µg/l	97.5
	Wood pulp mill 2	September 1989	13,400 µg/l	2,170 µg/l	84.3

Di Corcia et al. (1994) studied the behaviour of nonylphenol ethoxylates and nonylphenol in a mechanical-biological wastewater treatment plant in Italy over the period of 1 year. The average removal of nonylphenol ethoxylate by the plant was 94.3%. Based on the concentrations of nonylphenol in influent compared with effluent, the removal of nonylphenol was around 93%, mainly by adsorption onto sludge.

Kubek and Naylor (1990) used a simplified extraction technique to look at the behaviour of NPnEO in a US wastewater treatment plant. They reported that the presence of oxygen in the extraction and work-up procedure could lead to a skewing of the NPnEO oligomer distribution to those with a low value of n and this could, in part, explain the accumulation of these compounds seen in other results. Using the revised technique, influent and effluent NPnEO (n=1-18) concentrations were measured, which indicated a 93-98% removal of NPnEO during treatment. The oligomer distribution in effluent showed a slight difference (a slight increase in the proportion of low n NPnEO oligomers) when compared with the influent. Nonylphenol was detected in the effluent at concentrations of 0.5-4.0 µg/l, but no influent concentrations were measured so it is not possible to say anything about the possible formation and/or removal during wastewater treatment.

The degradation of nonylphenol ethoxylates in soil has been examined in field trials (Küchler et al. (1994). Over the period of 1 year, 10 areas of land were treated with two different sewage sludges or sanitary effluent containing nonylphenol ethoxylate (and also nonylphenol) at recommended rates. After application, the sewage sludge was incorporated into the top 5 cm of the soil. Subsequently soil samples were collected from various depths (0-10 cm, 10-20 cm and 20-30 cm) and analysed for the presence of nonylphenol and nonylphenol ethoxylates. The concentrations of nonylphenol ethoxylate rapidly decreased, with no compound being detected after 20 days. No leaching of nonylphenol ethoxylate was seen from the top (0-10 cm layer) indicating that removal was by biodegradation. An initial increase in the concentration of nonylphenol over the first 10 days of the experiment was seen, indicating that it was possibly formed from the degradation of nonylphenol ethoxylate, but no nonylphenol was detected after 20 days, indicating that this itself degraded.

### Experiments using octylphenol ethoxylates

Although the following tests were carried out with highly branched octylphenol based compounds, it is likely that the nonylphenol based compounds would behave similarly.

Ball et al. (1989) carried out an extensive study of the biodegradation of octylphenol ethoxylates (OPnEO) and the corresponding octylphenol ethoxylate carboxylic acids (OPnEC) under a variety of aerobic and anaerobic conditions. The OPnEO material used was a mixture of 13% OP1EO, 40% OP2EO, 29% OP3EO, 14% OP4EO and 4% OP5EO. In addition, the corresponding OPnEC (same relative composition of oligomers) was used in some test. Three test systems were used. Firstly 500 µg/l of the OPnEO was incubated at 20°C in BOD dilution water seeded with 180 mg/l of suspended solids from an activated sludge basin of a municipal wastewater treatment plant. Secondly, 10 mg/l of the OPnEO or OPnEC was incubated at 20°C in dilution water containing settled primary effluent from the wastewater treatment plant. Finally the same compounds (concentration around 25 µmole/l) were incubated at 35°C in an anaerobic medium seeded with anaerobic organisms maintained on a mixture of primary effluent and activated sludge. At periods throughout the experiment the media were analysed for the presence of degradation products. The results are shown in **Tables C to G**.

Table C Results of incubation of OPnEO with activated sludge

Components	Concentration (µ mole/l)					
	0 hr	2hr	6 hr	12 hr	18 hr	24 hr
<b>Starting compounds</b>						
OP1EO	0.18	0.05	0.03	0.02	0.01	tr
OP2EO	0.54	0.20	0.14	0.03	0.01	tr
OP3EO	0.40	0.06	0.02	nd	nd	nd
OP4EO	0.18	nd	nd	nd	nd	nd
OP5EO	0.10	nd	nd	nd	nd	nd
Total starting compounds	1.4	0.31	0.19	0.05	0.02	tr
<b>Products</b>						
Octylphenol		tr	tr	tr	tr	tr
OP1EC		0.26	0.17	0.19	0.23	0.14
OP2EC		0.61	0.39	0.50	0.85	0.72
OP3EC		0.19	0.12	0.08	0.20	0.15
Total components	1.4	1.4	0.87	0.82	1.3	1.0

Notes nd = not detected

tr = trace amount (<0.005 µ mole/l)

Table D Results of incubation of OPnEO with primary sewage

Components	Concentration ( $\mu$ mole/l)						
	day 0	day 2	day 5	day 17	day 36	day 64	day 127
<b>Starting compounds</b>							
OP1EO	3.6	2.3	2.9	0.13	nd	nd	nd
OP2EO	11	19	21	26	5.1	0.04	nd
OP3EO	8.0	0.58	0.33	0.19	0.03	nd	nd
OP4EO	3.7	tr	tr	nd	nd	nd	nd
OP5EO	0.88	nd	nd	nd	nd	nd	nd
Total starting compounds	27	22	24	26	5.1	0.04	nd
<b>Products</b>							
Octylphenol		nd	0.01	0.01	nd	nd	nd
OP1EC		nd	0.07	nd	nd	nd	nd
OP2EC		0.03	0.13	0.03	nd	nd	nd
OP3EC		tr	nd	0.03	0.03	0.02	0.03
Total components	27	22	24	26	5.2	0.06	0.03

Notes: nd = not detected

tr = trace amount (<0.005  $\mu$  mole/l)

Table E Results of incubation of OPnEC with primary sewage

Components	Concentration ( $\mu$ mole/l)						
	day 0	day 2	day 5	day 17	day 36	day 64	day 127
<b>Starting compounds</b>							
OP1EC	0.32	0.35	0.32	tr	nd	nd	nd
OP2EC	9.2	6.6	7.6	0.05	nd	0.01	nd
OP3EC	7.7	5.5	6.5	6.3	5.5	2.8	0.14
OP4EC	4.3	2.6	3.4	3.4	3.4	1.3	nd
OP5EC	2.0	1.0	1.3	1.2	1.3	0.01	nd
OP6EC	0.69	0.99	0.92	1.1	0.38	nd	nd
Total starting compounds	24	17	20	12	11	4.1	0.14
<b>Products</b>							
Octylphenol		0.02	0.01	0.01	0.01	0.01	nd
OP1EO		0.03	0.03	0.20	0.02	nd	nd
OP2EO		0.01	0.01	0.19	0.40	0.01	nd
OP3EO		nd	nd	tr	0.03	nd	nd
Total components	24	17	20	12	11	4.1	0.14

Notes:nd = not detected

tr = trace amount (<0.005  $\mu$  mole/l)



Table F Results of incubation of OPnEO under anaerobic conditions

Components	Concentration ( $\mu$ mole/l)						
	day 0	day 10	day 23	day 46	day 66	day 116	day 190
<b>Starting compounds</b>							
OP1EO	3.8	26	18	2.8	0.51	0.15	tr
OP2EO	11	0.23	0.03	nd	nd	nd	nd
OP3EO	8.3	0.26	nd	nd	nd	nd	nd
OP4EO	3.8	tr	nd	nd	nd	nd	nd
OP5EO	0.91	0.37	nd	nd	nd	nd	nd
Total starting compounds	28	27	18	2.8	0.51	0.15	tr
<b>Products</b>							
Octylphenol		0.19	1.1	2.2	5.1	2.7	2.2
OP1EC		tr	0.39	nd	nd	nd	nd
OP2EC		1.0	0.85	0.91	0.89	1.1	0.82
OP3EC		0.72	0.44	0.56	0.48	0.33	0.11
OP4EC		nd	nd	0.13	0.17	0.17	0.06
Total components	27	22	24	26	5.2	0.06	0.03

Notes:nd = not detected

tr = trace amount (<0.005  $\mu$  mole/l)

Table G Results of incubation of OPnEC under anaerobic conditions

Components	Concentration ( $\mu$ mole/l)						
	day 0	day 10	day 23	day 46	day 66	day 116	day 190
<b>Starting compounds</b>							
OP1EC	0.34	nd	nd	nd	nd	nd	nd
OP2EC	9.7	9.8	8.7	8.6	7.9	9.4	12
OP3EC	8.1	7.8	6.6	6.2	5.1	7.0	7.7
OP4EC	4.6	2.8	1.9	2.2	1.5	2.2	2.6
OP5EC	2.1	-	-	-	-	-	-
OP6EC	0.73	nd	nd	nd	nd	nd	nd
Total starting compounds	26	20	17	17	15	19	22
<b>Products</b>							
Octylphenol		0.27	0.19	0.19	0.19	0.17	0.17
OP1EO		0.24	0.13	0.11	0.07	0.05	0.04
Total components	26	21	18	17	15	19	23

Notes:nd = not detected

tr = trace amount (<0.005  $\mu$  mole/l)

- = not determined due to interferences

The experiments using activated sludge inoculation (**Table C**) the results clearly show that the OPnEO degrade to OPnEC (mainly OP2EC). The total mass balance indicates that little or no degradation to mineralised products (CO<sub>2</sub>, water etc.) was occurring in the system. Results from the primary sludge inoculated tests (**Table D**) show that the longer chain OPnEO (n≥3) degraded rapidly (within 2 days) with a concurrent increase in OP2EO. Degradation of OP1EO and OP2EO appeared to require an adaptation period of approximately 5 and 17 days respectively before degrading to unidentified products. Some oxidation of the OPnEO to OPnEC did occur, however this appears to be only a very minor route of degradation for OPnEO with n>3 since little or no OPnEC with n>3 were seen in the test (the results from **Table D** indicate that these OPnEC compounds become more resistant to biodegradation as n increases and so they would have been detected if they were a significant metabolic product of OPnEO). The data in **Table E** indicate that the OPnEC with n=1 or 2 are degraded to some extent under the conditions used, with the possible formation of small amounts of octylphenol and OPnEO. Under anaerobic conditions OPnEO was degraded firstly to mainly OP1EO within 10 days and this was then gradually degraded into octylphenol which appeared to be stable under the conditions of the test (**Table F**). The OPnEC were generally not degraded under anaerobic condition, with the exception of OP1EC which was rapidly degraded (**Table H**). Again octylphenol appeared to be produced during the degradation. In summary the results of Ball et al. (1989) clearly show that under aerobic conditions OPnEO are transformed to relatively stable OP2EO and OPnEC (n=2-3) which are then transformed further to unidentified products after an acclimation period. Under anaerobic condition degradation was not complete even after 190 days incubation. Octylphenol was a major degradation product formed. Although these results were obtained with octylphenol derivatives, similar trends would be expected with nonylphenol derivatives.

Lashan et al. (1966) carried out tests using radiolabelled p-tert. octylphenol ethoxylate (10 EO groups) using bench-scale activated sludge units. The compound used was <sup>14</sup>C-labelled in the ethoxylate chain and <sup>3</sup>H-labelled on the phenol ring to distinguish between degradation of the ethoxylate chain and the alkylphenol parts of the molecule. In shake-flask cultures inoculated with acclimated activated sludge, >90% primary biodegradation of the octylphenol ethoxylate was seen in 7 days. In the bench-scale activated sludge units operating with an hydraulic retention time of either 3 or 6 hours and inoculated with fresh sludge, acclimation of the units occurred within 5-11 days and after this time a high level (90-95%) of removal (primary degradation) of the octylphenol ethoxylate (concentration 20 mg/l in influent) was seen. Experiments using the radiolabelled compound showed that degradation of the octylphenol ethoxylate occurred almost entirely by degradation of the ethoxylate chain, with little or no degradation of the phenolic ring being seen. In a further experiment, the radiolabelled octylphenol ethoxylate was fed into a model anaerobic septic tank-percolation field system over several months. The hydraulic residence time of this system was 67 hours. The octylphenol ethoxylate showed overall degradation based on loss of foaming tendency and cobalt thiocyanate analysis of 84-93%, with an average loss of <sup>14</sup>C from the system of 46%. Again, no loss of <sup>3</sup>H was observed, indicating that little or no degradation of the phenolic ring was occurring. The results were again consistent with degradation of the ethoxylate chain only.

### Conclusion

All the available data appear to be reasonably consistent in the findings of nonylphenol ethoxylate degradation during surface water and sewage treatment.

The primary biodegradation of nonylphenol ethoxylates appears to occur rapidly during wastewater treatment, especially with acclimated microorganisms. The first step for NPnEO

(where  $n > 3$ ) appears to be rapid removal of the ethoxylate groups to form NP1EO and NP2EO. Once formed these can then be oxidised to form NP1EC and NP2EC or are degraded to nonylphenol or other degradation products where the aromatic ring is broken, leading to complete mineralisation. The NP1EC and NP2EC are then degraded further to mineralisation products (a recent report indicated that these two compounds exceeded 60% theoretical CO<sub>2</sub> generation in 28 days during a OECD 301B (Modified Sturm) ready biodegradation test, but did not fulfil the 10 day window (Williams et al., 1996)).

Under aerobic conditions, oxidation of NP1EO and NP2EO to NP1EC and NP2EC appears to be favoured over formation of nonylphenol. However, under anaerobic conditions, much larger amounts of nonylphenol appear to be formed from NP1EO and NP2EO.

**Table H** summarises the relevant data when considering degradation during wastewater treatment.

From the available data reasonable worst-case assumptions for the fate of nonylphenol ethoxylates during anaerobic wastewater treatment would be (based on % weight):

Mineralised/highly degraded	45%
Released as NP1EO/NP2EO/NPnEC in effluent	25%
Released as NPnEO ( $n > 3$ )	8%
Release as nonylphenol in effluent	2.5%
Nonylphenol in anaerobically digested sludge	19.5%

The nonylphenol ethoxylates released to the environment (NP1EO, NP2EO, NPnEO, NPnEC) will undergo further degradation. The information available indicates that nonylphenol is only a minor product from the aerobic degradation of these compounds in river water (indeed often no trace of nonylphenol was seen in river die-away test etc.) and soil. Thus as a worst case it could be assumed that a further 2.5% of the NPnEO released to the environment will eventually end up as nonylphenol. The overall conversion is likely to have a fairly long half-life, probably of the order of 100 days in water and 30 days in soil.

Table H Summary of behaviour of nonylphenol ethoxylates during wastewater treatment

Substance tested	Type of test	Results	Reference
NPnEO (n=9)	Coupled Units test	48.6% DOC removal; 97% primary degradation seen in OECD screening test.	Gerike, 1987
NPnEO (n=9)	Semi-continuous activated sludge test	Overall 93% removal of the NPnEO; 20.8% was mineralised to CO <sub>2</sub> , 23.1% converted to highly degraded metabolites, 26% in effluent as NPnEC. Conversion to nonylphenol could be around 4.5% of the NPnEO (by weight), of which around ¼ was found in effluent.	Varineau et al., 1996a
NPnEO (n=8; 10; 14; 16; and 30)	Lab-scale activated sludge system	82-96% removal of the original surfactant was seen.	Rudling and Solyom, 1974.
NPnEO (n=9)	Lab-scale bioreactors attached to sewage treatment plant, United States	>95% removal of the NPnEO. 35-50% of the hydrophobe was discharged in effluent from the system, probably as NPnEO/NPnEC, with n=0-3.	Kravetz et al., 1982).
NPnEO	Sewage treatment plants, Switzerland	50% on a molar basis and 17% on a mass basis of the NPnEO entering the plant was estimated to form nonylphenol ethoxylate during anaerobic sludge digestion.	Brenner et al., 1987.
NPnEO	Sewage treatment plants, Switzerland	Overall removal on NPnEO (n>2) is 92%. Of the total entering the plant: 19% release via effluent as NPnEC 11% release via effluent as NP1EO + NP2EO 25% released as nonylphenol (of which 90% is adsorbed onto digested sludge >2.5% released as nonylphenol in effluent) 8% released untransformed	Ahel et al., 1994b
NPnEO	Sewage treatment plants in the United States	>92% removal of the original surfactant	Naylor et al. (1992); Naylor (1992); Kubeck and Naylor (1990).

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## Appendix 2 EUSES Modelling

In the EUSES modelling that was used for the calculation of the PECs, the use patterns and life cycle stages are assigned to the following release scenarios from the risk assessment report. The EUSES export file can be downloaded from the ECB website: <http://ecb.jrc.it>

EUSES Use Pattern	EUSES Life Cycle Stage	RAR Scenario
1	Production	NP Production Site A
	Formulation	NP Production Site B
	Processing	NP Production Site C
	Private Use	NP Production Site D
	Recovery	
2	Production	Nonylphenol/formaldehyde resin production
	Formulation	TNPP production
	Processing	Epoxy resin production
	Private Use	Use in other plastic stabilisers
	Recovery	Phenolic oxime production
3	Production	NPEO Production Company B
	Formulation	NPEO Production Company C Sites 1 and 2
	Processing	NPEO Production Company C Site 3
	Private Use	NPEO Production Company D Site 1
	Recovery	NPEO Production Company D Site 2
4	Production	NPEO Production Company E
	Formulation	NPEO Production Company F
	Processing	NPEO Production Company G
	Private Use	
	Recovery	
5	Production	NPEO Formulation (Large)
	Formulation	NPEO Formulation (Medium)
	Processing	NPEO Formulation (Small)
	Private Use	NPEO Captive use by chemical industry
	Recovery	NPEO Electrical engineering industry
6	Production	NPEO Industrial and institutional cleaning
	Formulation	NPEO Leather processing (large)
	Processing	NPEO Leather processing (Average)
	Private Use	NPEO Metal extraction
	Recovery	
7	Production	NPEO Photographic industry (Large)
	Formulation	NPEO Photographic industry (Small)
	Processing	NPEO Polymer industry
	Private Use	NPEO Pulp, paper and board industry
	Recovery	NPEO Textile industry
8	Production	NPEO Paint manufacture
	Formulation	NPEO Paints (Domestic emulsion use)
	Processing	NPEO Paints (Industrial use)
	Private Use	NPEO Civil engineering
	Recovery	

### Appendix 3 Comparison of EU Nonylphenol Risk Assessment Report and US EPA RM-1 document for Para Nonylphenol (USEPA, 1996)

**The EU risk assessment concludes that there are widespread risks to the aquatic environment arising from the life cycle of this substance. The US assessment, however, concludes that “risks do not appear widespread, but there are some impacted areas where aquatic organisms could be affected.” Essentially the same data are used in both assessments, so this appendix briefly examines the reasons for this difference.**

#### PNEC or concern concentration

The US concern concentrations are 1 µg/l and 3 µg/l. The 1 µg/l value comes from a chronic test on the mysid shrimp, which gave a NOEC of 3.9 µg/l and a LOEC of 6.7 µg/l. The GMATC derived from this is 5.1 µg/l (geometric mean); a margin of exposure of 10 is applied to give a concern concentration which is rounded to 1 µg/l.

The value of 3 µg/l is the NOEC from the littoral zone enclosure study (effectively an in-situ mesocosm), with no margin applied as it is considered to be an actual field study.

The PNEC in the EU risk assessment is derived from an algal NOEC of 3.3 µg/l (this study is not included in the US report), with an assessment factor of 10 to give a PNEC of 0.33 µg/l.

The EU RAR discusses all of the data used to derive the concern concentrations; it uses the littoral study as supporting evidence for the choice of the NOEC for the PNEC. If the EU method was applied to the US data the PNEC would be 0.39 µg/l, as the NOEC from the shrimp study would have been used rather than the GMATC value. Hence although there appears to be a difference between 0.33 and 1 µg/l, this is due principally to different treatments of the data and not the data themselves.

#### *Exposure*

The RM-1 document assessment is based on measurements in selected rivers, including ones expected to receive significant inputs of nonylphenol. The highest measured concentration was 0.64 µg/l, the 95%ile value was 0.35 µg/l and the mean value was 0.12 µg/l (not detected values were treated as half the detection limit, i.e. 0.055 µg/l).

The assessment then considered the rivers with the highest concentrations, and calculated the levels expected under a range of conditions. For those where the concentration under low flow exceeded the concern concentration, a PDM3 analysis was carried out to estimate for how many days this level would be exceeded. Three rivers exceeded the 1 µg/l level for more than 20 days, and one of these was calculated to exceed the 3 µg/l level for more than 20 days. These results were interpreted as low risk.

In the EU assessment the aim is to associate levels in the environment with specific activities. Although the rivers targeted in the US were expected to have high inputs of nonylphenol, the source of these inputs was not specified. So although the actual monitoring results are included in the EU RAR, they are not used as a basis for the exposure assessment. In addition, monitoring data for the EU, although not as widespread, tend to show higher levels. The result is that the



assessment is based on the calculated levels (which relate to the specific activities), supported by the available measurements.

Note: Two rivers in the US had mean measured levels higher than the EU PNEC. Five rivers had calculated harmonic mean concentrations higher than the PNEC. Twenty-one rivers had calculated 7Q10 (low flow) concentrations higher than the PNEC. In other words, 70% of the sampled rivers would exceed the EU PNEC under low flow conditions. In the EU assessment scheme such results would have been interpreted as constituting a risk.

#### Sewage treatment works (STWs)

The RM-1 document assessment compares data on US and European STWs and comments that the US plants seem to be more efficient. The EU RAR contains an annex (Appendix 1) discussing removal in STWs, and when compared on the same basis concludes that the differences are not marked. The US data have been included in the derivation of values for the fate of nonylphenol in STWs for calculating concentrations.



European Commission

**EUR 20387 EN - European Union Risk Assessment Report  
4-Nonylphenol (branched) and nonylphenol, Volume 10**

*Editors: B.G. Hansen, S.J. Munn, J. De Bruijn, S. Pakalin, M. Luotamo, F. Berthault, S. Vegro, C.J.A. Heidorn, G. Pellegrini, K. Vormann, R. Allanou, S.Scheer.*

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Environment and quality of life series

The report provides the comprehensive risk assessment of the substance 4-Nonylphenol (branched) and nonylphenol. It has been prepared by The United Kingdom in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to man and the environment, laid down in Commission Regulation (EC) No. 1488/94.

The evaluation considers the emissions and the resulting exposure to the environment and the human populations in all life cycle steps. Following the exposure assessment, the environmental risk characterisation for each protection goal in the aquatic, terrestrial and atmospheric compartment has been determined. For human health the scenarios for occupational exposure, consumer exposure and humans exposed via the environment have been examined and the possible risks have been identified.

The human health risk assessment for 4-nonylphenol, branched and nonylphenol concludes that there is at present concern for workers. There is at present no concern for consumers. For humans exposed via the environment the risk assessment concludes that there is at present a need for further information on emissions to the local environment during production and use of nonylphenol. The risk assessment for the environment concludes that there is at present concern for the atmosphere, aquatic ecosystem, terrestrial ecosystem, for top predators via accumulation up the food chain and for micro-organisms in the sewage treatment plant.

The conclusions of this report will lead to risk reduction measures to be proposed by the Commission's Committee on risk reduction strategies set up in support of Council Regulation (EEC) 793/93.

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