European Union Risk Assessment Report

TRIS (NONYLPHENYL) PHOSPHITE

CAS-No.: 26523-78-4
EINECS-No.: 247-759-6

RISK ASSESSMENT

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RISK ASSESSMENT

Draft of October 2008

France

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Rapporteur for the risk assessment of tris(nonylphenyl) phosphite is the Ministry of Ecology and Sustainable Development as well as the Ministry of Employment and Social Affairs in co-operation with the Ministry of Public Health. Responsible for the risk evaluation and subsequently for the contents of this report is the rapporteur.

The scientific work on this report has been prepared by the National Institute for Industrial Environment and Risks (INERIS) and by the Chemical Risk Assessment Bureau (BERPC).

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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[1] 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[2], which is supported by a technical guidance document[3]. 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.

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Barry Mc Sweeney
Director-General
Joint Research Centre

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

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[1] O.J. No L 084 , 05/04/199 p.0001 – 0075

[2] O.J. No L 161, 29/06/1994 p. 0003 – 0011

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

0 OVERALL RESULTS OF THE RISK ASSESSMENT

CAS Number:	26523-78-4
EINECS Number:	247-759-6
IUPAC Name:	Phenol, nonyl-, phosphite (3:1)

Environment

Section not updated, see section 3.3.

Sections highlighted in grey in the document are pending information update from the Industry.

Human exposed via the environment

This section will be updated taking into account the refinement of the other parts of the risk assessment.

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1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION OF THE SUBSTANCE

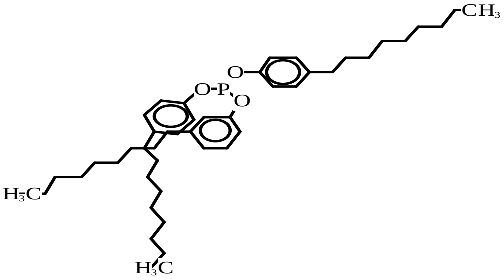
CAS No: 26523-78-4

EINECS No: 247-759-6

IUPAC Name: Phenol, nonyl-, phosphite (3:1)

Molecular formula: $C_{45}H_{69}O_3P$

Structural Formula:



Molecular weight: 689 $g.mol^{-1}$

Synonyms and tradenames: Alkanox TNPP, Doverphos, DP4, DP4HP, Lowinox TNPP, Irgafos TNPP, Tris(monononylphenyl)phosphite, Tris(nonylphenyl)phosphite, Weston 399, Weston TNPP, Irgastab CH 55, Naugard TNPP, Polygard, Polygard HR, Polygard LC, TNPP, Trisnonylphenylphosphit.

In this assessment, the name Tris(nonylphenyl)phosphite (TNPP) will be used for the substance as this is the most common name.

1.2 PURITY/IMPURITIES, ADDITIVES

1.2.1 Purity

There are two grades of TNPP that are sold in the marketplace.

The purity of the standard TNPP is reported as ca. 95 – 100% w/w. The following impurities may be found in standard TNPP :

- Nonylphenol (CAS 25154-52-3)	< 5% w/w,
- Phenol (CAS 108-95-2)	< 0.1% w/w,
- Di(nonylphenyl)phenylphosphite (CAS 25417-08-7)	0.05% w/w,

A high purity grade of TNPP was introduced into the market in the late 1990s. The impurities found in the high purity TNPP are:

- Nonylphenol (CAS 25154-52-3)	< 0.1% w/w,
- Phenol (CAS 108-95-2)	< 0.1% w/w,
- Di(nonylphenyl)phenylphosphite (CAS 25417-08-7)	0.05% w/w,

1.2.2 Additives

1,1’,1’’-nitrilotripropan-2-ol (CAS No: 122-20-3), also known as tri-isopropanol amine, or TIPA, is an additive commonly found in TNPP in the proportion of 0.5 to 1% w/w. TIPA acts as an acid scavenger and increases the hydrolytic stability of TNPP.

1.3 PHYSICO-CHEMICAL PROPERTIES

1.3.1 Physical state (at ntp)

TNPP is a viscous liquid at room temperature.

1.3.2 Melting point

Instead of a melting point, a pour point of 6°C ± 3°C was determined (Reimer&Associates, 2001c). A melting point could not be observed using the differential scanning calorimetric (DSC) method because an endothermic event was not observed in the heat flow *vs* temperature plot. The pour point (the lowest temperature at which the test substance is first observed to flow on warming) is an appropriate measurement for viscous liquid substances. The test was conducted according to ASTM Method D97, as recommended in the OECD 102 guideline.

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1.3.3 Boiling point

The boiling point was reported as >303°C (Reimer&Associates, 2001a). The test method was based on OECD 103 guideline. Bubbling was observed for the first 1 to 2 seconds of heating, and then stopped. This was probably due to the boiling of a minor component (<0.1%) present in the test substance. Consequently a new study was undertaken to assess the true boiling point. The TNPP producers have determined that TNPP will begin to degrade before boiling. According to a Thermal Gravimetric Analysis (TGA) of TNPP, the phosphite has an onset of degradation at 322°C under nitrogen.

1.3.4 Relative density

The relative density has been quoted at 0.98 $g.cm^{-3}$ at 20°C (Crompton, 2003).

1.3.5 Vapour pressure

A vapour pressure was estimated using structure activity relationships models developed by the U.S. Environmental Protection Agency and Syracuse Research Corporation (EPIWIN, v. 3.10, US EPA and Syracuse Research Corporation, 2001). The vapour pressure was estimated to 5×10^{-12} Pa (Staples, 2001).

A much higher value of 0.047 Pa at 20°C was extrapolated from results obtained by isoteniscope (method ASTM D2879) at temperatures ranging from 125 to 375 °C (Phoenix_Chemical_Laboratory, 1997). These measured values are displayed in Table 1.3-1.

Table 1.3-1: Vapour pressure data for TNPP (Phoenix Chemical Laboratory, 1997)

Temperature °C	Vapour Pressure (Pa)
125	22.7
150	65.3
175	160
200	373
225	747
250	1533
275	2800
300	4666
325	8133
350	15330
375	65330

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A strong relation between the temperature (1/T) and the vapour pressure is found. Excluding the last value measured at 375°C, the plot of the above results gives a linear regression with a good reliability (see Figure 1-1). Vapour pressures of respectively 0.039 Pa and 0.058 Pa at 20°C and 25°C could be derived from this equation. These results are consistent with the extrapolated value of 0.047 Pa at 20°C found in the study summary in the IUCLID file and for which no information on the extrapolation method was available.

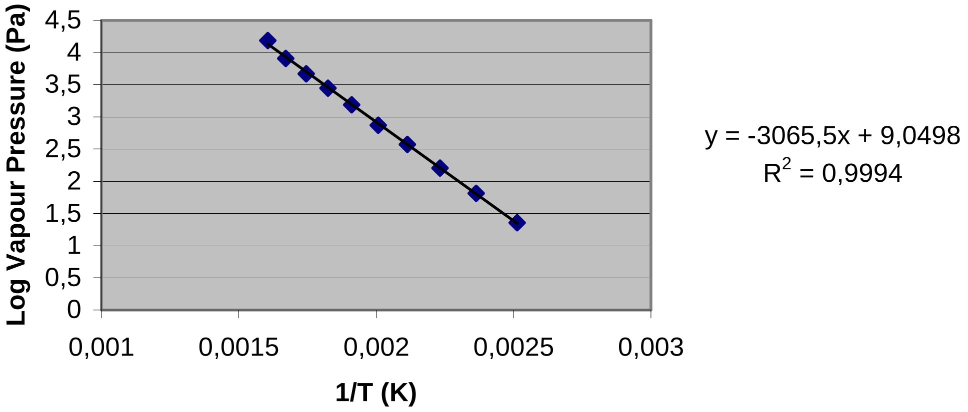

Figure 1-1: linear regression between the temperature (1/T) and the measured vapour pressures

The isoteniscope method is recommended for the measurement of vapour pressures between 10^2 and 10^5 Pa. The extrapolated value is three orders of magnitude below this range. However, almost all of the data used for the extrapolation were included in the valid range for vapour pressure.

There is speculation that the higher volatility reported in the 1997 study by Phoenix Chemical is due to the presence of high levels of nonylphenol as an impurity. To more accurately determine the vapour pressure of high purity TNPP, Industry commissioned a new vapour pressure determination study with standard TNPP and high purity TNPP. The results of this evaluation are reported in Table 1.3-2 (Phoenix Chemical Laboratory, 2007).

Table 1.3-2: measurements of vapour pressures (in Pa) for two grades (standard and high purity (HP)) of TNPP, nonylphenol (NP) and diisodecylphthalate (DIDP)

Temperature (°C)	**DP4**	**DP4HP**	**NP**	**DIDP**
0	0.27	0.93	12.67	2.93
20	**1.01**	**2.40**	40.00	8.00
38	2.80	5.07	95.99	16.67
66	11.73	14.67	333.30	49.33
93	37.33	34.66	933.24	122.65
121	102.66	71.99	2 199.78	259.97
149	253.31	139.99	4 932.84	519.95
177	573.28	253.31	9 732.36	959.90
204	1 119.89	419.96	17 464.92	1 599.84
232	1 999.80	639.94	29 997.00	2 533.08
260	3 333.00	959.90	50 661.60	3 799.62
288	5 732.76	1 339.87	89 324.40	5 732.76
316	8 665.80	1 933.14	-	17 331.60
343	17 331.60	4 666.20	-	-
Decomposition (°C)	338	334	243	302

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During this study on vapour pressures, several substances have been tested: two grades of TNPP, i.e. Doverphos 4 (DP4 containing around 2.5% NP as impurity) and Doverphos 4 Hi Pure (DP4HP, with less than 0.1% NP remaining as impurity), nonylphenol (NP) and diisodecylphthalate (DIDP). The latter compound has been tested in order to obtain comparable data between TNPP and DIDP which is taken as reference for low volatile compounds in the OECD Emission Scenario Document on plastic additives (OECD, 2004), see section 3.1.2.2.

The hypothesis of NP present in TNPP during the test would have contributed to the measurement of a higher vapour pressure (NP is more volatile than TNPP) is not fulfilled based on these results (at least for the lower temperatures). Vapour pressures measured during this study for TNPP are comparable with those available previously (see Table 1.3-1).

The extrapolated value of 0.058 Pa at 25°C determined above will be retained for this assessment.

1.3.6 n-octanol / water partition coefficient

The n-octanol-water partition coefficient was estimated using structure activity relationships models developed by the U.S. Environmental Protection Agency and Syracuse Research

Corporation (EPIWIN, US EPA and Syracuse Research Corporation, 2001). The log P_{ow} was estimated to 20.05 (US EPA and Syracuse Research Corporation, 2001).

According to Reimer & Associates, 2001c, it was not appropriate to conduct the partition coefficient measurement because the solubility of TNPP in water was too low (see section 1.3.7). Moreover, the reaction of TNPP with alcohol and consequently with octanol does not allow the measurement of adequate TNPP concentrations in octanol. The n-octanol / water partition coefficient was therefore calculated using the software from Advanced Chemistry Development Inc. (“ACD/LogP DB”). The result of the calculation was found to be 21.6 ± 0.6 (Reimer&Associates, 2001d).

The annex of the OECD guideline 117 presents some K_{ow} calculation methods that can be used to “provide an estimate when experimental methods cannot be applied”. However there are some limitations to the use of such methods. First, the reliability of calculation methods decreases as the complexity of the compound under study increases. Here, TNPP could be classified as a rather complex molecule with a high molecular weight and several functional groups. The domain of application of K_{ow} calculation methods is characterised in terms of chemical structures. For example, some calculation programs cannot be applied to the estimation of Kow for phosphorus compounds including phosphites. Second, the validity domain of the models is also restricted by the log K_{ow} range of their applicability. In general, clear estimates can be expected in the region of log K_{ow} 0-5. Some programs have shown good estimates for compounds with log K_{ow} > 5 but estimates for log K_{ow} around 10 or above should be considered rather as qualitative than quantitative information (TGD, Part III, Chapter 4, E.C., 2003). As an example, Table 1.3-3 presents calculation results for log Kow of TNPP obtained using several models.

Table 1.3-3: log Kow calculations for TNPP along with the validity domain of the calculation method used

Program	**Validity range***	**TNPP value**	**Remark**
CLOGP	0-5 (clear estimates in this range most of the time)	19.918	Very high LogP unrealistic in nature (this remark was associated to the result of the model) In general, CLOGP gives also better estimates with log Kow < 0.
LOGKOW (KOWWIN) Version 1.67	0-5 (clear estimates in this range most of the time)	20.05	
SPARC	>5	19.02	Better than KOWWIN and CLOGP for Kow >5.

* all estimates for Kow around 10 or above should be considered rather as qualitative than quantitative information.

Considering the high hydrophobic potential of TNPP which contains 27 aliphatic and 18 aromatic carbons, a high log Kow value could be expected for this compound. A sensitivity analysis was performed considering a range for log Kow between 6 and 20 (see Annex 1). This range takes into account both the highest result obtained using QSARs and the fact that this substance was expected to have a high log Kow based on its structure. **This section of the report is let for information as a log Kow has been experimentally estimated (Jakupca, 2007) and will be kept for risk assessment.**

Further testing for the log Kow determination

It was determined that a more appropriate approach at estimating the Kow was a HPLC method based on OECD guidelines 117 (Jakupca, 2007). The analysis of TNPP was conducted with gradient HPLC. Butyl benzene, diethylhexyl phthalate (DEHP), diisononylphthalate (DINP) and

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diisodecylphthalate (DIDP) were used as standards with known Kow's. Two percent water (98% acetonitrile) were chosen as the optimum mobile phase composition to allow the standards to be separated as well as keeping the retention time of TNPP to less than 90 minutes. The retention times of the standards were measured and the capacity factors calculated according to k = $(t_r - t_0)/t_o$ where t_r is the retention time of the analyte and t_o is the dead time/volume of the column or the retention time of solvent. The Kow of the standards were then plotted versus capacity factors, and a calibration curve was calculated using regression analysis. The capacity factor for TNPP was then measured, and its Kow was predicted based on extrapolation to the calibration curve.

Table 1.3-4 Retention time and capacity factor of standards and TNPP

Sample	Kow	Retention Time	Capacity Factor, k	Log k
Solvent		3.09		
Butyl Benzene	4.6	3.82	0.24	-0.63
DDT	6.5	3.97	0.28	-0.55
DEHP	7.5	5.95	0.93	-0.034
DINP	8.8	6.9	1.23	0.091
DIDP	9.3	8.52	1.76	0.24
TNPP		56.2	17.2	1.24

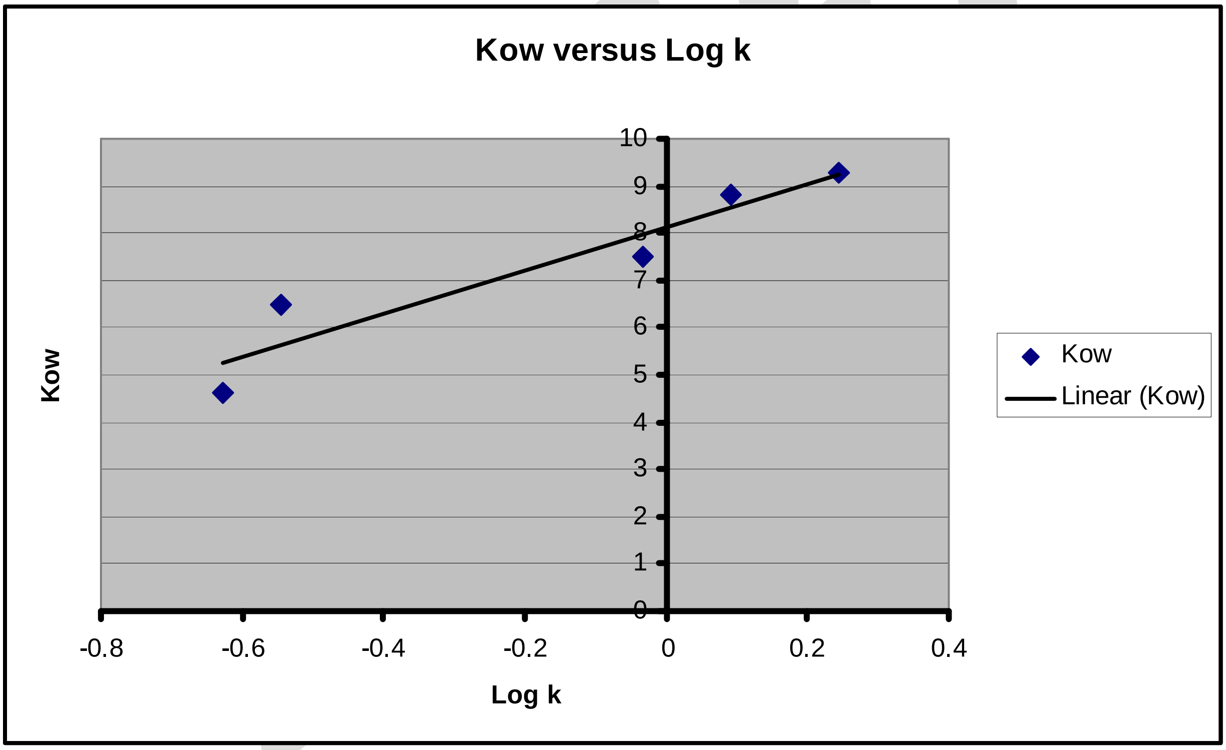

Figure 1.2 Calibration curve of standards (Butyl benzene, DDT, DEHP, DINP and DIDP)

Based on the calibration curve, TNPP was estimated with a **Kow of 14** or greater. A standard could not be found that had a Kow of 14 to test the calibration. However, it should be noted that the capacity factor of TNPP was 10 times greater than DIDP which had a Kow of 9.3. DIDP had a capacity factor only 30% larger than DINP, with a Kow of 8.8. The last three standards were closer to TNPP in terms of retention times, compared to the first two standards. If only the last three standards were used to construct the calibration curve, the Kow of TNPP would have been estimated at 16.

1.3.7 Water solubility

A water solubility was estimated using structure activity relationships models developed by the U.S. Environmental Protection Agency and Syracuse Research Corporation (EPIWIN, US EPA and Syracuse Research Corporation, 2001). The water solubility was estimated to 1.3×10^{-15} mg.L^{-1} (Staples, 2001). Other estimations have been obtained using a more recent version of EPI suite software (US-EPA and Syracuse Research Corporation, 2004): 3×10^{-16} and 6.9×10^{-7} mg/L calculated with a water solubility estimate from log Kow (WSKOW v1.41 with a log Kow of 20.05) and a water solubility estimate from fragments, respectively.

Experimental water solubility was determined by (Reimer&Associates, 2001e). The flask method based on OECD Guideline 105 was used. TNPP was not detected in the saturated aqueous test solution. Therefore it is concluded that the water solubility of TNPP is below the detection limit of the substance. This detection limit was estimated to be 0.6 mg.L^{-1}, the lowest TNPP concentration that produced a signal that is reliably distinguished from the background signal as determined from chromatograms of TNPP solutions. Therefore, the water solubility of TNPP would be < 0.6 mg.L^{-1} at 24°C.

The TNPP Industry commissioned a laboratory to develop a more sensitive analytical method for measuring TNPP so as to better approximate the true water solubility limit. Preliminary efforts were able to establish a new LOQ of 0.05 mg.L^{-1}. Solubility measurements have been attempted using this new analytical method. Considering the first results of this experiment, it seems that water solubility is still around or below this analytical limit (TNO, personal communication). This value has been used in the risk assessment but still need to be confirmed and validated.

Here again, in the absence of valid data for this endpoint, a sensitivity analysis will be made (see Annex 1) considering a range for water solubility between ~0.05 and 3×10^{-16} mg/L. This range takes into account both the highest result obtained using QSARs and the fact that this substance is expected to have a water solubility below the detection limit currently available for TNPP.

1.3.8 Flash point

Values of 183°C (internal reference, Great Lakes Chemical, Italia, Milan) and 195°C (Ciba MSDS) were reported using closed cup methods.

Besides, a value of 207°C was reported using the Pensky-Martin apparatus (closed cup) (Pittsburgh_Testing_Laboratory, 1978). This last value will be retained in this risk assessment because the analytical report was available.

1.3.9 Autoflammability

In a MSDS by Uniroyal, a value of 268°C was quoted. Moreover, using the Setchkin method, a result of 440°C was found (United States Testing Company, 1990).

1.3.10 Explosivity

No result could be found in the literature on any explosion limit. However, on the basis of its chemical structure, TNPP is not expected to have explosive properties.

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1.3.11 Oxidising properties

No oxidising property was reported for TNPP (internal reference, Great Lakes Chemical, Milan, Italia).

1.3.12 Viscosity

In a product information sheet, a value of 6000 cps at 25°C is quoted (Crompton, 2003). Other values are also presented in this document showing that the viscosity goes from 15000 cps at 15°C to 18 cps at 120°C. The value at 25°C will be retained for the risk assessment.

1.3.13 Henry's Law constant

The Henry's law constant was estimated using structure activity relationships models developed by the U.S. Environmental Protection Agency and Syracuse Research Corporation (EPIWIN, v. 3.10, sub-model HENRYWIN, US EPA and Syracuse Research Corporation, 2001). At 25°C, a value of 66.1 Pa.m^3.mol^{-1} was calculated (US EPA and Syracuse Research Corporation, 2001).

The Henry's law constant can also be estimated from the ratio of the vapour pressure to the water solubility (E.C., 2003):

$$HENRY = \frac{VP \cdot MOLW}{SOL}$$

Using a vapour pressure of 0.058 Pa, a molecular weight of 689 g.mol^{-1} and a water solubility of <0.05 mg.L^{-1} the Henry's Law constant would be >799 Pa.m^3.mol^{-1}.

In the risk assessment, the sensitivity analysis performed with log Kow and water solubilities will influence the value of the Henry's Law constant. This value will consequently range between 799 and 7.99x10^{16} Pa.m^3.mol^{-1} (the highest value obtained using the QSAR result for the water solubility of 3x10^{-16} mg/L). Additional comments on the Henry's Law constant will be found in section 3.1.1.2.3 on environmental behaviour and fate.

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1.3.14 Summary of physico-chemical properties

The physico-chemical properties of TNPP used in this risk assessment are summarised in the following table:

Table 1.3-5: Physical and chemical properties of the TNPP

Property	Value	Comments
Physical state at ntp	Viscous liquid	
Molecular weight	689 g.mol^{-1}	
Melting Point	6°C ± 3°C	Instead of a melting point, a pour point (more appropriate to viscous liquids) was determined
Boiling Point	322°C	Degradation
Relative density	0.98 g.cm^{-3}	
Vapour pressure	0.058 Pa at 25°C*	extrapolated from results obtained by isoteniscope (method ASTM D2879)
Partition coefficient	Log Kow = 14	Estimated by HPLC method based on OECD guideline 117
Water solubility	Upper value: <0.05 mg.L^{-1} * Lower value: 3.10^{-16} mg/L A sensitivity analysis will be performed in this risk assessment taking into account a water solubility ranging between 0.05 and 3.10^{-16} mg/L	Upper value: a saturated solution was not obtained and the water solubility result corresponds to the detection limit of the analytical method. Lower value: value obtained using QSAR calculation
Flash point	207°C	Pensky Martin apparatus (closed cup)
Autoflammability	440°C	Setchkin method
Explosivity	TNPP is not expected to have explosive properties	On the basis of chemical structure
Oxidising properties	No oxidising property	
Viscosity	6000 cps at 25°C	
Henry's law constant	Between 799 and 1.3.10^{17} Pa.m^{3}.mol^{-1} (Cf. sensitivity analysis on water solubility)	TGD calculation

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1.4 CLASSIFICATION

1.4.1 Current classification

TNPP chemical is not listed in Annex I to Directive 67/547 EEC.

1.4.2 Proposed classification

Waiting for additional information on the toxicity of TNPP.

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2 GENERAL INFORMATION ON EXPOSURE

2.1 PRODUCTION

TNPP is produced all over the world: Unites States, Europe, India, Korea, Russia, China, etc. (Chemical Information Services, 2002). Three facilities are currently producing TNPP in Europe[4]. On the other hand, the major source of TNPP to Europe is from the United States.

2.1.1 Production process

The basic manufacturing processes used to produce TNPP are reasonably similar in the various plants in the US and Europe, except that not all plants strip out nonylphenol to the same degree. Figure 2-1 is providing an overview of a typical production process.

TNPP production is carried out in a closed system where nonylphenol (NP) and phosphorus trichloride (PCl_3) are added to the reactor (ca. 3 :1) and held at greater than 110°C to ensure all the PCl_3 is consumed. The HCl by-product is vented to an absorber. The HCL by-product can be filtered and stored for sale or use in other processes. Excess nonylphenol is stripped from the product. The stripped nonylphenol can be recycled. The product TNPP in the reactor after stripping is pumped to a storage tank for packaging and sale. The product may be packaged into drums, isotaners, rail cars, or tank trunks.

<u>Environmental release and exposure</u>

The process is fully automated (computer controlled) in a closed system. The reactor is operated under 3-5 lbs (1.4 – 2.3 kg) of pressure. The vacuum pump vent is the only potential process release to the atmosphere, and it is passed through a carbon filter. The storage tank is kept under nitrogen preventing release to the atmosphere. Nitrogen is also used during transfer and packaging.

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[4] In this report, Europe will correspond to 15 member states (EU_{15}) as data on exposure were gathered before the enlargement of the European Union in 2004.

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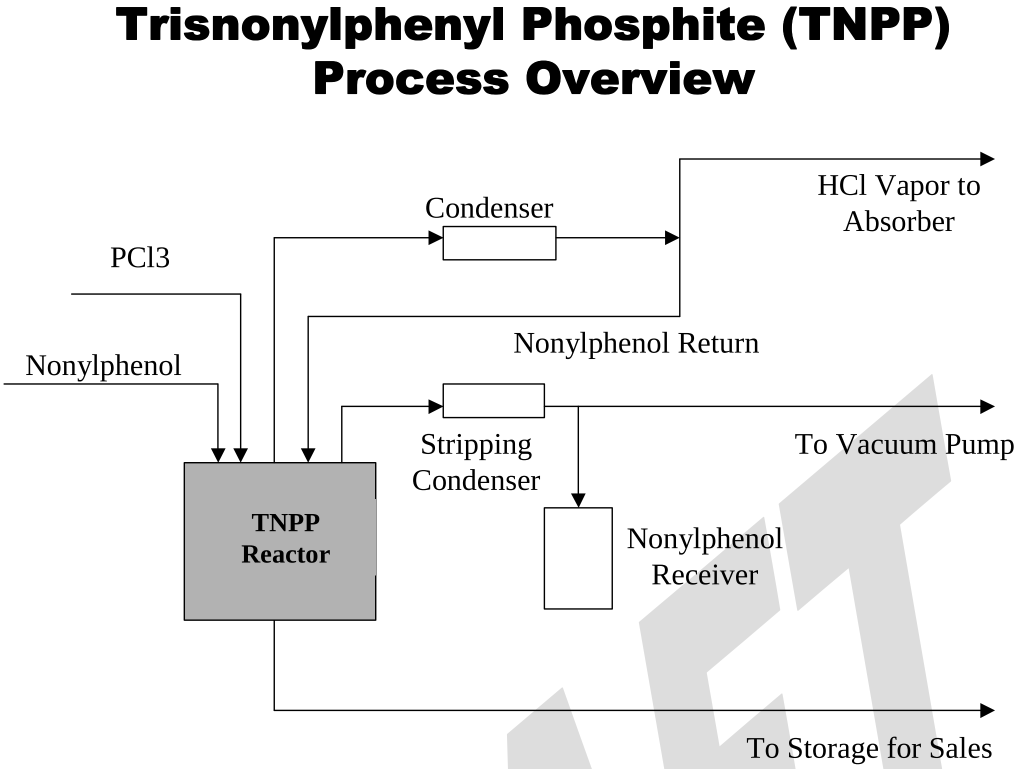

Figure 2-1: Process overview of tris(nonylphenyl)phosphite (TNPP) production

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2.1.2 Production capacity

European and North American TNPP producers are organised under the TNPP consortium, a not-for-profit trade association, whose members have commercial interest in TNPP. Information on production and imports of TNPP in EU_{15} were provided by the TNPP Consortium. Hardly any individual volume was provided for each producer/importer.

Three facilities are currently producing TNPP in EU_{15}. A fourth facility ceased TNPP production in 2001. Between 1990 and 1997, the production + import volumes were around 5,000 – 10,000 t/year.

Information is available on the combined estimate of TNPP produced within EU_{15} and imported into EU_{15} over the years 1999-2001:

- 1999 – approximately 5,565 tonnes
- 2000 – approximately 5,700 tonnes
- 2001 – approximately 6,800 tonnes

As this information is provided by the TNPP Consortium, it cannot be excluded that these volumes do not take into account shipments of product from producers in other parts of the world than Europe and North America. However, according to the TNPP Consortium, the quantity of TNPP from non-TNPP Consortium companies is not expected to be significant.

European production plants have also reported their production volumes for the year 2001. Imported volume for the same year is also available. Consequently, a total volume in EU_{15} of 8,000 t. calculated with all 2001 data will be used in this report.

2.2 USES

2.2.1 Introduction

TNPP is used as a stabiliser in the processing of various plastic and rubber products. They are used with hindered phenolic antioxidants in plastic food packaging. In the stabilisation process, TNPP is gradually oxidised and nonylphenol is released (Building Research Establishment Ltd., 2001).

TNPP is also used as a secondary antioxidant in polymer formulations (Ullmann, 1985).

An estimate of the breakdown of TNPP uses was developed based on an informal survey of North American and European manufacturers. Quantitative breakdown of TNPP uses are given in Table 2.2-1. The information pertains to sales of TNPP in 1999. It is expected that the breakdown of uses from the 1999 sales statistics is typical for the current year. Corresponding volumes are calculated using the total tonnage of 8,000 t.

Table 2.2-1: Typical quantitative breakdown of TNPP Uses

	Percentage of tonnage	Volume (tonnes)	Industrial Category / Use Category
Polyvinylchloride (PVC) film	35%	2,800	IC 11 / UC 49
Polyolefins linear low density polyethylene (LLDPE)	15%	1,200	IC 11 / UC 49
High density polyethylene (HDPE)	10%	800	IC 11 / UC 49
Rubber	37%	2,960	IC 11 / UC 49
Other/Unknown	3%	240	IC 55 / UC 0
TOTAL	100%	8,000	

In the SPIN Database (SPIN, 2007), the following industrial uses are described:

Table 2.2-2: Industrial uses of TNPP in the Nordic Countries: Denmark, Norway and Sweden (in Tonnes)

	2000	2001	2002	2003	2004	2005
Manufacture of chemicals and chemical products	27	62	4	17	20	9.5
Manufacture of rubber and plastic products	105	88	471.1	466.1	62	40
Manufacture of furniture; manufacturing n.e.c.	0.4	0.1	0.3	0.1	0.1	0.1
Manufacture of fabricated metal products, except machinery and equipment	0.2	0.1	0	0	0	0
Construction	0.2	0.1	0.2	0.2	0.2	0.2
Manufacture of wood and products of wood and cork, except furniture; manufacture of articles of straw and plaiting materials	0	0.1	0			
Total (including all other uses)	133.5	578.7	479.2	483.6	82.4	49.9

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TNPP is also mentioned in the following industrial categories: publishing, printing and reproduction of recorded media / sale, maintenance and repair of motor vehicles and motorcycles; retail sale of automotive fuel / manufacture of other transport equipment n.e.c. However, the volumes used in such industries and reported in this database could be considered as negligible (< 0.1 t/y in each country).

Besides, the following use pattern is described in the SPIN database:

Table 2.2-3: Use pattern of TNPP in the Nordic Countries: Denmark, Norway and Sweden (in Tonnes)

	2000	2001	2002
Process regulators	n. i.	n. i.	421.3
Stabilizers	120	91	46
Intermediates	1	n. i.	n. i.
Others	1	3	7
Adhesives, binding agents	0.5	1	1.7
Paints, lacquers and varnishes	0.3	0	0.1
Fillers	0	0.2	0.2
Total	122.8	95.2	476.3

n.i.: not indicated

TNPP is also mentioned in the following use categories: lubricants and additives / reprographic agents. However, the volumes used in such applications could be considered as negligible (< 0.1 t/y in each country).

From these tables, it could be stated that TNPP is mainly used as a stabiliser for the manufacture of rubbers and plastic products. The breakdown of TNPP uses described in Table 2.2-1 will be used in this risk assessment.

2.2.1.1 Industrial use

Formulation and processing steps are necessary to manufacture plastic and rubber products. Formulation could be defined as the stage where TNPP is combined in a process of blending and mixing into a polymer or into another material while during the processing step, the TNPP containing material is formed. It is not known to what extent formulation and processing may occur at the same site. In the rubber industry, these two steps can often not be viewed separately (E.C., 2003, Emission Scenario Document for IC 15: others: rubber industry).

Therefore, as a worst assumption, formulation and processing stages will be assumed to occur at one site for every use.

Without any specific information, it could be considered that TNPP is used for polymer processing, in the sub-category "processing of thermoplastics" as a processing aid. This categorisation will be used in the risk assessment for the determination of the default releases factors.

All calculations will be performed using EUSES default parameters and, when available, emission factors issued from the emission scenario document on plastics additives (OECD, 2004).

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2.2.1.2 Production of Polyvinylchloride (PVC) film

PVC containing TNPP may be used in many products like shower curtains, floorings and wall coverings.

2.2.1.3 Production of Polyolefins linear low density polyethylene (LLDPE)

LLDPE films containing TNPP are used for the manufacture of bags and food packaging. Many national regulations are covering the use of TNPP in food contact materials (Table 2.2-4)

Table 2.2-4: Global food contact regulations specific to TNPP

Country	Regulation
USA	Food and Drug Administration (FDA) – 21 CFR Part 178.2010
Japan	Self-restrictive Requirements on Food-Contact Articles Japan, Hygienic Olefin and Styrene Plastics Association (JHOSPA) (March 1996), Section A4-2, maximum 1.2%
European Union	Plastics Directive 2002/72/EC, pm/ref. No. 74400, specific migration limit 30 mg/kg
Germany	BfR Recommendation VI, maximum 2.0% total of all stabilisers BGA: maximum 6% in plastics
Netherlands	Food Packaging and Utensils Decree of 01.10.1979 as amended Chapter 1
France	Brochure 1227 (Avril 1990) maximum 1.0%
Italy	Min. Decree of 21.03.1973 maximum 0.3% Min. Decree of 0.04.1985
Spain	Royal Decree 125/1982 of 30.04.1982 Resolution of 4.11.1982
Belgium	Royal Decree of 11.05.1992, specific migration limit 30 mg/kg
United Kingdom	BIBRA/BBF Code of Practice (1991) Rec. No. C.159, maximum 1.0%

2.2.1.4 Production of High density polyethylene (HDPE)

HDPE containing TNPP is used in the manufacture of many products like blow-molded plastic drums or outer wrapping (film) of cigarette boxes or tea boxes.

2.2.1.5 Production of rubber

Rubber containing TNPP are used for example in tires and shoes soles.

2.2.2 Other applications

TNPP is used in other applications than plastic and rubber productions. Using the information provided in the SPIN database, it could be supposed that these other applications include the use of TNPP in publishing, printing and reproduction activities, in the manufacture of products of

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wood, of fabricated metal products, of furniture and in the construction activities. However, no more specific information is available.

2.2.2.1 Use of end-products (service life)

Shower curtains, flooring and wall coverings, bags and food packaging, blow-molded plastic drums, outer wrapping films, tires and shoes soles are examples of plastic and rubber end-products containing TNPP. For all these products, both private and professional end-uses can occur and releases are expected during their service life. This will be considered in the EUSES program ({E.C., 2008 #29}) taking into account the information available in OECD Emission Scenario Documents. However, it could be expected that TNPP or NP releases due to the use of end-products are low.

2.2.2.2 Recovery and disposal

No information on recovery has been submitted. In view of the end-products containing TNPP that are manufactured, it could be assumed that products containing TNPP may be either recycled into new products, disposed in landfill or incinerated. Therefore, this stage could be considered in the EUSES calculation ({E.C., 2008 #33}). However, no default value is currently available for this stage in version 2.1 of the software. Nevertheless, qualitative information available for example in Emission Scenario Documents have been considered (see section 3.1.2.2).

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3 ENVIRONMENT RISK ASSESSMENT

3.1 ENVIRONMENTAL EXPOSURE

3.1.1 Environmental fate

3.1.1.1 Degradation in the environment

3.1.1.1.1 Atmospheric degradation

In the atmosphere, TNPP may be degraded by reactions with photochemically generated species like hydroxyl radicals. This atmospheric photo-oxidation potential can be estimated using structure activity relationships models developed by the U.S. Environmental Protection Agency and Syracuse Research Corporation (EPIWIN, v. 3.10, sub-model AOPWIN US EPA and Syracuse Research Corporation, 2001). The corresponding specific rate constant with OH radicals (k_{OH}) was estimated to be 50.6×10^{-12} $cm^3.molec^{-1}.s^{-1}$. Then the pseudo first order rate constant for degradation in air ($kdeg_{air}$) is determined with the following equation:

$$k\deg_{air} = k_{OH} \cdot OHCONC_{air} \cdot 24 \cdot 3{,}600$$

Using the global annual average OH radicals in the atmosphere (5×10^5 $molec.cm^{-3}$), $kdeg_{air}$ is calculated to 2.19 d^{-1} and the half life for the reaction of hydroxyl radical with TNPP in the atmosphere is calculated as 0.32 days (7.6 hours).

Assuming another value for the OH radicals in the atmosphere (1.5×10^6 $molec.cm^{-3}$) and 12 hours of daylight, $kdeg_{air}$ is calculated to 3.28 d^{-1} and the half life for the reaction of hydroxyl radical with TNPP in the atmosphere is calculated as 0.21 days (5.07 hours) (Staples, 2001).

The 1.5×10^6 $molec.cm^{-3}$ value for daylight hours is based on recent experimental observations (Leifer, 1993; Mount and Eisele, 1992 in US EPA and Syracuse Research Corporation, 2001).

The use of the 12 hours daylight period is justified by the U.S. EPA considering that OH radicals were existing only during sunlight hours. Therefore, the 12 hours period was chosen as an average daylight for a whole year and the pseudo first order rate constant was calculated with this new information. This last result (half life of 5.07 hours) will be used in the risk assessment.

Anyway, there are chances that TNPP will not be transported far from its emission source when it is emitted to the atmosphere. With such a low half life, TNPP will be rapidly degraded in the air and it is therefore not expected that TNPP will contribute to ozone depletion in the stratosphere.

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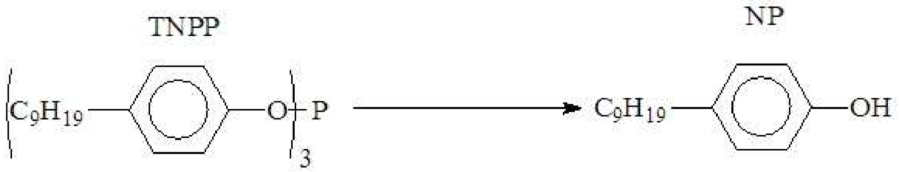
3.1.1.1.2 Aquatic degradation - hydrolysis

TNPP can be hydrolyzed to form NP (Nonylphenol).



The ability to resist this decomposition is called “hydrolytic stability”. Hydrolytic stability can occur in several different ways, depending upon where the actual hydrolysis is predicted to take place. The potential of TNPP to hydrolyse can be considered under different conditions as a consequence of the production, process and releases of TNPP:

- During the production, shipment and storage of TNPP: the bulk stock of TNPP can be subject to hydrolysis from atmospheric humidity. Information from handling hydrolytic stability is available)
- In-polymer during the processing: In polymer, TNPP mainly takes place has TNPP phosphate, as a result of its action as secondary antioxidant. This aspect is considered under section 3.1.1.1.3.
- Hydrolytic stability of TNPP in an aqueous compartment (small amounts of TNPP in an aqueous solution),

The information available to quantify the hydrolytic stability of TNPP is presented hereafter in order to show thoroughly degradation properties of this substance. However, only results originating from the last test can be used in the risk assessment in order to estimate the behaviour and fate of TNPP in the environment (surface water).

Bulk storage and handling hydrolytic stability of TNPP

The bulk storage and handling hydrolytic stability of a phosphite can be measured by placing the neat phosphite in a Petri dish, and exposing it to elevated temperatures and humidity. This is an accelerated test. This accelerated test uses a temperature of 35°C (95°F) and 85% humidity. The stability was measured by analyzing for nonylphenol with HPLC, since nonylphenol is formed as the product hydrolyzes.

TNPP may contain a residual amount of nonylphenol that is left over from the synthesis/reaction. Dover Chemical offers two grades of TNPP, regular DP4 and a high purity grade called DP4HP that contains less than 0.1% free/residual nonylphenol.

Some hydrolysis rate constant calculations have been performed using a product datasheet from a producer (Dover Chemical Corporation, 2001). Degradation constants for three different TNPP formulated products have been determined based on the measurement of free nonylphenol formed from TNPP formulated products at 35°C and with 85% relative humidity (see Figure 3-1**Erreur ! Source du renvoi introuvable.**).

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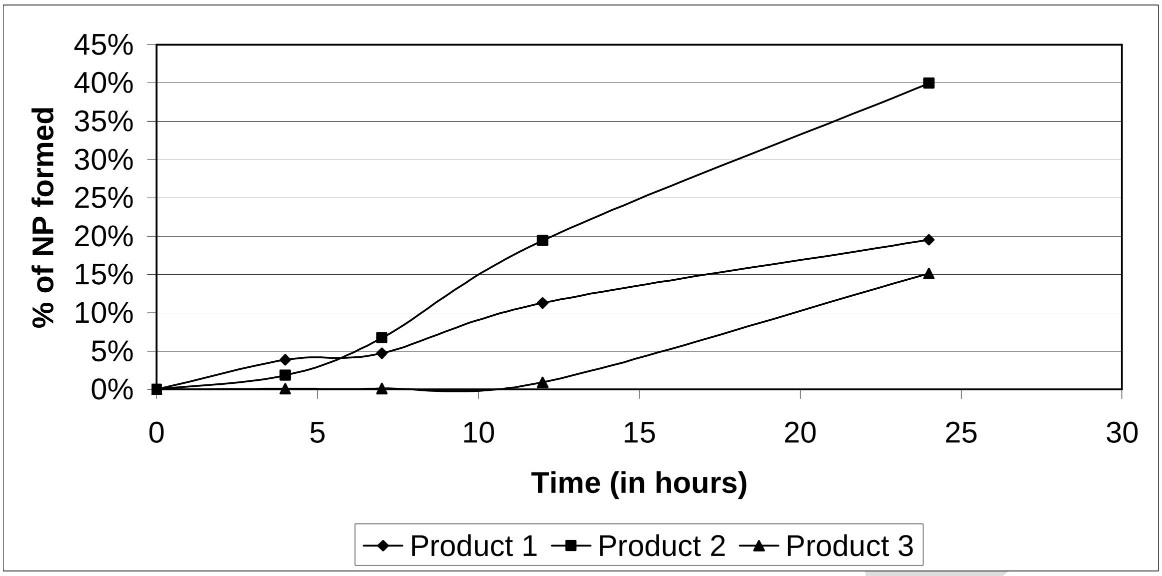

Figure 3-1: hydrolysis of different TNPP grades at 35°C and 85% relative humidity

Products 1 and 2 are “classical” TNPP formulation used in processing operations whereas product 3 is a high-pure grade of TNPP (containing less than 0.1% NP). Half-lives have been calculated by regression analysis and range between 1.6 and 4.4 days at 35°C (see Table 3.1-1**Erreur ! Source du renvoi introuvable.**). This information could be used as supportive data in the risk assessment report particularly in order to assess to which extent NP could be formed during the use of TNPP for the processing of TNPP.

Table 3.1-1: hydrolysis half-lives of three TNPP grades

	Degradation constants at 35°C, 85% hum. **(%NP_{formed}.h^{-1})**	**Half-lives at 35°C, 85% hum. (d.)**
Product 1	0,0082	3,5
Product 2	0,0177	1,6
Product 3	0,0065	4,4

Other examples have been provided by Dover to illustrate the hydrolytic stability of TNPP during storage or handling and this is illustrated by Figure 3-2 (Dover, unpublished). TNPP is usually sold with an additive present at 0.5-1.0%. The additive, tri-isopropanol amine, or TIPA (CAS #122-20-3), acts as an acid scavenger and increases the hydrolytic stability of TNPP. ~78% of the TNPP Dover Chemical sells in Europe contain TIPA (DP4HR and DP4HPHR). Some applications such as PVC do not need TIPA since the polymer contains other types of acid scavengers. DP4HP with TIPA is very stable, with less than 3% hydrolyzed even after 80 days.

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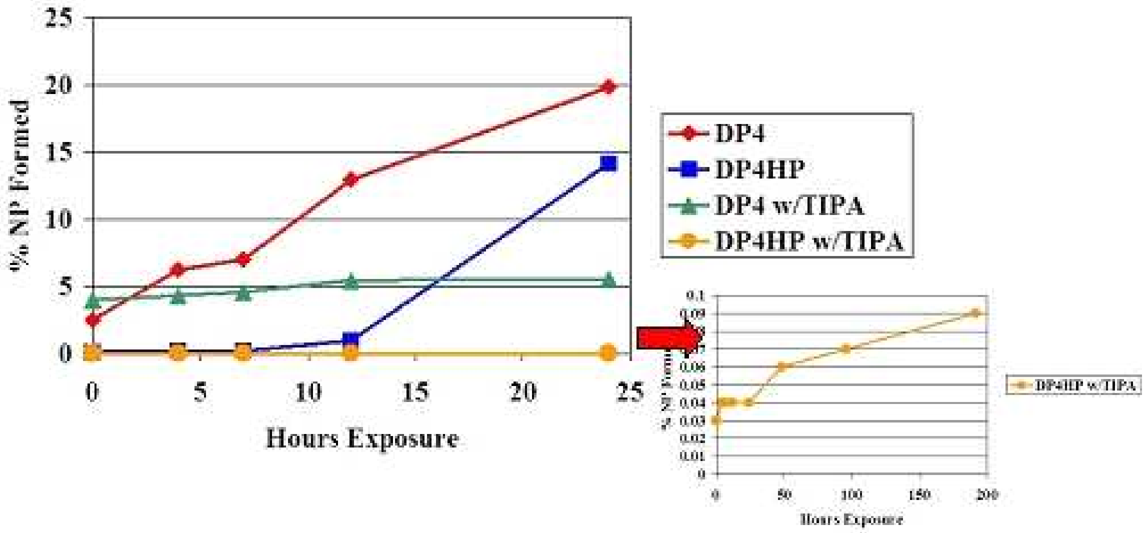

Figure 3-2: hydrolytic stability of TNPP (different purities and with/without TIPA) exposed at 35°C with 85% humidity

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These test results can be used to support the fact that TNPP has a potential to hydrolyse during handling and storage. However this information cannot be used for the quantitative estimation of the hydrolysis potential of TNPP in the environment. Indeed, temperature conditions are different and the very low solubility of TNPP will influence its behaviour in the aquatic compartment.

Instead of measuring the hydrolytic stability of TNPP in the neat state, you can also measure the hydrolytic stability of TNPP when placed into an aqueous solution or environment (TNPP by itself is essentially insoluble in water).

<u>Hydrolysis of TNPP in an aqueous compartment</u>

In the literature, it is indicated that some organic phosphites are hydrolytically unstable with the general pathway described below (Goghova M. et al., 1989; Stevenson D.R., 1997 in Reimer&Associates, 2001b):

$$(RO)_3P \rightarrow (RO)_2 - P(O)H + ROH \rightarrow (RO) - P(O)H(OH) + ROH \rightarrow P(O)H(OH)_2 + ROH$$

With R = organic group; alkyl or aryl.

For TNPP, the final hydrolysis products are nonylphenol (NP) and phosphoric acid. Theoretically, with excess of water, the hydrolysis should be complete, yielding 3 molecules of NP and 1 molecule of phosphorous acid for each molecule of TNPP (see Figure 3-3). However, laboratory data reveal that TNPP resists hydrolysis.

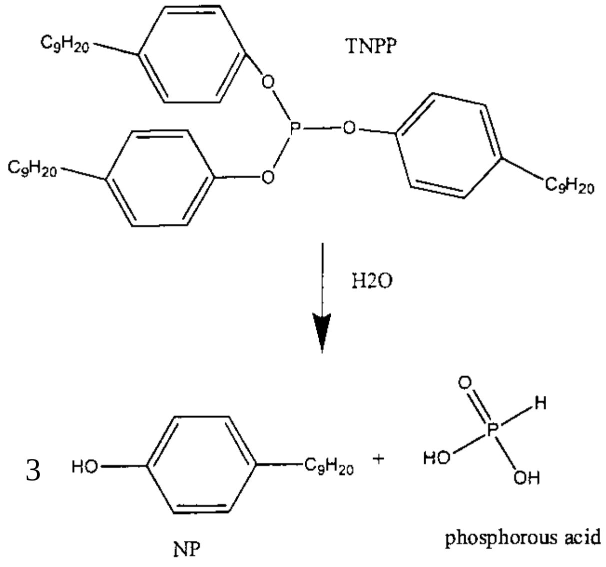

Figure 3-3: complete hydrolysis of TNPP

Any further breakdown of nonylphenol would be biodegradation.

① First hydrolysis study (Reimer&Associates, 2001b) – invalid study (included for information)

An experiment was conducted on TNPP to determine its hydrolysis potential as a function of pH (): TNPP was dissolved in buffers (pH 4, 7, and 9) with CH_3CN co-solvent (1/1; v/v). These solutions were placed at 22°C and analysed repeatedly for NP as the hydrolysis product.

During the hydrolysis experiment, nonylphenol was detected but concentrations remained small and constant. This constant, low concentration of nonylphenol during hydrolysis was explained by the authors by the surfactant properties of NP which may have resulted in its adsorption to the glass surface of the vial (the hydroxyl group(-OH) of NP is responsible for hydrogen bonding with the glass). These adsorption properties of nonylphenol to the walls of vessels were also reported in some adsorption isotherm studies on nonylphenol (Roy F. Weston Inc, 1990d in). Due to its high Kow and low water solubility TNPP probably also adsorbed to the glass surface of the vial and/or aggregated at the water surface. The measured decrease in TNPP could also be due to these phenomena. Another plausible explanation for the constant concentration of NP observed during the experiment could be the initial contamination of the test substance with NP. Indeed the test material in this study contained about 5% of nonylphenol.

For this hydrolysis experiment on TNPP, the apparent half-life of TNPP in solutions of buffer/CH_3N (1/1; v/v) was estimated between 13 and 14 h at 22 °C. The hydrolysis was also found to be independent from pH conditions, i. e. TNPP concentrations decreased identically at pH 4, 7 and 9, which is different from what is usually observed with other alkyl phosphites (see Annex 2, OECD, unpublished). As described further, in subsequent experiments, these initial half-life determinations, were likely not accurately measuring the degradation of TNPP.

We should also consider that TNPP concentration used in this hydrolysis study (589 mg/L) is well above its water solubility (~50 µg/L based on the limit of quantification and a QSAR value of $3x10^{-16}$ mg/L has been calculated). The truly dissolved TNPP could hydrolyse faster but the resulting NP concentration would be well below the detection limit.

② Second hydrolysis study (TNO, 2004)

TNO has confirmed a very low limit of quantification for NP of 23 ng/L. The TNPP Industry therefore undertook a modified hydrolysis study to measure the rate of formation of NP from low concentration solutions of TNPP.

Since it was difficult to measure TNPP at low concentrations (see section 1.3.7 on water solubility), the TNPP Industry therefore undertook a modified 24-hour hydrolysis study where the rate of formation of NP was measured from water samples containing TNPP at 0.1 and 1 µg/L. These solutions were made from a stock solution prepared using acetone. It is also mentioned that at both concentrations tested, the solutions were clear. During this test the level of NP was below the level of quantification (23 ng/L) in all the samples over the 24-hour period indicating no formation of NP.

Under the assumption that the half-life of TNPP was between 13-14 hrs, TNO should have been able to detect NP formed at the two (0.1 and 1 µg/L) concentrations used for the hydrolysis experiment. Also it has been established that NP is likely not adsorbing to the glass containers since TNO was able to find a very good recovery of NP in the calibration solutions prepared similar to the TNPP hydrolysis samples. Based on this experiment, it can be concluded that under ambient conditions TNPP in the aquatic environment will not hydrolyze to any meaningful degree to NP.

③ Third hydrolysis study (DAT Laboratories, 2007)

The TNPP hydrolysis study was performed to determine the extent to which TNPP hydrolyzes to NP in aqueous media. Solutions of the TNPP(DP4HPHR)/buffer system were directly injected into a LC-MS, and the amount of nonylphenol was measured. The nonylphenol calibration curve was calculated using the same technique with a branched industry standard nonylphenol. Percent hydrolysis was defined as weight NP * 100/weight TNPP.

Table 3.1-2 NP analysis and calculated TNPP hydrolysis

Time(hr)	ppb NP	% NP (relative to TNPP)	% Hydrolysis
0	5.43	0.0543 %	NA
1	6.81	<0.1%	<0.05%
2	4.72	<0.1%	<0.05%
18.5	4.73	<0.1%	<0.05%
24	8.57	<0.1%	<0.05%
68	10.47	0.1047%	0.0504%
92.5	15.82	0.1582%	0.1039%
241.5	15.36	0.1536%	0.0993%

The level of NP after the first 18.5 hours was assumed equivalent or within experimental error. Thus the hydrolysis of TNPP was less than 0.05%. After 92.5 hours there was a slight increase in the NP level. Percent hydrolysis was calculated at 0.10%. This level was maintained at 0.1% over 241.5 hours.

In conclusion, although it cannot be totally ruled out that there might be environmental conditions where hydrolysis could occur, hydrolysis of TNPP in the aquatic environment will not be considered as an important phenomenon. This is based on the expected very low water solubility of the substance that would not enable hydrolysis to occur in large amount. Furthermore, the high hydrophobicity of TNPP (high log Kow) will contribute to a large adsorption of the substance on sediment when entering the aquatic compartment thus reducing its availability for hydrolysis.

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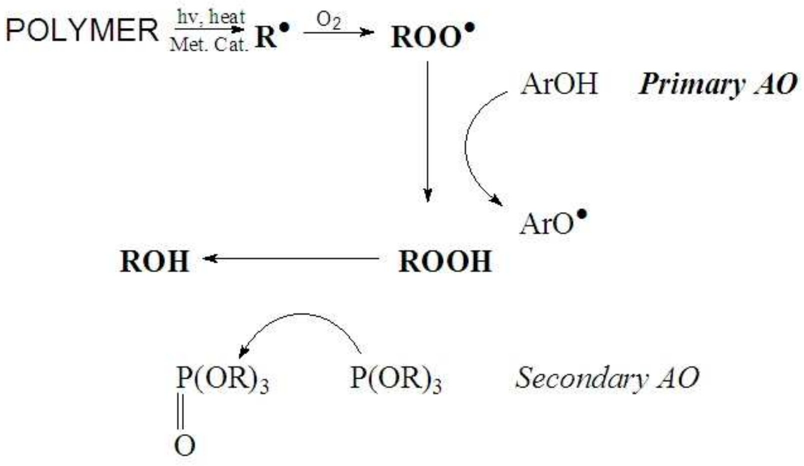
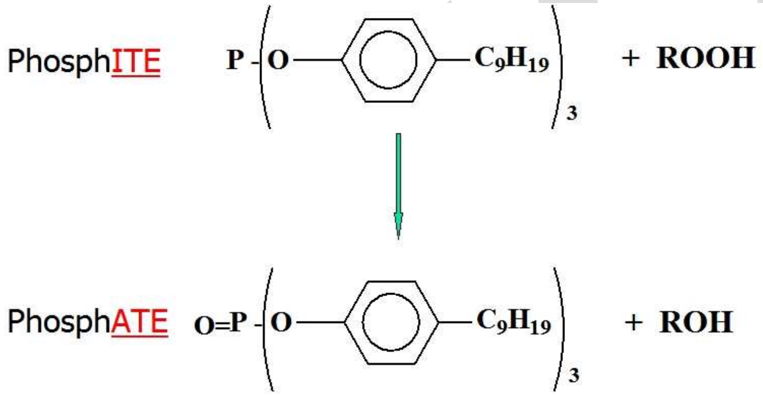
3.1.1.1.3 Aquatic degradation - oxidation

TNPP is used as a secondary antioxidant in polymers. It is placed into the polymer to decompose hydroperoxides, thus partially transforming TNPP into TNPP-phosphate while the polymer is being processed. In the polymer the following oxidation reaction occurs:



The following figure shows the chemical structures of TNPP and TNPP-phosphate:



Bulk storage and handling hydrolytic stability of TNPP-phosphate

During the processing of the polymers, TNPP is oxidised partly and TNPP-phosphate is produced. TNPP-phosphate is more hydrolytically stable than TNPP as illustrated by Figure 3-4:

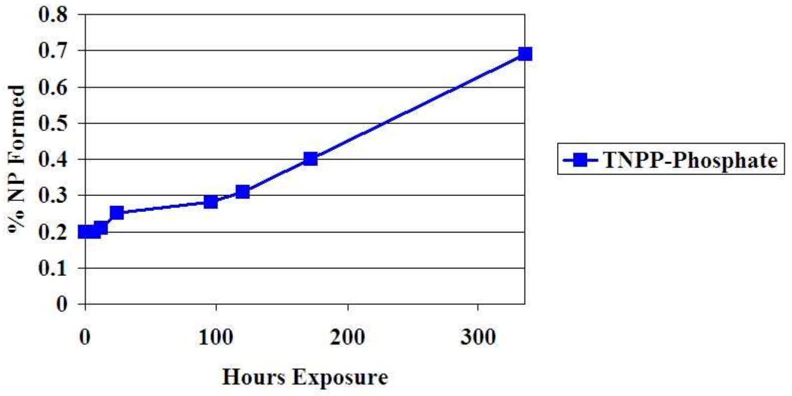


Figure 3-4: hydrolytic stability of TNPP-phosphate exposed at 35°C with 85% humidity

In an experiment (Dover, unpublished) with TNPP-phosphate, it has been shown that less than 1% of this substance is hydrolyzed after two weeks (without TIPA).

3.1.1.1.4 Aquatic degradation - biodegradation

Test #1: the ready biodegradability of TNPP was studied in the closed bottle test (OECD 301D) (Hydroqual Laboratories Ltd, 2001c). TNPP solutions were inoculated with a commercial bacterial preparation (Polyseed) and incubated at 20 ± 1°C.

The biological oxygen demand (BOD) of the test substance was measured at 0, 7, 14, 21 and 28 days and compared to the theoretical oxygen demand ($ThODNO_3$) of the nominal concentration of TNPP. TNPP concentration was 15.4 $mg.L^{-1}$ which was theoretically corresponding to a Chemical Oxygen Demand of 13.2 mg. Beside the TNPP solution, there were 3 controls: a test control (inoculated mineral medium), a procedure control (degradation of a reference substance) and a toxicity control (degradation of the reference substance in the simultaneous presence of TNPP).

All controls passed the acceptability criteria of the test: oxygen depletion in the test control did not exceed 1.5 mg per litre after 28 days incubation, biodegradation of the sodium acetate reference substance met the criterion of > 60% of the $ThODNO_3$ within 14 days. TNPP did not inhibit the degradation of the reference substance by more than 25% after 14 days. Finally, the variance amongst duplicate test bottles was less than 20%.

Less than 4% of TNPP was biodegraded after 28 days experiment. According to this test, TNPP is not readily biodegradable.

Test #2: the ready biodegradability of TNPP was studied in another test following the OECD guideline 301B (CIBA-Geigy, 1994). Test substance has been tested in duplicates at a concentration of 18.1 mg/L which corresponds to 15.3 mg ThOC/L. The inoculum was constituted with activated sludge collected from the sewage treatment plant of Reinach (Switzerland). The pH after collection was 7.0. Before application, the inoculum was pre acclimated to the test medium overnight. The test was performed at a temperature of 22 +/- 2°C with a carbon dioxide free air supply.

To take into account the very low solubility of the test substance, its preparation was as follow: a stock solution was prepared dissolving 1.36 g. of test substance in 10 mL dichloromethane. From this stock solution, for each replicate, 27.2 mg (200 µL) were applied onto a filter paper as small drops. After the filter paper was completely dry (no remaining of dichloromethane was present), it was cut to small pieces (10-15) and added to the test medium. Thereafter, the medium volume was completed to 1.5L with 300 mL water and the flasks were immediately connected to the CO_2 scrubber. Within a few hours the filter paper was homogeneously distributed in the test medium (so that it could not be seen anymore).

A deviation from the guideline should be noted. Indeed, only one CO_2 scrubber was used during the test. However, theoretically, a solution of 0.05 M NaOH is sufficient to trap at least twice more CO_2 than the maximum $ThCO_2$ which can be produced in each test bottle (including CO_2 possibly evolved from the bacteria, e.g. endogenous respiration). Moreover, experimentally it was confirmed that no measurable CO_2 carry over has ever occurred with the scrubbers used.

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A test has also been conducted with sodium benzoate as reference substance, at a concentration corresponding to 15 mg DOC/L. After 7 days and 20 days, the biodegradation of the reference substance reaches respectively 71 and 86%.

Only 1% of TNPP was biodegraded after 29 days experiment. According to this test, TNPP is not readily biodegradable.

TNPP will be considered as non-readily biodegradable in this risk assessment.

3.1.1.1.5 Degradation in soil

No result could be found on degradation processes of TNPP in soils.

3.1.1.1.6 Summary of environmental degradation

TNPP released to the atmosphere is expected to degrade by reaction with hydroxyl radicals. A rate constant for degradation in air of 3.28 d^{-1} with a corresponding half-life of 5.07 hours were estimated.

TNPP is not biodegradable in aquatic environments and the corresponding rate constant for biodegradation is 0 d^{-1} with an infinite corresponding half-life.

As far as hydrolysis of TNPP in the aquatic environment is concerned, different sources indicate a potential of TNPP to hydrolysis. However TNPP hydrolysis will not be considered as an important degradation phenomenon in the risk assessment. This is based on the expected very low water solubility of the substance that would not enable hydrolysis to occur in large amount. Furthermore, the high hydrophobicity of TNPP (high log Kow) will contribute to a large adsorption of the substance on sediment when entering the aquatic compartment. However it should be taken into account that during the processing of polymers using TNPP as antioxidant, TNPP will undergo hydrolysis resulting in the release of nonylphenol in the environment. This hydrolysis during processing is due to the conditions of temperature in the process reactor.

The hydrolysis of TNPP leading to the formation of NP during processing will be considered in the risk assessment.

3.1.1.2 Distribution

3.1.1.2.1 Adsorption

The partition coefficients for TNPP have been calculated using EUSES ({E.C., 2008 #33}) based on log Kow of 14. They are presented as an example in Table 3.1-3.

Table 3.1-3: Calculated partition coefficients for TNPP

	Log Kow 14	
K_{oc}	2.76×10^{11}	Partition coefficient organic carbon-water ($L.kg^{-1}$)
Kp_{susp}	2.76×10^{10}	Partition coefficient solid-water in suspended matter ($L.kg^{-1}$)
Kp_{sed}	1.38×10^{10}	Partition coefficient solid-water in sediment ($L.kg^{-1}$)

Kp_{soil}	5.51 x10^{09}	Partition coefficient solid-water in soil (L.kg^{-1})
$K_{soil-water}$	8.27 x10^{09}	Soil-water partition coefficient (m^3.m^{-3})
$K_{susp-water}$	6.89 x10^{09}	Suspended matter-water partition coefficient (m^3.m^{-3})
$K_{sed-water}$	6.89 x10^{09}	Sediment-water partition coefficient (m^3.m^{-3})

3.1.1.2.2 Precipitation

Based upon the reaction with hydroxyl radicals, a half-life of 5.07 hours was calculated (see section 3.1.1.1.1). With such a short half-life, TNPP is unlikely to be transported a long distance from its point of emission and therefore neither enter the atmosphere in large amounts. Besides, TNPP being insoluble in water, concentrations in rainwater could be assumed to be negligible.

3.1.1.2.3 Volatilisation

A Henry's law constant between 799 and 1.33.10^{17} Pa.m^3.mol^{-1} was calculated from TGD (see section 1.3.13) taking into account the range of values chosen for water solubility. Indeed, in the risk assessment, the sensitivity analysis performed with water solubility (see Annex 1) will influence the value of the Henry’s Law constant.

The resulting air-water partition coefficient (Kair-water) would then range between 0.337 and 5.62x10^{13} m^3.m^{-3} by EUSES ({E.C., 2008 #33}). These values should be interpreted with care, as it should also be taken into consideration that with the increase of hydrophobicity (lower solubility), higher adsorption of the substance on organic matter will occur. In that conditions, the property that will effectively limit the volatility of the substance will be the strong adsorption onto sediment and soil rather than the Henry’s law constant.

Thus, volatilisation of TNPP from water is not expected to be a major phenomenon.

3.1.1.2.4 Distribution in waste water treatment plants

The distribution of TNPP in sewage treatment plants have been calculated using the model SIMPLETREAT integrated to EUSES ({E.C., 2008 #33}) based on a log Kow of 14 and Henry’s law constant. They are presented as an example in Table 3.1-4.

Table 3.1-4: Estimation of removal of TNPP in STPs according to EUSES

	Log Kow 14 H = 799 Pa.m^{-3}.mol^{-1} (calculated using a solubility of 0.05 mg/L)
% to air	1.7x10^{-5}
% to water	8
% to sludge	92
% degraded	0
% removal	92

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TNPP being insoluble, not volatile and considered as not biodegradable, releases through production or processing will mainly go to sludge.

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3.1.1.2.5 Accumulation and metabolism

Measured data on bioaccumulation of TNPP are not available. A calculated BCF has been obtained using EpiWin: 3.162 L/kg.

Bioaccumulation potential of TNPP could also be evaluated through EUSES calculation.

Based on the high Kow expected for TNPP, there are indications that TNPP may be bioaccumulated through trophic chains. Using EUSES calculation a bioconcentration factor of 479 L/kg could be calculated for fish taking into account a log Kow >10 (the worst case for BCF obtained when using the parabolic equation giving the BCF for fish based on the K_{ow}, [E.C., 2003 #28]).

Besides, bioaccumulation of nonylphenol due to TNPP releases into the aquatic compartment will also have to be considered (BCF for NP: 1,280 L/kg for fish - E.C., 2002).

For earthworms, a partition coefficient earthworm-porewater could be calculated using EUSES model ({E.C., 2008 #33}): $K_{worm\text{-}porewater} = 1.2\times10^6$ L/kg taking into account a log Kow of 8 (worst case of the QSAR application range). Concerning the calculation of the BCF for earthworm, it should be noticed that contrary to QSARs available for fish, there is only one formula for the derivation of BCF for earthworm based on the log Kow. This leads to the determination of high BCFs for high Kow values (with a validity domain between 1 and 8) whereas for fish a maximum is calculated for the log BCF at a log Kow of 6.85.

The bioaccumulation factors calculated for TNPP based on log Kow of 8 and >10 as a worst case indicate a high bioaccumulation potential. Nevertheless, the bioaccumulation potential of TNPP based on these calculations should be considered with precaution for the following reasons:

- molar weight is near 700 g/mol (689 g/mol) and certain classes of substances with molecular mass greater than this threshold are not readily taken up by fish and are unlikely to bioaccumulate significantly.
- Information on the molecular size of TNPP is also available (personal communication, Kazumi Kawahara, CERI, 20th October 2005). Based on this study, it seems that, taking into account the calculated molecular size of TNPP, the bioaccumulation potential is negligible. The calculation of the mean diameter for six different three dimension structures of TNPP has led to a lowest value of 13.9 angstrom. This conclusion has been reached based on a cut-off value for the ability of a chemical to pass through fish gill membrane has been established at 9.5 angstrom (Opperhuizen *et al.*, 1985). However, it should also be considered that the current cut-off value proposed by the PBT subgroup is a mean diameter higher than 17 angstroms.
- A worst case value has been taken into account for the calculation of BCFs for TNPP. However, there are some indications that the Kow of TNPP could be much higher than this value (HPLC method estimated log Kow of 14).
- The molecular dimensions (D_{max} and D_{eff}) of two representative isomers of commercial TNPP were estimated with a demonstration version of Molecular Operating Environment software (version 2006.08) (Schocken, 2007). The TNPP isomers, comprised of nonylphenol ligands that are "slightly or highly branched" were each sorted into their lowest potential energy state conformations in aqueous solution and the lowest-energy conformations averaged to obtain the requisite molecular dimensions. The approach

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taken was to use two different programs of MOE, namely, conformational import and dynamics simulation. Results showed that D_{max} average, currently considered the most important molecular dimension and defined as the average diameter of the smallest spheres circumscribing the low-energy conformations for a given TNPP isomer, ranged from 23.7 Å for the slightly branched TNPP isomer to 22.8 Å for the highly branched TNPP isomer using the conformational import approach and from 24.3 Å to 21.2 Å for the slightly branched and highly branched TNPP isomer using the dynamics simulation method, respectively. These values all exceed the 17.4-Å cutoff currently used to preclude absorption of organic chemicals via fish gills. Coupled with TNPP's high experimentally determined log Kow (14) and its high molecular weight (689 grams/mole), it is unlikely that this chemical would be bioaccumulative in the aquatic environment.

- Mammalian toxicity of TNPP is described in section 4 of this report. In animals, TNPP has a very low acute toxicity by the oral route, with a LD50 value of about 19.5 +/- 3.3 g/kg bw for the rat. Two-year studies provide a profile of limited repeated dose toxicity for TNPP. In these 2-year studies, 3300 ppm of TNPP in the diet (corresponding to 167 mg/kg/d in rats), was derived as a NOAEL, both for rat and dog. A possible effect on reproduction at the dose of 500 mg/kg/d was reported in rats, based on those results a NOAEL for reproduction of 167 mg/kg bw/day can be derived.

The low mammalian toxicity of TNPP could be linked to a limited absorption potential. However in the absence of specific toxicocinetic study, only quantitative information were derived from the physico-chemical properties of the substance (see section 4.1.2.1). The screening B/vB criterion is fulfilled based on the bioaccumulation potential determined with log Kow worst case values for QSAR models. However, while considering the measured log Kow of 14 and additional information on the molecular weight and the size of the molecule, there might be indications that the above calculations overestimate the bioaccumulation potential of the substance.

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3.1.2 Environmental releases

3.1.2.1 General information

Releases of TNPP and/or NP (nonylphenol) to the environment occur during production, transport, storage, formulation and processing of plastic and rubber products. In addition, releases may also take place through the uses of the end-products. Finally, waste disposal of the end-products may also release TNPP or NP into the environment.

The different industry categories (IC), use categories (UC) and main categories (MC) used in the EUSES calculations are described in Table 3.1-5.

Table 3.1-5: Industrial Categories (IC), Use Categories (UC) and Main categories (MC) used in EUSES calculations

Life cycle stages		**IC**	**UC**	**MC**
Production		11	49	I b
PVC films (2,800 t)	**Formulation**	11	49	III
	Processing	11	49	II
LLDPE films (1,200 t)	**Formulation**	11	49	III

Life cycle stages		**IC**	**UC**	**MC**
	Processing	11	49	II
HDPE films (800 t)	**Formulation**	11	49	III
	Processing	11	49	II
Rubber (2,960 t)	**Formulation**	11	49	III
	Processing	11	49	II
Others (240 t)	**Formulation**	15	55	III
	Processing	15	55	II

About 25 to 35 facilities are processing TNPP in EU_{15}. Their consumption ranges from a few tonnes to around 700 tonnes/year. The highest value comes from an identified site where near 10% of the total TNPP used in EU_{15} is processed. As the type of use taking place at this site is not known, this worst case will be taken into account for each category of use identified. In the exposure assessment, it will also be considered by default that only one site processes TNPP in a region with an annual tonnage of 700 t.

Table 2.2-1 shows the order of magnitude of the sizes of European sites where TNPP is used. These data come from a survey where 21 sites were identified using a total of 4,269 t. of TNPP.

Table 3.1-6: order of magnitude of TNPP volumes processed in identified sites

Use	**Number of sites identified in the specified volume range**		
	< 45 t. ("small" site)	**45-227 t. ("medium" site)**	**>227 t. ("large" site)**
Polyolefins linear low density polyethylene (LLDPE)		1	1
High density polyethylene (HDPE)		3	
Rubber	2	6	1
Polyvinylchloride (PVC) film		1	3
Other	1	1	1

The regional tonnage will be defined in the following way:

- Where a "large" site has been identified for a type of use, the regional volume will be set at 700 t. (the highest site identified), except for the other uses to which only 240 t. have been attributed. It will be considered that there is only one site in a region.
- When only medium sites have been identified, e. g. for TNPP used for HDPE, only one site will be considered in a region with a volume of 227 t.

Consequently, for tonnage input in the B tables, regional tonnage of TNPP was set to 700 t for the uses for PVC, LLDPE and rubber (maximum reported consumption range for TNPP processing facilities). For the uses in HDPE and other uses, the regional tonnage was respectively set to 227 t and 240 t.

A default fraction of TNPP in formulation is suggested in TGD (E.C., 2003) Emission Scenario Document for rubber Industry: up to 1.5 % (wt) for processing aids used as stabilisers. However,

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TNPP manufacturers have submitted better approximations of this value, for different formulated products (Personal communication from TNPP consortium, 1st April 2004):

PVC film	0.8-1.5 %
Polyolefins	0.1-0.2 %
Rubber	0.4-1.0 %

As a worst case, the upper limit of these intervals will be used for the exposure assessment. Then, in the absence of more specific information, fractions of the main source and number of days are derived from Tables B using the tonnage as such for each use.

Releases of TNPP have to be estimated during the production of the substance and during its uses. TNPP has several applications in Polymer Industry (Industrial Category 11) where it is mainly used as a stabiliser (Use Category 49). Both formulation and processing steps have to be considered in the risk assessment.

Releases due to the use of TNPP containing products have also to be considered.

Local releases due to formulation and processing of TNPP are calculated using default scenarios presented in the TGD (E.C., 2003) and other available Emission Scenario Documents. Details of calculation parameters are given in Table 3.1-8.

3.1.2.2 Use of the OECD ESD for plastic additives with TNPP

TNPP is used as an antioxidant and volatility of antioxidants is the same as the substances used in plasticizers. Considering its vapour pressure, TNPP should be classified in the high volatility group (Cf. Table 8.1 in OECD, 2004). However, The TNPP consortium commissioned new vapour pressures measurement for TNPP and DIDP which is the reference substance for the low volatility group in the Emission Scenario. Thus the study provided results which can be directly used so as to compare the volatility of TNPP to the one of DIDP. It appears that the vapour pressures measured for TNPP in this study are lower than those for DIDP. Consequently, TNPP will be considered a low volatility compound for the selection of figures from the Emission Scenario. Emission factors are detailed hereafter. Worst case emission factors available in the ESD for plastic additives have been used (OECD, 2004).

- Raw material's handling (formulation)

To estimate TNPP releases, it may be considered that antioxidants are analogous to plasticizers with respect to handling, and that the ESD for plastic additive can apply. However, the initial state of TNPP is liquid and the scenario only considers losses from the handling of solid materials. Thus, default emission factors of the scenario for antioxidants cannot be applied in its case. Plasticizers are almost in a liquid form. They are usually transported and handled in bulk through enclosed storage systems. So minimal loss by spillage can be assumed.

Consequently, $F_{handling,water} = 1x10^{-4}$. It is considered that loss by volatilisation should be minimal.

- Compounding (formulation)

Two cases should be taken into account depending on the method used for the compounding. Here again, the factors for plasticizers are used.

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Release factors used for dry blending and Banbury blending are used as a worst case: $F_{compounding,water} = F_{compounding,air} = 1x10^{-5}$ and (emission factors for the low volatility group).

For the formulation stage, emission during handling are taken into account, the following emission factors will be used: $F_{air} = F_{water} = 1.1x10^{-4}$.

- Conversion (processing)

For the low volatility group, losses during conversion are estimated using the following emission factors. As a worst case, the processing performed in open processes (solid articles) will be applied: $F_{conversion,water} = F_{conversion,air} = 5x10^{-5}$.

- Service life

The following emission factors have been chosen for the service life of products containing TNPP:

- Indoor service, leaching to liquid waste: $F_{service\ life,water} = 5x10^{-4}$ over lifetime
- Indoor service, volatility to atmosphere: $F_{service\ life,air} = 5x10^{-4}$ over lifetime
- Outdoor service, leaching to environment: $F_{service\ life,water} = 1.6x10^{-3}$ x $T_{service}$ ($T_{service}$ is the service life of product in years)
- Outdoor service, volatility to atmosphere: $F_{service\ life,air} = 5x10^{-4}$ over lifetime

This results in fractions of emission to water of 0.016 (taking into account, as a worst case, a lifetime of 10 years for TNPP containing products) and $5x10^{-4}$ to air (the worst case of outdoor service is taken into account).

The releases occurring during this stage of the life cycle of TNPP will be taken into account at the regional scale.

- Disposal

In landfill, leaching losses to water will depend on many factors, relating to the type of landfill as well as to the properties of TNPP and the nature of the polymer in which it has been used. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal, but it is very unlikely that this amount would be released. The volatilisation loss from landfill is also likely to be limited. Consequently, in this assessment, releases during disposal are assumed to be negligible.

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3.1.2.3 Use of the OECD ESD for additives used in rubber industry with TNPP

For this scenario, the production of two main product types identified in this assessment will be considered: tyres and soles.

- Formulation and processing

The emission rate into waste water for formulation and processing is calculated using the following equation:

Equation 3-1: calculation of daily releases into wastewater during formulation and processing of TNPP used in rubber industry

$$Elocal_{water} = Q_{prod} \cdot \frac{Q_{additive}}{100 \cdot F_{recipe}} \cdot \left(1 - F_{remaining}\right)$$

For TNPP, the amounts of the product types produced per day (Q_{prod}) are taken by default as 26,400 kg/d for tyres and 550 kg/d for soles. The part of additive introduced into the rubber is 0.25 phr (parts per hundred rubber parts) for tyres (default value) and 3 phr in soles (default for other rubber products). The fraction of TNPP remaining in the rubber product ($F_{remaining}$) is set at 0.943 (the default value, 0.99, minus the fraction of NP formed during processing) for tyres and 0.933 for soles (the default value, 0.98, minus the fraction of NP formed during processing). Finally, F_{recipe} is set at 2 when $Q_{additive}$ is given in phr.

For the releases in air and soil, the calculations are made as follow:

Equation 3-2: calculation of daily releases to air and soil during formulation and processing of TNPP used in rubber industry

$$Elocal_{air} = Q_{prod} \cdot \frac{Q_{additive}}{100 \cdot F_{recipe}} \cdot F_{air}$$

or F_{soil}

With F_{air} and F_{soil} set at $5x10^{-4}$ and $1x10^{-4}$ respectively.

- Service life: for this stage of the life cycle, only the emission resulting from the abrasion of tyres will be considered. The emission calculated using the equation proposed in the Emission Scenario Document for Rubber Industry will be allocated to the region.

Equation 3-3: calculation of the annual releases to water at the regional level due to the abrasion of tyres containing TNPP

$$Eregional_{breakdown\_product} = Q_{ann\_prod} \cdot F_{abrasion} \cdot \frac{MW_{additive}}{MW_{breakdown\_product}}$$

With Q_{ann_prod} the amount of additive used per year in the region (by default, the tenth of the amount of TNPP used in EU_{15} in rubber products will be used, 296 t/a). $F_{abrasion}$ the emission factor for abrasion from tyres (0.12). The ratio of molecular weights will be set at 1 since here the additive is considered (TNPP).

- Disposal: this stage is not taken into account due to a lack of data to estimate the emission rates and leachate processes.

3.1.2.4 Calculation of NP releases due to the processing of TNPP

During the use of TNPP, nonylphenol is present as an impurity and could, to some extent and under the conditions of temperature and humidity occurring in the process, be formed due to the hydrolysis of TNPP. It should be noted that NP formation during the processing of TNPP is limited as much as possible, using very pure TNPP or employing stabilisers in TNPP formulation for example, because it has a negative impact on the production of plastics. TNPP is used as a stabiliser in the processing of various plastic and rubber products. The primary mechanism of polymer stabilisation of phosphites is oxidation, not hydrolysis. It is extremely critical during the

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process to minimise the generation of NP from TNPP, as this will destroy the stabiliser properties.

Information that can be used to quantify the amount of NP formed during the manufacture of plastics can be estimated from a study by Howe *et al.*, 2001. This assessment was performed using two grades of TNPP differing with respect to the level of residual NP. These grades have been chosen to be representative for the TNPP available on the market. The concentrations of residual NP were ~1.5% (sample 1) and <0.1% (sample 2). Using these samples of TNPP grades resulting in the measurement of the following concentrations in plastics:

Plastic sample	**p-nonylphenol**		**TNPP**		**TNPP phosphate**	
	ppm	**% of total $TNPP_{total}$**	**ppm**	**% of total $TNPP_{total}$**	**ppm**	**% of total $TNPP_{total}$**
LLDPE Resin 1	58	4.7	819	66.2	360	29.1
LLDPE Film 1	10	0.9	631	54.1	526	45.1
LLDPE Resin 2	14	1.2	847	69.9	350	28.9
LLDPE Film 2	5	0.4	891	70.4	370	29.2
PVC film 1	160	2.4	3170	47.4	3360	50.2
PVC film 2	120	1.7	3390	47.3	3650	60.0

It has to be noticed that this source of information is considered relevant to estimate the fraction of NP in plastics. Indeed, the initial residual NP concentrations in TNPP samples were known and these TNPP grades have been taken as representative for the TNPP on the market.

Taking the maximum value for NP concentration, it will be assumed that during the process, 4.7%[5] of TNPP is hydrolysed leading to a similar amount of NP (in mass). Indeed, considering the hydrolysis pathway (three molecules of NP formed for each molecule of TNPP hydrolysed) and the molecular weights of the substances, it can be assumed that 1 mg of TNPP would yield to 0.96 mg of NP.

The following properties have been taken for the risk assessment of NP due to the use of TNPP. They have been taken from the EU RAR for nonylphenol (E.C., 2002).

Table 3.1-7: main characteristics of nonylphenol used for the risk assessment

Molecular weight	220,34 g/mol	$F_{STP-air}$	0.0669
Melting point	-8°C	$F_{STP-water}$	0.35
Boiling point	290°C (degradation)	$F_{STP-sludge}$	0.344
Relative density	0.95	K_{psusp}	$5.36.10^{2}$
Vapour pressure	0.3 Pa	K_{psed}	$2.68.10^{2}$
Log Kow	4.48	K_{psoil}	$1.07.10^{2}$
Water solubility	6 mg/L	K_{oc}	$5.36.10^{3}$
Henry's Law constant	11.02 $Pa.m^{-3}.mol^{-1}$	**BCF**	1,280
Half-life for biodegradation in soil	300 days		

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[5] This fraction of TNPP converted into NP during the process is based on limited information on the fraction of NP in product samples taken during processing. Further information is required concerning this issue.

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3.1.2.5 General parameters used for the calculation of local releases

Table 3.1-8: Parameters used for the calculation of local releases due to formulation and processing of TNPP

Life cycle stages	Tonnage				Stage	Emission factors				Local characteristics		
Uses	**Fraction**	**Tonnage for application**	**Regional tonnage of substance**	**Fraction of TNPP in formulation**		**A-Table or scenario**	**F released to air**	**F released to waste water**	**F released to industrial soils**	**B-Tables**	**Number of days of emission**	**Fraction of main source**
PVC films	0.35	2,800	700	0.015	Formulation	PA ESD[2]	0.00011	0.00011	0	B 2.3	300	1
					Processing	PA ESD[2]	0.00005	0.00005	0	B 3.9	300	1
					Service life[1]	PA ESD[2]	0.0005	0.016*	0	B 4.1	365	0.002
LLDPE films	0.15	1,200	700	0.002	Formulation	PA ESD[2]	0.00011	0.00011	0	B 2.3	300	1
					Processing	PA ESD[2]	0.00005	0.00005	0	B 3.9	300	1
					Service life[1]	PA ESD[2]	0.0005	0.016*	0	B 4.1	365	0.002
HDPE films	0.1	800	227	0.002	Formulation	PA ESD[2]	0.00011	0.00011	0	B 2.3	300	1
					Processing	PA ESD[2]	0.00005	0.00005	0	B 3.9	300	1
					Service life[1]	PA ESD[2]	0.0005	0.016*	0	B 4.1	365	0.002
Rubber	0.37	2,960	700	0.01	Formulation	RI ESD[3]	Specific calculations for this scenario are explained in section 3.1.2.3					
					Processing	RI ESD[3]						
					Service life[1]	RI ESD[3]						
Others	0.03	240	240	0.015	Formulation	PA ESD[2]	0.00011	0.00011	0	B 2.3	300	1
					Processing	PA ESD[2]	0.00005	0.00005	0	B 3.14	300	1

[1] Emission considered at the regional level

[2] OECD Emission Scenario Document on plastic additives

[3] OECD Emission Scenario Document on additives in rubber industry

* Releases to surface water

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3.1.2.6 Regional releases

Based on the exposure scenarios introduced previously, the following regional releases can be estimated:

Table 3.1-9: regional releases of TNPP

	TNPP regional releases (kg/d)
Air	8.32
Waste water	48.3
Surface water	181
Industrial soil	0.688

3.1.2.7 Regional concentrations

The following regional concentrations for TNPP have been calculated using EUSES and taking into account the different releases identified in the previous section of the exposure assessment.

The regional concentrations of NP are also reported in Table 3.1-11.

Table 3.1-10: regional concentrations for TNPP

	TNPP regional PEC Log Kow 14; sol. 50 µg/L
Surface water - dissolved (µg/L)	2.04×10^{-7}
Sea water - dissolved (µg/L)	1.98×10^{-8}
Freshwater sediment (µg/kg ww)	2.44×10^{3}
Seawater sediment (µg/kg ww)	237
Agricultural soil (mg/kg ww)	4.9
Natural soil (mg/kg ww)	2.05×10^{-2}
Air (mg/m^3)	4.49×10^{-8}

Table 3.1-11: regional concentrations for NP

	NP regional PEC (E.C., 2002) / estimation after implementation of the Risk Reduction Strategy
Surface water (µg/L)	0.60 / **0.18**
Freshwater sediment (µg/kg ww)	103 / **30.9**
Agricultural soil (mg/kg ww)	0.265 / **0.08**
Natural soil (mg/kg ww)	1.44×10^{-5} / **4.32×10^{-6}**
Air (mg/m^3)	3.14×10^{-6} / **9.42×10^{-7}**

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Since the completion of the risk assessment report, risk reduction measures have been applied to reduce the amounts of NP released in the environment. Consequently, this should have had an impact on the regional concentrations calculated initially. UK Competent Authorities estimated that the measures proposed to reduce the risk for nonylphenol would result in a reduction of emissions by 70%. The concentrations indicated in bold in Table 3.1-11 takes into account this reduction of the regional concentrations calculated in the nonylphenol risk assessment report (E.C., 2002). These estimates have been used for the calculation of PEC_{local} for NP in this assessment.

3.1.2.8 Releases during TNPP production

Three facilities are currently producing TNPP in EU_{15}. A fourth facility ceased TNPP production in 2001. In general, companies do not routinely monitor TNPP or NP and hence meaningful monitoring data from most facilities are likely not available. To estimate the daily releases of TNPP, TGD Tables A1.1. and B1.4. were used (E.C., 2003).

Site specific information was used to complete the exposure assessment of the three facilities manufacturing TNPP in EU_{15}. To ensure the confidentiality of the data, detailed calculations for real production sites are not included at this stage. PEC calculated using site specific information will appear at point 3.1.3.1.1.

One production facility conducted periodic monitoring for nonylphenol of the waste stream leaving their waste treatment facility prior to entering the municipal treatment plant. In 2002, the NP concentrations were non-detectable, with a sensitivity of 1 mg/m^3. In 2003, the results were also non-detectable with a sensitivity of 0.1 mg/m^3. Consequently, at the production step, releases of NP from the production of TNPP will not be taken into account.

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3.1.2.9 Releases during the use in PVC films or LLDPE films

Remark: both scenarios are compiled since there are driven by the same parameters.

Table 3.1-12: Local TNPP and NP (in brackets) emissions due to use in PVC films or LLDPE films

	Emission to waste water	**Emission to Air**
	kg/d	**kg/d**
Formulation	0.257 (0.0121)	0.257 (0.0121)
Processing	0.117 (5.48x10^{-3})	0.117 (5.48x10^{-3})
Disposal / Recovery	Not considered	

3.1.2.10 Releases during the use in rubber

Table 3.1-13: Local TNPP and NP (in brackets) emissions due to use in rubber

	Emission to waste water	**Emission to Air**
	kg/d	**kg/d**
Formulation and processing - **tyres** - **soles**	 - 0.017 (0.016) - - 4x10^{-3} (7.76x10^{-3})	 - 1.881 (7.75x10^{-4}) - - 0.553 (3.88 x10^{-5})

Disposal / Recovery	Not considered

3.1.2.11 Releases during the use in HDPE films

Table 3.1-14: Local TNPP and NP (in brackets) emissions due to use in HDPE films

	Emission to waste water	Emission to Air
	kg/d	kg/d
Formulation	0.083 ($3.91x10^{-3}$)	0.083 ($3.91x10^{-3}$)
Processing	0.038 ($1.78x10^{-3}$)	0.038 ($1.78x10^{-3}$)
Disposal / Recovery	Not considered	

3.1.2.12 Releases during the use in other applications

Table 3.1-15: Local TNPP and NP (in brackets) emissions due to use in other applications

	Emission to waste water	Emission to Air
	kg/d	kg/d
Formulation	0.09 ($4.14x10^{-3}$)	0.09 ($4.14x10^{-3}$)
Processing	0.04 ($1.88x10^{-3}$)	0.04 ($1.88x10^{-3}$)

3.1.3 Aquatic compartment (incl. sediment)

3.1.3.1 Predicted environmental concentrations in water

The Predicted Environmental Concentrations (PECs) for local water are calculated using the environmental releases detailed in section 3.1.2 using the equations set out in the TGD. By default and in the absence of specific information, the following values are used: $EFFLUENT_{STP}$ = 2000 m^3/d (flow of the STP), DILUTION = 10 (dilution factor).

In calculating the local PEC, the regional PEC is added to the local concentrations.

3.1.3.1.1 $PEC_{local(water)}$ at TNPP production sites

Final results of the PECs calculations for the three European TNPP production sites are presented in Table 3.1-16. The calculations have been performed using specific information available (e.g. flows of the STPs and receiving waters). Although these specific data are kept confidential, the type of data available for each site is indicated in Table 3.1-16.

Site C is presented in the report for information as the production of TNPP was stopped in 2007 (M. Schocken personal communication, 4th of February 2008).

Table 3.1-16: PEClocal for the three European TNPP production sites

	Site-specific information available	**PEC_{STP} for TNPP (µg/L)**	**PEC_{local} for TNPP (µg/L)**
		Log Kow 14; sol. 50 µg/L	
Site A	Production volume (2001) Waste water treatment plant flow Flow of receiving waters Releases of TNPP Processing takes place on-site (included)	84.1	4.08×10^{-7}
Site B	Production volume (2001) Waste water treatment plant flow Flow of receiving waters	136	1.33×10^{-5}
*Site C**	*Production volume (2001)*	*857*	*2.07×10^{-4}*

*** Only for information, TNPP has not been produced at this site for at least a year (M. Schocken personal communication, 4th of February 2008).**

3.1.3.1.2 $PEC_{local(water)}$ at sites using TNPP

Site specific information for releases during the use of TNPP for LLDPE films production

In 2003, water samples were collected at one TNPP processing facility. These samples were analysed for nonylphenol concentrations by High Performance Liquid Chromatography. The highest concentration of 82.7 µg/L was measured in the process wastewater.

At the same site, nonylphenol concentrations up to 10.3 µg/L were measured in sewer. At this site, the stream further undergoes primary treatment prior to discharge but it is not subjected to secondary treatment. Therefore, as a worst case estimation (no further removal), nonylphenol concentration in effluent of 10.3 µg/L could be considered at this site as a concentration resulting from TNPP processing.

This monitoring result shows that nonylphenol releases due to TNPP uses in polymer industry can not be neglected. However, as on one hand the end-products processed at this site are not known and on the other hand the TNPP volumes used are not specified, these values could not be used as a general scenario for estimating nonylphenol releases due to TNPP processing.

Therefore, default releases estimations will have to be used in the risk assessment for each use pattern.

Default releases estimation

It is assumed that formulation and processing stages can take place at the same site. Therefore, in calculating local concentrations, releases due to both stages are added.

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Table 3.1-17: PEClocal for water for sites using TNPP

Uses	PEC$_{local}$ (µg/L)		PEC$_{STP}$ (µg/L)	
	TNPP Log Kow 14; sol. 50 µg/L	NP	TNPP Log Kow 14; sol. 50 µg/L	NP
PVC films **LLDPE films**	3.82×10^{-6}	0.504	15	3.26
Rubber				
- **tyres**	3.68×10^{-7}	0.466	0.68	2.88
- **soles**	2.43×10^{-7}	0.323	0.16	1.44
HDPE films	1.37×10^{-6}	0.285	4.84	1.06
Other uses	1.44×10^{-6}	0.291	5.12	1.12

3.1.3.2 Calculation of Predicted Environmental Concentration for Sewage Treatment Plants (PEC$_{stp}$)

For the risk characterisation of a substance upon micro-organisms in the STP, it can be assumed that homogeneous mixing in the aeration tank occurs which implies that the dissolved concentration of a substance is equal to the effluent concentration. In addition, no intermittent release is assumed for production or uses of TNPP. Therefore, PEC$_{STP}$ are equal to the concentration of TNPP in STP effluents (Clocal$_{eff}$). See above section 3.1.3.1 for the results.

3.1.3.3 Calculation of PEC$_{sediment}$

The concentration in bulk sediment can be derived from the corresponding water body concentration, assuming a thermodynamic equilibrium (see equation 50 in TGD).

In calculating the local PEC, the regional PEC is added to the local concentrations.

Results of PEClocal$_{sediment}$ are given in Table 3.1-18.

Table 3.1-18: PEClocal for sediment for sites using TNPP

Uses	PEC$_{sed}$ for TNPP (mg/kg ww) Log Kow 14; sol. 50 µg/L	PEC$_{sed}$ for NP (mg/kg ww)
Production site A	2.44	-
Production site B	79.9	-
*Production site C**	*1.24×10^{3}*	-
PVC films, LLDPE films (formulation and processing)	22.9	0.059
Rubber		
- **tyres**	2.21	0.055
- **soles**	1.45	0.038
(formulation and processing)		

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Uses	**PEC$_{sed}$ for TNPP (mg/kg ww)** **Log Kow 14; sol. 50 µg/L**	**PEC$_{sed}$ for NP (mg/kg ww)**
HDPE films **(formulation and processing)**	8.24	0.033
Other uses **(formulation and processing)**	8.64	0.034

*** Only for information, TNPP has not been produced at this site for at least a year (M. Schocken personal communication, 4th of February 2008).**

3.1.4 Marine compartment

This section will be added when the exposure part for the aquatic compartment (freshwater and freshwater sediment) will be refined.

3.1.5 Terrestrial compartment

3.1.5.1 Calculated PEC for soil

PECs can be calculated for natural soil, agricultural soil and grassland using equations 51 to 67 in the TGD. These predicted environmental concentrations in soils take into account possible direct release of TNPP to soils, application of sewage sludge in agriculture and dry and wet deposition from the atmosphere.

Direct releases of TNPP to soils are expected to be negligible (see Table 3.1-8). In a same way, soil concentrations due to air deposition could be expected to be negligible because of low amount of TNPP released to air and a rapid degradation of TNPP in the atmosphere (see section 3.1.1.1.1).

The main contribution to TNPP concentration in soils is then expected to come from the application of sewage sludge (Cf. the high log Kow).

In calculating the local PEC, the regional PEC for natural soil is added to the local concentrations.

3.1.5.1.1 PEClocal$_{soils}$ at TNPP production sites

Final results of the PECs calculations for the three European TNPP production sites are presented in Table 3.1-19.

Table 3.1-19: PEClocal for the three European TNPP production sites

	PEClocal$_{agr.soil}$ mg.kg^{-1} wet wt. (averaged over 30 days) **Log Kow 14; sol. 50 µg/L**	**PEClocal$_{agr.soil}$ mg.kg^{-1} wet wt. (averaged over 180 days)** **Log Kow 14; sol. 50 µg/L**	**PEClocal$_{grassland}$ mg.kg^{-1} wet wt. (averaged over 180 days)** **Log Kow 14; sol. 50 µg/L**
Site A	36	36	14.4

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	$PEClocal_{agr.soil}$ mg.kg^{-1} wet wt. (averaged over 30 days) **Log Kow 14; sol. 50 µg/L**	**$PEClocal_{agr.soil}$ mg.kg^{-1} wet wt. (averaged over 180 days)** **Log Kow 14; sol. 50 µg/L**	**$PEClocal_{grassland}$ mg.kg^{-1} wet wt. (averaged over 180 days)** **Log Kow 14; sol. 50 µg/L**
Site B	58	58	23.2
*Site C**	*2.05 x10^{-2}*	*2.05 x10^{-2}*	*2.05 x10^{-2}*

*** Only for information, TNPP has not been produced at this site for at least a year (M. Schocken personal communication, 4th of February 2008).**

3.1.5.1.2 $PEClocal_{soils}$ at sites using TNPP

It is assumed that formulation and processing stage can take place at the same site. Therefore, in calculating local concentrations, releases due to both stages are added.

Table 3.1-20: $PEClocal,_{soil}$ for European TNPP processing sites

	Uses	**$PEClocal_{agr.soil}$ mg.kg^{-1} wet wt. (averaged over 30 days)**	**$PEClocal_{agr.soil}$ mg.kg^{-1} wet wt. (averaged over 180 days)**	**$PEClocal_{grassland}$ mg.kg^{-1} wet wt. (averaged over 180 days)**
TNPP **Log Kow 14; sol. 50 µg/L**	**PVC films** LLDPE films	6.42	6.42	2.58
	Rubber			
	- **tyres**	0.317	0.317	0.148
	- **soles**	0.09	0.09	0.051
	HDPE films	2.1	2.1	8.49
	Other uses	2.21	2.21	0.897
NP	**PVC films** LLDPE films	0.018	0.015	0.005
	Rubber			
	- **tyres**	0.016	0.013	0.005
	- **soles**	0.008	0.006	0.002
	HDPE films	0.006	0.005	0.002
	Other uses	0.006	0.005	0.002

3.1.6 Atmospheric compartment

In the calculation of PEClocal for air, emission from a point source as well as emission from a STP are taken into account.

For the generic TNPP production site, the concentration calculated at 100 m distance from the STP represents the major input for the PEClocal calculation whereas for all uses, TNPP concentration in air is mainly due to direct emission. Annual average predicted concentrations in air are calculated below.

In calculating the local PEC, the regional PEC is added to the local concentrations.

3.1.6.1.1 PEClocal$_{air}$ at TNPP production sites

Final results of the PECs calculations for the three European TNPP production sites are presented in Table 3.1-21**Erreur ! Source du renvoi introuvable.**.

Table 3.1-21: PEClocal,$_{air}$ for the three European TNPP production sites

	PEClocal$_{air,ann.}$ (µg.m^{-3}) **Log Kow 14; sol. 50 µg/L**
Site A	0.225
Site B	4.54 x 10^{-5}
*Site C**	*4.59 x 10^{-5}*

*** Only for information, TNPP has not been produced at this site for at least a year (M. Schocken personal communication, 4th of February 2008).**

3.1.6.1.2 PEClocal$_{air}$ at sites using TNPP

It is assumed that formulation and processing stage can take place at the same site. Therefore, in calculating local concentrations, releases due to both stages are added.

Table 3.1-22: PEClocal for air for sites using TNPP

Uses	**PEC$_{air}$ for TNPP (µg.m^{-3})** **Log Kow 14; sol. 50 µg/L**	**PEC$_{air}$ for NP (µg.m^{-3})**
PVC films **LLDPE films**	0.086	0.005
Rubber		
- **tyres**	0.430	0.001
- **soles**	0.126	0.001
HDPE films	0.028	0.002
Other uses	0.030	0.002

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

EUSES has been used to calculate the concentrations of TNPP in fish and earthworms. As a worst case values of 0.05 mg/L and 14 have been used for water solubility and log Kow, respectively. Considering the chosen value for log Kow, a BMF of one is applied to the calculation of the PECs for TNPP and a BMF of 1 is taken for NP concentrations.

Table 3.1-23: Predicted Concentrations for secondary poisoning

Life Cycle Stage	**Concentration of TNPP in fish from surface water for predators (mg.kg^{-1})**	**Concentration of TNPP in earthworms from agricultural soils (mg.kg^{-1} wet weight)**	**Concentration of NP in fish from surface water for predators (mg.kg^{-1})**	**Concentration of NP in earthworms from agricultural soils (mg.kg^{-1} wet weight)**
TNPP use in PVC films and LLDPE films	5.86 x 10^{-7}	0.475	0.401	0.0301

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Life Cycle Stage	**Concentration of TNPP in fish from surface water for predators (mg.kg^{-1})**	**Concentration of TNPP in earthworms from agricultural soils (mg.kg^{-1} wet weight)**	**Concentration of NP in fish from surface water for predators (mg.kg^{-1})**	**Concentration of NP in earthworms from agricultural soils (mg.kg^{-1} wet weight)**
(formulation and processing)				
TNPP used in rubber				
- **tyres**	1.3 x 10^{-7}	0.266	0.381	0.027
- **soles**	1.05 x 10^{-7}	0.255	0.306	0.016
(formulation and processing)				
TNPP use in HDPE films **(formulation and processing)**	3.28 x 10^{-7}	0.357	0.286	0.0125
TNPP use in other applications **(formulation and processing)**	3.41 x 10^{-7}	0.363	0.286	0.014

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

3.2.1 Aquatic compartment (including sediment)

3.2.1.1 Fish

3.2.1.1.1 Acute toxicity

Table 3.2-1 shows a summary of the acute toxicity tests that were performed with fish species. The toxicity limits reported are above the upper limit of the estimated water solubility (solubility < 50 µg/L).

Table 3.2-1: Summary of acute toxicity tests with fish

Test #	Species	References	Comment	Validity*
1	Species: *Oncorhynchus mykiss* LC_{50} (96 hours) > 100 mg/L Method: OECD GL 203	Guterson, 2001	Concentrations tested were far above the solubility of the substance. No effect was seen at the highest concentration tested although no analytical monitoring was performed.	2
2	Species: *Brachydanio rerio* LC_{50} (96 hours) = < 10 mg/L LC_{50} (48 hours) = 16 mg/L Method: Dir. 84/449/EEC C.1	CIBA-Geigy, 1992a	The tested concentrations were probably very far above the actual water solubility of the substance. No analytical follow-up of the test concentrations was performed. As there was no equilibration time to allow dissolution of the substance during the preparation of the test concentration, it is not even clear that the maximum solubility in the test medium was achieved. The report mentions that undissolved substance was observed at all test concentrations.	3
3	Species: *Leuciscus idus* LC_{50} (48 hours) = 7.1 mg/L Method: DIN 38412-L15	CIBA-Geigy, 1988a	Concentrations tested were above the solubility of the substance and the results show no effect below the estimated upper limit of the water solubility of TNPP.	3

* 1 = valid; 2 = valid with restrictions; 3 = invalid; 4 = not assignable

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Detailed descriptions of the tests are presented hereafter.

Test #1: the acute toxicity of an hydrolysed solution of TNPP (purity 99.8%) has been tested on *Oncorhynchus mykiss* according to the OECD guideline 203 (Guterson, 2001).

The fish were held 33 days before initiating the test on TNPP. Mortality in the stock culture was less than 0.1 % the week prior to test initiation. The fish were fed a daily ration of trout chow equal to 5 % of their body weight but were not fed 24 h prior to test initiation or during the test. The dilution water was dechlorinated City of Calgary tap water (charcoal filtered and aerated) and had a hardness of 198 mg $CaCO_3$/L, alkalinity of 140 mg $CaCO_3$/L, pH of 7.6, and a conductance of 446 ms/cm.

The test solutions were prepared from a stock solution initially containing 100.0 mg/L of TNPP. The solutions were gently aerated for 78 h at room temperature (20 ± 2 °C). The supernatants containing the hydrolysis products of TNPP were then decanted for preparation of the test solutions. The stock solutions and 200 L of dilution water were cooled to the test temperature overnight in a controlled environment chamber (15 °C with aeration).

At test initiation, dissolved oxygen, temperature, and pH ranged from 8.7 to 9.2 mg/L (98% to 100% saturation), 14 to 16 °C, and 7.7 to 8.0 units, respectively. At test termination, the temperature and pH of the test solutions were 15 °C and 7.8, respectively. Dissolved oxygen levels ranged from 6.2 to 6.8 mg/L (69 to 75 % saturation). The test solutions were only analysed for nonylphenol but nonylphenol was not detected in any of the test solutions collected at test initiation and termination.

There were no signs of stress or unusual behaviour exhibited by the fish in any of the treatment concentrations. No fish died at any concentration at any time point. The highest non-lethal concentration tested was set as greater than or equal to the 100 mg/L of TNPP hydrolysis products. LC50 was > 100 mg/L after 24, 48, 72 and 96h.

This study should be considered as valid with restrictions. Indeed, tested concentrations were far above the water solubility of TNPP. Nonylphenol has been measured but not detected in any sample. The way test solutions were prepared should have enable the observation of effects triggered off by metabolites (nonylphenol). The result from this test can be used to support the fact that no toxicity of TNPP is expected above its water solubility (< 50 µg/L).

Test #2: the acute toxicity of TNPP (purity >94%) has been tested on *Brachydanio rerio* according to Directive 84/449/EEC, C.1 (CIBA-Geigy, 1992a). Five concentrations plus one control were tested (10, 18, 32, 58 and 100 mg/l). The control was performed in the test medium, i.e. dechlorinated tap water with an hardness of 171 mg $CaCO_3$/L. Other test parameters were as follow: pH between 7.3 and 7.9, temperature = 22 +/- 1°C. During the test, 10 fish were disposed per aquarium. They were acclimated 125 days prior the test and adapted to test medium 24 hour prior testing and no food was delivered 24 hours prior to exposure. A gentle aeration was started after 48 hours exposure. The test was conducted under a fluorescent light, 16 hours daily. The stock solution contained a mixture of 4 g. test substance and 160 mg Alkylphenol-Polyglycol-Ether (ARKOPAL) completed to 2 L with water.

During the test, the oxygen saturation ranged from 89-97% at 24 hours, 68-83% at 48 hours, and 60-76% at 72 hours. In the preliminary test, 10 mg/L TNPP had no effect to the fish after 96 hours of exposure. In the main test, 10 mg/L showed no effect to the fish after 48 hours. However, the oxygen concentration in the water was determined to be low at 48 hours and a gentle aeration was started at this time. After 72 hours of exposure with the test substance, all fish were dead. It is also important to notice that a small part of the test substance was swimming at the surface of the test vessels at all test times and concentrations.

No LC_{50} could be estimated after 96h but some results were calculated at intermediate times: LC_{50}(48h)=16 mg/L (95% CL 12-19 mg/L) ; LC_{50}(24h)=29 mg/L (95% CL 23-36 mg/L). No mortality occurred in blank and in the vehicle controls.

Test #3: a static test was performed with *Leuciscus idus* (CIBA-Geigy, 1988a). Test organisms were acclimated 22 days with no food distribution three days prior to testing and for the test, mean fish size and weight were respectively 44 mm (35-50 mm) and 0.59 g. (0.29-0.85 g.). This led to a loading of 0.39 g/L in the test aquariums (test volume = 15 L.). 10 fish were disposed per concentration and control and dechlorinated tap water was used as dilution water. A hardness of 254 mg $CaCO_3$/L (Ca/Mg = 4/1) was measured. During the test, dissolved oxygen, pH and temperature were measured at 0, 24 and 48 hours: $[O_2]$ > 91% saturation, pH = 7.9-8.2 and T = 20 +/- 1°C. The test medium was gently aerated during the test and a fluorescent light was used 16 hours a day.

The stock solution of TNPP was prepared using a vehicle solvent, DMF. 5 g. of TNPP were dissolved in made up to 50 mL with DMF. This resulted in a concentration of DMF of 950 mg/L for the highest TNPP concentration tested.

Fish were exposed during 48 hours to six TNPP concentrations (5.8, 10, 18, 32, 58 and 100 mg/L) plus a blank and a control with the vehicle solvent used. Different symptoms were observed at the different test concentrations: moderate effects on swimming behaviour were observed after 24 and 48 hours at the concentration of 5.8 mg/L. Slight effects on the respiratory function has been observed after 48 hours, at 5.8 mg/L (one fish died at this concentration). All fish died at concentrations down to 10 mg/L. A LC_{50} of 7.1 mg/L was calculated.

Study #2 and #3 have to be considered as invalid:

- The tested concentrations were probably very far above the actual water solubility of the substance.
- No analytical follow-up of the test concentrations was performed. As there was no equilibration time to allow dissolution of the substance during the preparation of the test concentration, it is not even clear that the maximum solubility in the test medium was achieved. The report mentions that undissolved substance was observed at all test concentrations.
- All fish died at the lowest test concentration during aeration of the test system at t = 48 h.

3.2.1.1.2 Long-term toxicity

No chronic toxicity test with fish is available.

3.2.1.2 Aquatic invertebrates

3.2.1.2.1 Acute toxicity

Table 3.2-2 shows a summary of the acute toxicity tests that were performed with aquatic invertebrate species.

Table 3.2-2: Summary of acute toxicity tests with aquatic invertebrates

Test #	Species	References	Comment	Validity
1	Species: *Daphnia magna* EC_{50} (48 hours) = 0.009 mg/L Method: OECD GL 202	Hydroqual Laboratories Ltd, 2001a	The toxicity value is expressed as nonylphenol measured concentration (nonylphenol is the main hydrolysis product of TNPP).	2
2	Species: *Daphnia magna* EC_{50} (48 hours) = 0.42 mg/L Method: Dir. 84/449/EEC C.2	CIBA-Geigy, 1992b	No analytical monitoring was conducted neither for TNPP nor for its degradation product (nonylphenol). However, test result is comparable with the results of test #1 and other tests conducted with nonylphenol.	3

* 1 = valid; 2 = valid with restrictions; 3 = invalid; 4 = not assignable

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Detailed descriptions of the tests are presented hereafter.

Test #1: (Hydroqual Laboratories Ltd, 2001a) The test was initiated with young daphnids less than 24 h old from in-house cultures. Mortality in the stock culture was less than 1% in the week prior to test initiation. Dilution water was dechlorinated City of Calgary tap water (charcoal filtered and aerated). The dilution water had a hardness of 188 mg $CaCO_3$/L, alkalinity of 100 mg $CaCO_3$/L, pH of 8.1, and conductivity of 421 ms/cm. The ratios of calcium-to-magnesium and sodium-to-potassium on a weight-to-weight basis were 3.4 and 4.0 respectively. The concentration of dissolved oxygen was 8.2 mg/L (100 % saturation at the test temperature 20 +/- 1°C).

The test solutions were prepared from a stock solution initially containing 100 mg/L of TNPP. The mass of TNPP selected for the test was based on initial attempts to get enough of the hydrolysis products in solution to be acutely toxic to *Daphnia magna*. The method detailed below provided a stock solution that was acutely lethal to *Daphnia magna*.

TNPP (100 mg) was weighed onto a glass Petri dish. The dish and test substance were placed into a two-litre, glass Erlenmeyer flask containing 1 L of dilution water. A magnetic stir bar was added and the mouth of the flask sealed with Parafilm®. The test substance was gently stirred for 78 h at room temperature (20 ± 2 °C). The supernatant containing the hydrolysis products of TNPP was then decanted for preparation of the test solutions. A stock was prepared from the hydrolysed TNPP solution by diluting 100 mL of the supernatant with 900 mL of dilution water (10 mg/L nominal). This solution was then serially diluted with laboratory dilution water to obtain the other eight test concentrations (5.00, 2.50, 1.25, 0.63, 0.31, 0.16, 0.08, and 0.04 mg/L). The concentrations were nominal values based on the total mass of TNPP initially added to the flask and hydrolysed for 78 h (100.0 mg/L).

The organisms were then added to the test vessels in a random fashion (final loading density of one organism per 10 mL of test solution). There were four replicates for each test concentration containing 5 daphnids. The daphnids were not fed during the test. Beakers were placed on a tray and covered with a glass sheet. The test was conducted at conditions similar to the culture conditions. The test vessels were examined at 24 and 48 h, and the number of immobilised organisms recorded along with any observations of unusual behaviour.

The samples of the test solutions were analysed for the major hydrolysis product of TNPP, nonylphenol. Nonylphenol was only detected in the highest treatment at test initiation (0.3 mg/L based on the results of duplicate analyses; detection limit of 0.2 mg/L). Toxicity values were derived based on this measured concentration of nonylphenol. The test concentrations for toxicity values were derived from the single measured value available for nonylphenol (starting value that was serially diluted by a factor of 2 to obtain the numerical values for the test concentrations, all of which were below the detection limit of 0.2 mg/L for nonylphenol).

At test initiation the concentration of dissolved oxygen, temperature, and pH ranged from 8.2 to 8.3 mg/L (99% saturation), 19°C, and 8.1 to 8.3 units, respectively. At test termination, the concentration of dissolved oxygen, temperature, and pH ranged from 7.6 to 7.8 mg/L (96 to 100% saturation), 21°C, and 8.2 to 8.3 units, respectively. Dead organisms were considered immobilised.

Toxicity values were derived based on nominal concentrations for the mixture of TNPP hydrolysis products. These nominal values were likely higher than actual concentrations because of the sparingly soluble nature of the test substance and hydrolysis products. The concentrations and 95 % confidence limits of the hydrolysis products that immobilised 50 % of the daphnids at 24 and 48 h were 2.2 mg/L (1.7 to 3.0 mg/L) and 0.3 mg/L (0.2 to 0.4 mg/L), respectively. This would correspond to a 24-h LC50 of 66 µg/L and a 48-h LC 50 of 9 µg/L expressed as estimated nonylphenol. The toxic response and presence of detectable levels of the hydrolysis product in solution confirmed that the TNPP had undergone hydrolysis during preparation of the stock solution. TNPP is not soluble in water and the only major hydrolysis product is nonylphenol. Hence, nonylphenol is likely the toxic agent present in the test solutions. The low effect concentration could also be attributed to physical effect although there was no identification of the presence of undissolved material during this test.

No explanation can be found to explain the low toxicity observed during this short-term toxicity testing with daphnids. Indeed, the toxicity observed could not be attributed solely to nonylphenol measured in the test medium if we refer to the EU risk assessment available on this substance.

Industry is asked to perform another test to solve this issue (and to analyze both TNPP – if possible, and NP). This study could also be used in order to test the possible constraints of the realisation of a long-term test that should be performed subsequently. Indeed, TNPP being suspected to be highly hydrophobic, other exposure routes should be studied.

Test #2: (CIBA-Geigy, 1992b) Calculated amounts of the test material to produce the desired concentrations were added to the water and were homogeneously distributed. Values are based on the nominal concentrations. Parts of the test substance were visible on the surface of the water at concentrations of 0.1-1.0 mg/L.

One day before the start of exposure, reproductive *Daphnia* are separated from the young (0-24 hours old) by sieving all individuals through an 800 mm sieve. This procedure is repeated immediately prior to exposure and the young are retained for the test. The *Daphnia* (4 replicates of 5 *Daphnia* each) were then transferred into the beakers. Cultures of *Daphnia* were maintained in glass vessels containing approximately 2.5 litres of reconstituted water and maintained at 20 +/- 1°C. The oxygen content ranged from 97 to 103%, the pH ranged from 7.8 to 8.0, and the water temperature was maintained at 21-24°C throughout the experiment.

The EC-50 values were calculated according to the maximum likelihood method, probit model. EC-values were graphically determined on gausso-logarithmic probability paper. The EC_{50} values at 24 and 48 h were 2.6 and 0.42 mg/L, respectively.

This study has to be considered as invalid:

- The tested concentrations were probably very far above the actual water solubility of the substance.
- No analytical follow-up of the test concentrations was performed. As there was no equilibration time to allow dissolution of the substance during the preparation of the test concentration, it is not even clear that the maximum solubility in the test medium was achieved. The report mentions that undissolved substance was observed at all test concentrations.

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3.2.1.2.2 Long-term toxicity

A 28-day sediment-water toxicity test using spiked sediment was conducted with *Lumbriculus variegatus*, following OECD guideline 225 (Picard, 2008). Artificial sediment was prepared (6.0% sphagnum peat, 20% kaolin clay, 37% fine sand and 37% of coarse sand) and characterized (organic carbon content 1.8%, pH of 6.3, and a percent moisture 11.8%). TNPP was applied to sediment at dose levels of 63, 130, 250, 500 and 1000 mg a.i./kg. Prior to test termination, no observations of mortality or abnormal behavior were evident during this study. However, turbidity of the overlying water caused by oligochaete burrowing activity made accurate observations of the test organisms difficult. The total number of oligochaetes recovered at test termination and mean biomass for each replicate of each treatment level observed throughout the exposure period are presented in Table 3.2-3.

At test termination (day 28), the number of living oligochaetes recovered within the 63, 130, 250, 500 and 1000 mg a.i./kg treatment levels was 21, 19, 14, 15 and 12, respectively. There was a missing individual in one test vessel of the 1000 mg/kg treatment level. This individual oligochaete was assumed to have died. A statistically significant difference in number of total oligochaetes recovered in all treatment levels tested compared to the pooled control organisms was established.

Mean biomass in the 63, 130, 250, 500 and 1000 mg a.i./kg treatment levels was 20, 21, 15, 15 and 8.7 mg, respectively. A statistically significant difference in mean biomass in all treatment levels tested compared to the pooled control organisms was established.

Since all concentrations of TNPP caused a statistically significant reduction of both oligochaete reproduction and biomass, the NOEC value for these endpoints was empirically estimated to be < 63 mg a.i./kg. The LOEC for this exposure was determined to be 63 mg a.i./kg. Based on linear regression, an EC10 value was calculated as an estimate of the NOEC for reproduction and biomass. The NOEC values for reproduction and biomass were estimated to be 44 and 25 mg a.i./kg, respectively.

One deviation from the OECD guideline 225 was observed in the report, the total ammonia content was analysed only in Solvent control and in the highest dose. The guideline indicates the analysis at least in one replicate of the controls and in one test vessel of each concentration level at the start of the exposure period, and subsequently 3 x per week.

Table 3.2-3 Nominal sediment concentrations, number of oligochaetes and biomass of oligochaetes at test termination of the 28-day exposure with TNPP

Nominal Sediment Concentration (mg a.i./kg)	Control	Solvent Control	Pooled Control	63	130	250	500	1000
Mean Number Of Oligochaetes per Replicate (SD[b])	27 (1.9)	24 (2.6)	25 (2.5)	21 (1.5)[c]	19 (1.8)[c]	14 (2.5)[c]	15 (2.6)[c]	12 (2.1)[c]
Mean Biomass per Replicate per Concentration in Milligrams (SD)	28.11 (5.39)	32.28 (4.82)	30.19 (5.34)	19.79 (6.36)[c]	20.86 (4.29)[c]	15.08 (6.42)[c]	14.98 (4.19)[c]	8.66 (5.73)[c]

[b] SD = Standard Deviation

[c] Statistically different ($p \leq 0.05$) compared to the pooled control data, based on Bonferroni's t-Test.

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3.2.1.3 Algae

Table 3.2-4 shows a summary of the toxicity tests that were performed with algae species.

Table 3.2-4: Summary of toxicity tests with algae

Test #	Species	References	Comment	Validity*
1	Species: *Selenastrum capricornutum* NOEC (72 hours) 100 mg/L (growth rate) Method: OECD GL 201	Hydroqual Laboratories Ltd, 2001b	No significant effects upon algae growth were observed at any test concentration. On the contrary, it seems that the hydrolysis of TNPP during the experiment has increase the phosphorous content of the test medium causing growth stimulation.	2
2	Species: *Scenedesmus subspicatus* NOEC (72 hours) 100 mg/L (biomass) Method: Dir. 87/302/EEC, part C., p. 89	CIBA-Geigy, 1992c	No significant effects upon biomass were observed at any test concentration.	2

* 1 = valid; 2 = valid with restrictions; 3 = invalid; 4 = not assignable

Detailed descriptions of the tests are presented hereafter.

Test #1: (Hydroqual Laboratories Ltd, 2001b) The test was initiated with exponentially growing cells from in-house cultures maintained at 23 ± 2°C under continuous light (3,770 lux). The cultures were grown under axenic conditions in 2-L flasks containing 1 L of artificial media, aerated with filtered sterile air. Cell numbers were obtained from optical density measurements at 430 nm calibrated against particle and cell counts at test termination. The dilution water was dechlorinated City of Calgary tap water (charcoal filtered and aerated) spiked with nutrients. The dilution water had a hardness of 198 mg $CaCO_3$/L, alkalinity of 146 mg $CaCO_3$/L, pH of 7.6, and conductance of 446 ms/cm.

The test solutions were prepared from a stock solution initially containing 100 mg of TNPP in 1 L of dilution water. The substance was weighed on a glass Petri dish (100 mg) and the dish placed into a 2 L glass, Erlenmeyer flask containing 1 L of dilution water. A magnetic stir bar was added and the mouth of the flask sealed with Parafilm®. The test substance was stirred gently for 78 hours at room temperature (21 ± 2 °C). The test solutions were then prepared from the stock solution of TNPP hydrolysis products as recommended by the OECD for the testing of difficult substances. A 100 mL volume of the hydrolysed stock solution was poured into a 250 mL plastic container for the highest test concentration (100 mg/L nominal test concentration). A second 100 mL volume of the stock solution was poured into another 250-mL container and serially diluted with 100-mL volumes of dilution water to obtain the remaining test concentrations (50.0, 25.0, 12.5, 6.3, 3.1, and 1.6 mg/L nominal test concentrations).

The solutions were spiked with 1 mL of a concentrated nutrient solution and then inoculated (1 mL) to give an initial cell density of 9,664 + 154 cells/mL. The inoculum was taken from an exponentially growing culture, washed twice with a sodium bicarbonate solution, and the cell number adjusted to give the desired initial cell density in the 100-mL test volume.

The test was conducted in a controlled environment chamber at 23 + 2°C under continuous light with intensity at the plate surface of 4,370 lux provided by cool white fluorescent lights.

Two sets of samples were collected for chemical analysis. The first set consisted of samples of the test solutions and control at test initiation. The second set consisted of samples of the test

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solutions and control incubated under the test conditions for 72 h. The samples were not analysed for TNPP because it is insoluble in water. The samples of the test solutions were analysed for nonylphenol however it was not detected in any of the samples (detection limit of 0.2 mg/L).

The pH at test initiation and termination in the controls and 100.0 mg/L test solution ranged from 7.0 to 8.0. The initial and final control cell densities were 9,664 cells/mL and 404,000 cells/mL, respectively. This was a 42-fold increase in cell density over the 72-h test period. A 16-fold increase was required for a valid test. The test medium contains 0.65 mg/L phosphate. Complete hydrolyses of the test substance (100 mg/L) would yield approximately 12 mg/L of phosphorous acid. The cell density in the highest test concentration at 72 h was 344 % greater than the controls. This represents approximately 1.5 additional doublings of the cell population exposed to the hydrolysed TNPP solution when compared to the controls. The result indicates that hydrolysis of TNPP causes growth stimulation due to the liberation of phosphorous. The LOEC as well as the 24, 48 and 72 h EC50 values were >100 mg/l. The NOEC was the highest concentration tested of 100 mg/l. The level of nonylphenol present in the test solutions under the conditions in which the stock solution was prepared, diluted, and tested was not toxic to unicellular green alga, *Raphidocelis subcapitata*.

Test #2: (CIBA-Geigy, 1992c) Nominal test concentrations of 0, 1.23, 3.7, 11, 33 and 100 mg/L were used (three replicates for the test concentrations and 6 replicates for the blank).

The stock solution was prepared by mixing 200 mg of the test substance with 80 mL water and 1 mL of a 0.8% alkylphenol-polyglycol ether and made up to 100 mL with water. This 100 mL solution was then made up to 1 liter with water. Calculated amounts of the stock solution to produce the desired test concentrations were added to the water. The algae were then transferred into the flasks (100 mL Erlenmeyer flasks, stoppered with aluminium caps, on Lab-Shaker). The cell densities were measured at 24, 48, and 72 hour. The temperature was continuously measured and maintained at 23 +/- 1°C. The pH was measured at 0 and 72 hours and ranged from 7.8 to 8.1. The test was conducted under continuous illumination, cold white fluorescent light, 118 µE/m² sec +/- 20% (approx. 8000 lux.).

No significant effects upon biomass were observed at any test concentration.

3.2.1.4 Micro-organisms

A respiration inhibition test was conducted using TNPP on activated sludge from the sewage treatment plant of CH-4153 Reinach (CIBA-Geigy, 1988b). The OECD guideline 209 was followed. Sludge concentration was 1.6-1.7 g/L and the temperature was 20 +/- 2°C during the test. The test was performed with dechlorinated drinking water. A reference substance (3,5-dichlorophenol) was also tested and an IC_{50} of 16 mg/L was determined. A deviation from the guideline is highlighted: instead of a centrifuged sludge, a settled sludge was used. Due to the very low solubility and the expected low toxicity of the substance, only one concentration (100 mg/L) was tested in duplicates during three hours. The test substance was directly added to the test vessel. In one replicate, no inhibition was recorded, in the other, an inhibition of 24% was observed. This test must be considered invalid as 25% inhibition were found in a replicate. Consequently a NOEC cannot be determined.

As TNPP is not considered as readily biodegradable, the result of the first biodegradability test presented in this report (Hydroqual Laboratories Ltd, 2001c) is not useable for the determination of the $PNEC_{microorganisms}$. However a supplementary assay was conducted during test #2 of this report (CIBA-Geigy, 1994). Indeed the test substance has also been tested with the reference substance in presence of the inoculum in order to control the toxicity and inhibition of the bacteria's activity by the test substance. The controls of reference and reference together with the test substance meet the specification for ready biodegradability. Therefore, it can be concluded that the test substance has no inhibitory effect on the bacteria at the concentration tested (18.1 mg/L) which is above the solubility limit of TNPP.

3.2.1.5 Calculation of Predicted No Effect Concentration (PNEC)

3.2.1.5.1 Surface water

The PNEC derived in the risk assessment report of nonylphenol will be used for the risk characterisation relating to the NP formed during the use of TNPP

$\text{PNEC}_{\text{water}}$ (NP) = 0.33 µg/L (based on a chronic study with the algae *Scenedesmus subspicatus* and an assessment factor of 10).

Toxicity tests available for TNPP tend to indicate that no toxicity is expected above its water solubility (< 50 µg/L).

3.2.1.5.2 Sewage treatment plants

No valid test with micro-organisms is available. However, a supplementary test conducted during a ready biodegradability test tends to demonstrate that TNPP has no inhibitory effect on bacteria at concentrations below its solubility limit. According to the TGD, a PNEC for sewage treatment plants can be derived using an assessment factor of 10 on the non-inhibitory concentration from a ready biodegradation test, i.e. a PNEC of >1.8 mg/l can be derived for TNPP.

For nonylphenol, the PNEC_{STP} of 9.5 mg/L will be retained (E.C., 2002).

3.2.1.5.3 Sediment

The PNEC_{sed} can be calculated using the NOEC values for biomass estimated to be 25 mg a.i./kg dw (Picard, 2008). The experimental NOEC is normalised to a standard NOEC taking in account the Organic Carbon content of the tested sediment versus the standard sediment:

$$\text{NOEC}_{\text{standard}} = \text{NOEC}_{\text{experiment}} \text{ x } (\text{Foc}_{\text{sediment standard}} / \text{Foc}_{\text{sediment experiment}})$$

$$\text{NOEC}_{\text{standard}} = 25 \text{ x } (0.05/0.018) = 69.4 \text{ mg/kg dw}$$

An Assessment Factor of 100, corresponding to one long-term sediment test available in the dataset, is applied to derive the $\text{PNEC}_{\text{sediment}}$.

$$\text{PNEC}_{\text{sediment}} = 69.4 / 100 = 0.694 \text{ mg/kg dw}$$

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PNEC Conversion dry weight/wet weight: $PNEC_{\text{wet sediment}} = (PNEC_{\text{dry sediment}} * Fsolid_{susp} * RHOsolid) / RHOsusp$
with
Fsolidsusp= 0.1
RHOsolid=2500
RHOsusp=1150
(TGD 2ed chap 2 Table 5 p43; E.C., 2003)

$PNEC_{\text{wet sediment}} = (0.694 * 0.1 * 2500) / 1150$

$PNEC_{\text{wet sediment}} = 0.150$ mg/kg ww

For TNPP, a $PNEC_{sed}$ of 150 µg/kg ww can be derived.

For nonylphenol, the $PNEC_{sed}$ of 39 µg/kg ww will be retained (E.C., 2002).

3.2.2 Marine compartment

This section will be added when the exposure part for the aquatic compartment (freshwater and freshwater sediment) will be refined.

3.2.3 Terrestrial compartment

3.2.3.1 Terrestrial effect data

No data available.

3.2.3.2 Calculation of $PNEC_{soil}$

In the absence of any ecotoxicological data for soil organisms, the $PNEC_{soil}$ could be provisionally calculated using the equilibrium partitioning method. However, according to the toxicity tests conducting with aquatic organisms, it seems that TNPP will not have a toxic effect below the upper limit of the estimated water solubility, no $PNEC_{water}$ could have been derived for TNPP. Consequently, the equilibrium partitioning method cannot be applied to calculate a $PNEC_{soil}$ for TNPP.

For nonylphenol, the $PNEC_{soil}$ of 300 µg/kg ww will be retained (E.C., 2002).

3.2.4 Atmosphere

No data available.

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

A $PNEC_{oral}$ can be calculated based on a NOAEL of 167 mg/kg bw/d determined during a 90-d repeated dose toxicity study on rats.

From this NOAEL, a NOEC of 3340 $mg.kg_{food}^{-1}$ can be calculated using a conversion factor of 20 (applicable to a test performed on *Rattus norvegicus* - > 6 weeks).

The $PNEC_{oral}$ is then determined using an assessment factor of 90 (duration of the test on mammals is 90 days):

$$PNEC_{oral} = \frac{TOX_{oral}}{AF_{oral}} = \frac{3340}{90} = 37 \ \text{mg.kg}_{food}^{-1}$$

For nonylphenol, a $PNEC_{oral}$ of 10 $mg.kg_{food}^{-1}$ has been determined (E.C., 2002).

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3.3 RISK CHARACTERISATION

Nota: the risk assessment is based on the use of standard TNPP. It should be noticed that two grades of TNPP are put on the marketplace, one with around 5% residual NP ("standard TNPP" in the RAR), the other one containing less than 0.1% residual NP. The risk assessment of the high pure TNPP would lead to the calculation of local concentrations of NP reduced to approximately one third of the one currently available in this report.

3.3.1 Aquatic compartment (including sediment)

Surface water

Results of the RCR calculations for the three European TNPP production sites and for the sites where TNPP is used are presented in Table 3.3-1 and Table 3.3-2 for sewage treatment plants for TNPP and NP and water for NP. Only RCRs for STP for TNPP have been calculated as no effect has been shown for TNPP above its water solubility. However, works are still needed on this aspect and the risk characterisation for TNPP in surface water could be updated based in the results of the conclusion (i) program.

Table 3.3-1: RCR for STP for the three European TNPP production sites

	RCR_{STP} for TNPP Log Kow 14; sol. 50 µg/L
Site A	<0.047
Site B	<0.076
*Site C**	*<0.476*

*** Only for information, TNPP has not been produced at this site for at least a year (M. Schocken personal communication, 4th of February 2008).**

RCR for STP are below the trigger value of 1, indicating an acceptable risk from the production of TNPP. During the production step, it has been estimated that no NP emission occurs[6].

Table 3.3-2: RCR for STP and water for sites using TNPP

Uses	**RCR_{STP} for TNPP** Log Kow 14; sol. 50 µg/L	**RCR_{STP} for NP**	**RCR_{water} for NP**
PVC films **LLDPE films**	<0.008	3.43×10^{-4}	**1.52**
Rubber			
- **tyres**	$<3.8 \times 10^{-3}$	3.03×10^{-4}	**1.41**
- **soles**	$<8.9 \times 10^{-5}$	1.52×10^{-4}	0.97
HDPE films	<0.003	1.12×10^{-4}	0.86
Other uses	<0.003	1.18×10^{-4}	0.88

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[6] This is in accordance with the RAR for NP where no risk has been identified for the use of NP for TNPP production

No risks are identified according to the calculation of RCR in STP for both TNPP and NP.Some local PEC_{water} for NP are above the $PNEC_{water}$ that is derived from the risk assessment on NP (0.33 µg/L). A risk is identified for the uses of standard TNPP in PVC and LLDPE films and in rubber (for tyres).

Sediment compartment

Results of the RCR calculations for TNPP for the three European TNPP production sites are presented in Table 3.3-3.

RCRs calculated from the exposure to TNPP and NP due to the use of standard TNPP are presented in Table 3.3-4. For nonylphenol a PNEC of 39 µg/kg ww has been derived (E.C., 2002).

Table 3.3-3: RCR for sediment for the three European TNPP production sites

	RCR_{sed} for TNPP **Log Kow 14; sol. 50 µg/L**
Site A	**16**
Site B	**533**
*Site C**	8267

*** Only for information, TNPP has not been produced at this site for at least a year (M. Schocken personal communication, 4th of February 2008).**

Table 3.3-4: RCR for sediment for sites using TNPP

Uses	**RCR_{sed} for TNPP** **Log Kow 14; sol. 50 µg/L**	**RCR_{sed} for NP**
PVC films **LLDPE films**	**153**	**1.51**
Rubber		
- **tyres**	**15**	**1.41**
- **soles**	**10**	0.97
HDPE films	**55**	0.85
Other uses	**58**	0.87

Based on TNPP exposure, a risk is identified for the use of TNPP in PVC films, LLDPE films, rubber (tyres and soles), HDPE films and other uses.

Based on NP exposure due to the use of TNPP, a risk is identified for the use of TNPP in PVC and LLDPE films and in rubber (for tyres).

Conclusions to the risk assessment for the aquatic compartment

Sewage treatment plants (exposure to TNPP and NP)

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(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.

This conclusion applies to all stages of the life cycle of TNPP.

Freshwater (exposure to TNPP)

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

This conclusion applies to all stages of the life cycle of TNPP.

- There is a need for more information for the effect assessment of TNPP. A long-term testing on *Daphnia* is requested.

Update on the work performed to answer this request: a short-term test with daphnids has been performed by Industry. However, some drawbacks associated with the chemical analysis were identified during the test and the study should be considered invalid (low recovery rates found with the TNPP analysis; too high nominal concentrations of TNPP tested leading to sufficient residual NP concentrations to generate an effect). Based on this experience, a new test is currently being setting-up.

Freshwater (exposure to NP)

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

This conclusion applies to the use of standard TNPP in PVC and LLDPE films and in rubber (for tyres).

The exposure concentrations of NP due to the use of standard TNPP lead to a risk for the aquatic compartment. The PNEC for nonylphenol (E.C., 2002) has been calculated using an assessment factor of 10 on the lowest result of three chronic tests on different trophic levels. Therefore, it is not expected that the PNEC for NP can be realistically refined.

OR

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

The $PNEC_{water}$ for Nonylphenol and Octylphenol are currently being revised by the UK RMS on the basis of the Risk Assessment Report (E.C., 2002) and completed with new data that are derived from a literature search at web of science for the most recent years 2003 to September 2008.

The risk characterisation of TNPP (exposure to NP) could be refined based on monitoring studies (NP measurements) at processing sites.

Sediment (exposure to TNPP)

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

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This conclusion applies to all stages of the life cycle of standard TNPP.

OR

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

This conclusion applies to all stages of the life cycle of standard TNPP.

- Concerning the sediment compartment, one long term study is available on the toxicity of TNPP toward endobenthic organisms and associated with an Assessment Factor of 100 to calculate the PNEC. Considering the low solubility in water and the high adsorption potential of TNPP, toxicity on sediment dwelling organisms should be further studied. Toxicity testings on sediment organisms should be done for the refinement of the $PNEC_{sed}$.
- A refinement of the information used to calculate the PEC or site monitoring should be considered afterward if a RCR >1 is calculated and a risk is still identified.

Sediment (exposure to NP)

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

This conclusion applies to the use of TNPP in PVC and LLDPE films and in rubber (for tyres).

OR

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

As the exposure assessment of NP is based on the equilibrium partitioning method, any refinement of the exposure assessment of NP in freshwater will lead to a refinement of the exposure assessment in sediment (see conclusion (**i**) for freshwater).

The $PNEC_{sediment}$ for Nonylphenol and Octylphenol are currently being revised by the UK RMS on the basis of the Risk Assessment Report (E.C., 2002) and completed with new data that are derived from a literature search at web of science for the most recent years 2003 to September 2008.

3.3.2 Marine compartment

This section will be added when the exposure part for the aquatic compartment (freshwater and freshwater sediment) will be refined.

3.3.3 Terrestrial compartment

There is a lack of toxicity data that does not enable the determination of a PNEC for this compartment. Consequently, no risk characterisation can be done for TNPP.

RCRs calculated from the exposure to NP due to the use of TNPP are presented in the following table. For nonylphenol a PNEC of 0.3 mg/kg ww has been derived (E.C., 2002).

Table 3.3-5: RCR for soil for sites using TNPP

Uses	**RCR_{soil} for NP**
PVC films **LLDPE films**	0.06
Rubber	
- **tyres**	0.053
- **soles**	0.026
HDPE films	0.02
Other uses	0.02

Based on NP exposure and effect assessment, no risk is identified for sites using standard TNPP (formulation and processing combined).

No risk characterisation can be done for TNPP as ecotoxicological test results are lacking.

Conclusions to the risk assessment for the terrestrial compartment

Soil (exposure to TNPP)

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

This conclusion applies to all stages of the life cycle of TNPP.

- Considering the suspected high adsorption potential of TNPP, toxicity on soil organisms should be studied. Based on the outcome of the long-term *Daphnia* study a $PNEC_{soil}$ sould be calculated with the equilibrium partitioning method. Toxicity testing on soil organisms should be performed subsequently for the determination of the $PNEC_{soil}$ in case a risk is identified for this compartment.

Soil (exposure to NP)

(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.

This conclusion applies to all stages of the life cycle of TNPP.

3.3.4 Atmosphere

No risk characterisation can be carried out for the air compartment since there is no specific effect data.

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

Results of the risk characterisation for secondary poisoning are presented in Table 3.3-6.

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Table 3.3-6: RCRs for secondary poisoning

Uses	RCR$_{food}$ for TNPP	RCR$_{terr,food,ch}$ for TNNP	RCR$_{food}$ for NP	RCR$_{terr,food,ch}$ for NP
PVC films LLDPE films (formulation and processing)	1.58 x 10^{-8}	0.013	0.04	3.01 x 10^{-3}
Rubber - tyres - soles (formulation and processing)	3.51 x 10^{-9} 2.83 x 10^{-9}	7.18 x 10^{-3} 6.89 x 10^{-3}	0.038 0.031	2.7 x 10^{-3} 1.6 x 10^{-3}
HDPE films (formulation and processing)	8.86 x 10^{-9}	9.64 x 10^{-3}	0.029	1.25 x 10^{-3}
Other uses (formulation and processing)	9.21 x 10^{-9}	9.81 x 10^{-3}	0.029	1.4 x 10^{-3}

For TNPP, no risk is identified based on exposure and effect assessment.

For NP, no risk is identified for the releases due to the use of TNPP.

Conclusions to the risk assessment for secondary poisoning

Secondary poisoning (exposure to TNPP)

(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.

This conclusion applies to all stages of the life cycle of TNPP.

- There are already indications that the bioconcentration factor of TNPP could be low (Cf. Annex 2 and section 3.1.1.2.5).

Secondary poisoning (exposure to NP)

(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.

This conclusion applies to all stages of the life cycle of TNPP.

3.3.6 PBT assessment

3.3.6.1 PBT assessment for TNPP

- The P/vP screening criterion is fulfilled as the substance is non readily biodegradable based on a negative result at a test on ready biodegradability performed according to OECD guidelines 301B and 301D. It has been shown than the substance can be hydrolysed into nonylphenol, this hydrolytic product being readily biodegradable. However, hydrolysis was not considered to be significant in environmental conditions.

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The low mineralization observed in ready biodegradation test would allow considering the substance as P/vP although further testing would be necessary for a definite assignment.

- The screening B/vB criterion is fulfilled based on the bioaccumulation potential determined with log Kow worst case values for QSAR models. A log BCF of 2.68 has been calculated for fish (TNPP log Kow >10) and a log BCF of 6.07 has been calculated for earthworm (TNPP log Kow maximum value of 8). However, while considering the measured log Kow of 14 and additional information on the molecular weight and the size of the molecule, there might be indications that the above calculations overestimate the bioaccumulation potential of the substance (section 3.1.1.2.5). Further testing would be necessary for a definite assignment.

- Concerning the T criterion, no aquatic toxicity is expected at concentrations above the water solubility of TNPP based on the available set of information. However, a long-term test with daphnids is requested.

Conclusions to PBT assessment

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

- Based on the available data, TNPP would be classified as vPvB. However, only the screening criteria are fulfilled for the P/vP criterion. Likewise, the vB criterion is fulfilled based on a BCF calculated from an estimated log Kow taken as a worst case. The T criterion remains inconclusive, pending the results of a new long-term toxicity test on daphnids. Refinement of these 3 parameters is necessary to conclude the PBT assessment of this chemical.

3.3.6.2 PBT assessment for NP

Properties of NP have been extracted from the EU risk assessment report available for this substance (E.C., 2002).

- Nonylphenol is considered inherently biodegradable. However, a half-life in surface water has been estimated at 150 days. Hence the vP criterion is fulfilled (half-life > 60 days).

- The B criterion is not fulfilled based on the BCF of 1,280 used in the European risk assessment report (BCF < 2000).

- The T criterion is fulfilled since NOECs < 0.01 mg/L have been identified for fish and invertebrates for example.

Based on the properties of nonylphenol, it appears that nonylphenol is neither PBT nor vPvB.

4 HUMAN HEALTH

4.1.1 Human exposed via the environment

The following sections will be updated when agreement will be found in the environmental exposure assessment.

4.1.1.1 Indirect exposure via the environment

4.1.1.2 Human exposed via the environment

4.1.1.2.1 Summary of risk characterisation for exposure via the environment

5 RESULTS

5.1 ENVIRONMENT

Conclusions to the risk assessment for the aquatic compartment

Sewage treatment plants (exposure to TNPP and NP)

(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.

This conclusion applies to all stages of the life cycle of TNPP.

Freshwater (exposure to TNPP)

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

This conclusion applies to all stages of the life cycle of TNPP.

- There is a need for more information for the effect assessment of TNPP. A long-term testing on *Daphnia* is requested.

Update on the work performed to answer this request: a short-term test with daphnids has been performed by Industry. However, some drawbacks associated with the chemical analysis were identified during the test and the study should be considered invalid (low recovery rates found with the TNPP analysis; too high nominal concentrations of TNPP tested leading to sufficient residual NP concentrations to generate an effect). Based on this experience, a new test is currently being setting-up.

Sediment (exposure to TNPP)

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

This conclusion applies to all stages of the life cycle of standard TNPP.

OR

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

This conclusion applies to all stages of the life cycle of standard TNPP.

- Concerning the sediment compartment, one long term study is available on the toxicity of TNPP toward endobenthic organisms and associated with an Assessment Factor of 100 to calculate the PNEC. Considering the low solubility in water and the high adsorption potential of TNPP, toxicity on sediment dwelling organisms should be further studied. Toxicity testings on sediment organisms should be done for the refinement of the $PNEC_{sed}$.
- A refinement of the information used to calculate the PEC or site monitoring should be considered afterward if a RCR >1 is calculated and a risk is still identified.

Conclusions to the risk assessment for the marine compartment

This section will be added when the exposure part for the aquatic compartment (freshwater and freshwater sediment) will be refined.

Conclusions to the risk assessment for the terrestrial compartment

Soil (exposure to TNPP)

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

This conclusion applies to all stages of the life cycle of TNPP.

- Considering the suspected high adsorption potential of TNPP, toxicity on soil organisms should be studied. Based on the outcome of the long-term *Daphnia* study a $PNEC_{soil}$ sould be calculated with the equilibrium partitioning method. Toxicity testing on soil organisms should be performed subsequently for the determination of the $PNEC_{soil}$ in case a risk is identified for this compartment.

Conclusions to the risk assessment for the air compartment

No risk characterisation can be carried out for the air compartment since there is no specific effect data.

Conclusions to the risk assessment for secondary poisoning

Secondary poisoning (exposure to TNPP)

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(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.

This conclusion applies to all stages of the life cycle of TNPP.

- There are already indications that the bioconcentration factor of TNPP could be low (Cf. Annex 2 and section 3.1.1.2.5).

5.2 HEALTH

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GLOSSARY

Standard term Abbreviation	Explanation/Remarks and Alternative Abbreviation(s)
Ann.	Annex
AF	assessment factor
BCF	bioconcentration factor
bw	body weight / *Bw*, *b.w.*
°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_{50}	period required for 50 percent dissipation (define method of estimation)
DT_{50lab}	period required for 50 percent dissipation under laboratory conditions (define method of estimation)
DT_{90}	period required for 90 percent dissipation (define method of estimation)
$DT_{90field}$	period required for 90 percent dissipation under field conditions (define method of estimation)
EC	European Communities
EC	European Commission
EC_{50}	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_{oc}	Fraction of organic carbon
G	gram(s)

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PNEC(s)	Predicted No Effect Concentration(s)
$PNEC_{water}$	Predicted No Effect Concentration in Water
(Q)SAR	Quantitative Structure Activity Relationship
STP	Sewage Treatment Plant
TGD	Technical Guidance Document[7]
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 / *h*
HPLC	High Pressure Liquid Chromatography
IARC	International Agency for Research on Cancer
C_{50}	median immobilisation concentration or median inhibitory concentration 1 / *explained by a footnote if necessary*
ISO	International Standards Organisation
IUPAC	International Union for Pure Applied Chemistry
kg	kilogram(s)
kPa	kilo Pascals
K_{oc}	organic carbon adsorption coefficient
K_{ow}	octanol-water partition coefficient
Kp	Solids water partition coefficient
l	litre(s)
log	logarithm to the basis 10
$L(E)C_{50}$	Lethal Concentration, Median
LEV	Local Exhaust Ventilation
m	Meter
µg	microgram(s)

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[7] 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.
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mg	milligram(s)
MAC	Maximum Accessibility Concentration
MOS	Margins Of Safety
NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration
NOEL	No Observed Effect Level
OEL	Occupational Exposure Limit
OECD	Organisation for Economic Co-operation and Development
OJ	Official Journal
pH	potential hydrogen -*logarithm* (to the base 10) of the hydrogen ion concentration (H^+)
pKa	-*logarithm* (to the base 10) of the acid dissociation constant
pKb	-*logarithm* (to the base 10) of the base dissociation constant
Pa	Pascal unit(s)
PEC	Predicted Environmental Concentration
STP	Sewage Treatment Plant
WWTP	Waste Water Treatment Plant

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The report provides the comprehensive risk assessment of the substance Trisnonylphenylphosphite (TNPP). It has been prepared by France 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.

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