RISK ASSESSMENT

TERTIARY BUTYL HYDROPEROXIDE (TBHP)

CAS-No.: 75-91-2

EINECS-No.: 200-915-7

Final report, 11 October 2006

ENVIRONMENT

Rapporteur for the risk evaluation of TBHP is the Ministry of Housing, Spatial Planning and the Environment (VROM) in consultation with the Ministry of Social Affairs and Employment (SZW) and the Ministry of Public Health, Welfare and Sport (VWS). 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 Netherlands Organisation for Applied Scientific Research (TNO) and the National Institute of Public Health and the Environment (RIVM), by order of the Rapporteur.

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0 OVERALL CONCLUSIONS / RESULTS OF THE RISK ASSESSMENT

CAS No.:	75-91-2
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IUPAC Name:	Tert-butyl hydroperoxide

ENVIRONMENT

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

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

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

Conclusion iii) is reached, because:

- the local PEC/PNEC is >1 for the aquatic environment (including WWTP) and/or terrestrial environment for one production site and a number of processing sites. Although the exposure assessment is based on a number of default assumptions, no additional data were submitted by industry that may rebut the currently followed approach for the PEC calculations.

  It is stressed that from a scientific perspective, a conclusion (**i**) would have been more appropriate, as refinement of both PEC values (now based on a number of default assumptions instead of site-specific data) and the PNEC values (now based on very limited data) may be possible. However, Industry has not supported to provide additional exposure data or to conduct additional ecotoxicological studies (see further Section 3.5) and thereby implicitly accepted a conclusion (**iii**) for a number of sites. Furthermore, it can be questioned if all PEC/PNEC values would be lowered sufficiently by a refinement of PEC and PNEC values, as some of the current PEC/PNEC values are far above 1.

1 GENERAL SUBSTANCE INFORMATION

Identification of the substance

CAS-No.: 75-91-2

EINECS-No.: 200-915-7

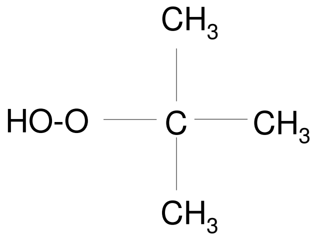
IUPAC name: tert-Butyl hydroperoxide

Synonyms: TBHP, 2-Hydroxyperoxy-2-methylpropane, (1,1-)Dimethylethyl hydroperoxide, tert-Butyl hydrogen peroxide,

Trade names: TBHP-70 (T-Hydro), Cadox TBH, Trigonox AW70, Perbutyl H

Molecular formula: $C_4H_{10}O_2$

Structural formula:



$$\begin{array}{ccc} & CH_3 & \\ & | & \\ HO\text{-}O\ - & C & - CH_3 \\ & | & \\ & CH_3 & \end{array}$$

Molecular weight: 90.1

Purity/impurities and additives for TBHP-70 (T-Hydro)

Purity:	68.4-69.6%	
Impurity:	2-Methylpropano-2-ol	< 0.5%
	Dialkyl peroxide	≤ 0.1%
	Ketones	≤ 0.2%
	Other hydroperoxides	≤ 1%
	Other organics	≤ 0.4%
Additives:	Water	≤ 30%

Physico-chemical properties

In table 1 the physico-chemical properties for TBHP (pure substance) and TBHP-70 are summarised.

Table 1. Physico-chemical properties of TBHP and TBHP-70

Property	**Result**	**Note**	**References**
Physical state	liquid (TBHP and TBHP-70)		
Melting point	-8 to –3°C 3 to 5.5°C (crystals)	1	MSDS, 1996; Merck Index, 1989; Beilstein, 1990; HSDB, 1999.
Boiling point	96°C at 760 mm Hg 35 °C at 20 mm Hg (TBHP-pure) 160 °C	1	MSDS, 1994; Merck Index, 1989; Beilstein, 1990; HSDB, 1999. ChemFinder 2001.
(Relative) density	Liquid: 935-964 kg/m^3 at 25°C Liquid: 791-902 kg/m^3 at 20°C (TBHP-pure) Vapour: 3.1	1	MSDS, 1994; MSDS, 1996; Beilstein, 1990; HSDB, 1999.
Vapour pressure	**2700 Pa at 20°C (experimental)** 3070 Pa at 21°C 730 Pa at 25 °C (experimental)	4	Hooidonk, 1992. MSDS, 1994. SRC PhysProp, 2001; HSDB, 1999
Surface tension	56 dynes/cm		ARCO, 1994.
Water solubility	> 100 mg/l at 25 °C and pH 4.3 20,000 mg/l at 20 °C (estimate) **≥ 100,000 mg/l at 22 °C** ca. **100,000** to 150,000 mg/l at 0-50 °C 700,000 mg/l	5 6	MSDS, 1996. SRC PhysProp, 2001. ChemFinder, 2001. ARCO, 1994. OECD/SIDS, 1995.
Solubility in other solvents	Soluble in ethanol, ether, chloroform; very soluble in alkali metal hydroxy solution .		HSDB, 1999.
Dissociation constant (pKa)	12.8 at 20 °C (experimental)		SRC PhysProp, 2001; HSDB, 1999.
Partition coefficient n-octanol/water (log Kow)	**0.7 at 25 °C (experimental)** 0.94 (estimate)	4	Hooidonk, 1992. SRC PhysProp, 2001.
Henry's Law constant (H)	**2.43 Pa*m^3/mole (estimate)** 1.63 Pa*m^3/mole at 25 °C (estimate)	7	EUSES calculation. Howes et al., 1995.
Atmospheric OH rate Constant	**3E-12 cm^3/molecule*second at 25 °C (experimental)**	1, 8	Anastasi et al., 1978
Flash point	43 °C 62 °C	2	MSDS, 1994. Chemfinder, 2001.
Flammability	Flammable	1	MSDS, 1994.
Autoflammability temperature	238 °C	1	MSDS, 1994.
Explosive properties	Not explosive	3	.
Oxidizing properties	Oxidizing	3	ARCO, 1994.
Granulometry	Not applicable (TBHP is liquid)		

Values printed in bold are used in the environmental exposure assessment (see also footnotes)

1. The same or similar results were found in several literature sources.
2. The hazard of peroxides is not determined by its flammability but by its decomposing properties.
3. Conclusion based on theoretical, and/or structural considerations.
4. Full test report available.
5. Range of concentrations derived from the phase diagram for TBHP-70. The diagram shows one liquid phase up to

100,000-150,000 mg/l (solubility), two liquid phases at ca. 100,000-150,000 mg/l to ca. 650,000 mg/l (above water solubility, but TBHP and water not miscible) and one liquid phase above ca. 650,000 mg/l (TBHP completely miscible with water).

6. Based on composition of TBHP-70 (70% TBHP and 30% water). Concentration is above the water solubility, see above.
7. Henry's Law Constant (H) of 2.43 Pa*m^3/mole: EUSES (version 1.00) calculation, from a vapour pressure (VP) of 2700 Pa and a water solubility (WS) of 100,000 mg/l and the molecular weight (MW) of 90.1 g/mole (H ={[VP*MW]/WS}), according to the EU Technical Guidance document, TGD (EC, 2003). These values have been used in the further EUSES calculations underlying the environmental exposure assessment (section 3.3). The Henry's Law Constant of 1.63 Pa*m^3/mole was calculated with the "Henry's Law Constant Program", using the "bond contribution method" (Howes et al., 1995).
8. The atmospheric OH rate constant of 3E-12 cm^3/molecule*second (Anastasi et al., 1978, also cited in Atkinson 1989, 1990 and SRC PhysProp, 2001), has been used in the further EUSES calculations underlying the environmental exposure assessment (section 3.3).

Conclusion

TBHP is commercially available and used mostly as TBHP-70 (T-Hydro), an aqueous solution of approximately 70 weight percent TBHP and 30 weight percent water[1]. The physico-chemical properties listed in Table 1 include some values for the pure substance. TBHP-70 is a highly reactive peroxide with an active oxygen content of about 12%. Experimental data on explosive properties and oxidising properties were not submitted by industry. In view of theoretical and structural considerations, however, experimental determination of these properties is considered to be not necessary (TBHP is a hydroperoxide with a reactive oxygen-oxygen bond (–O-O-) resulting in significant physical hazards, viz. flammability, thermal decomposition and decomposition due to contamination). All other required physico-chemical data were submitted by industry. Most of these data are based on information from databases, material safety data sheets (ARCO, 1994; MSDS, 1994, 1996) or general published information summarizing experimental or estimated physico-chemical properties. Only the vapour pressure of 2700 kPa at 20 °C and the log Kow of 0.7 at 25 °C are based on full test reports (Hooidonk, 1992). Nevertheless, the available data on the physico-chemical properties of TBHP and TBHP-70 are considered to meet the Annex VIIA requirements.

The substance is flammable, but does not need to be classified as flammable according to the criteria. However, the flashpoint indicates labelling with R10. The substance should be classified as oxidising (symbol O) and labelled with the R-sentence R7, because it is an organic peroxide. Furthermore, the following S-sentences are applicable based on the physico-chemical properties: S3, S7, S14, S43.

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[1] TPHP solutions with a higher purity, up to 90%, are also commercially available (HSDB, 1999)

Classification

- EU Classification in Annex I: The substance is not yet included in Annex I, but the indicated Classification and Labelling (as proposed by the rapporteur) has been approved by the EU Commission Working Group on the Classification and Labelling of Dangerous Substances, in April 2006 (environmental effects) and October 2006 (physico-chemical properties and human health effects), respectively. In October 2006 the Working Group did not yet make a final decision on the assignment of R68. For the final decision on c&l for human health endpoints reference is made to the final version of the human health risk assessment report.

- Classification:
  O; R7
  R10
  Xn; R21/22
  T; R23
  C; R34
  R43
  Mutagenic, Category 3; R68 (provisionally)
  N; R51/53

- Labelling:

Symbols:	O, T, N
R- phrases:	7, 10, 21/22, 23, 34, 43, 68, 51/53
S-phrases:	3/7, 14, 26, 36/37/39, 43, 45, 60, 61

2 GENERAL INFORMATION ON EXPOSURE

2.1 PRODUCTION

The production of tert-butyl hydroperoxide (hereafter referred to as TBHP) is located at three sites in the European Union (Table 2.1). The total EU production volume is around 14,500 tonnes/year (based on the combined 2000 data of the three production companies). The total EU processing volume is around 14,200 tonnes/year (based on the submitted data for 1996-2000). Import into and export outside the EU are 143 and 164 tonnes/year, respectively. The difference of about 300 tonnes/year between production volume and processing volume is thought to be caused by the difference in the year of record of the reported amounts.

The annual market growth in the European Union is expected to be below 3 percent in the near future as indicated by industry.

Table 2.1. Production sites of TBHP in the EU in the year 1996.

COMPANY	LOCATION	TONNAGE (tpa)
Arco Chemical Nederlands LTD	Rotterdam, Netherland	Confidential
Peroxid-Chemie GmbH	Pullach, Germany	Confidential
ATOFINA	Günzburg, Germany	Confidential

2.1.1 Production process

The production of TBHP takes place in a closed batch or closed continuous process. The main types of production of TBHP are:

- Direct reaction of isobutane and liquid oxygen.

  (Used by one of the three EU producers. Overall reaction: $(CH_3)_3CH + O_2 \rightarrow (CH_3)_3CO\text{-}OH$. This reaction produces numerous minor by-products such as t-butyl alcohol and di-butyl peroxide which are removed during the purification by distillation which involves a TBHP-water azeotrope. Decanting of the aqueous phase of the distillation process leaves an organic phase containing around 70% TBHP and 30% water.).

- Preparation from tertiary-butyl alcohol and 30% hydrogen peroxide in presence of sulphuric acid
  (Used by one of the three producers. Overall reaction: $(CH_3)C\text{-}OH + H_2O_2 \rightarrow (CH_3)CO\text{-}OH$.)
- Oxidising of tertiary-butylmagnesium chloride.
- Epoxidation of propylene catalysed by a molybdenum complex.
- Oxidation of t-butyl alcohol in a 50% hydrogen peroxide solution with a reaction catalyst of silicotungstic acid.

2.2 USE PATTERN

Tert-butyl hydroperoxide (TBHP) is primarily used in the chemical industry (HEDSET, 1997). TBHP is used as starting material (or intermediate) and as a reactive ingredient (catalyst, initiator or curing agent). Applications are:

- the epoxidation of propylene to propylene oxide (intermediate);

- free radical initiator for polymerisations, copolymerisations, graft polymerisations and curing of polymers (plastic industry);

- free radical initiator to polymerise unsaturated monomers, usually to high polymers. Mainly used by manufacturers of synthetic lattices or water borne dispersions. Also used as a component of catalysts systems for unsaturated polyester resins (resin industry; see Annex 3 for additional data on the use of TBHP in the resin industry);

- the synthesis of other organic peroxy molecules (as a precursor of initiators) such as perester, persulphate, dialkyl peroxide and perketal derivatives;

- the preparation of speciality chemicals required by fine chemical and performance chemical industries, such as pharmaceuticals and agrochemicals (fungicide).

- the use as an ingredient of hardeners for plastics. These products contain 5 - 20 % TBHP. Hardeners for plastics are also used in the plastic industry.

According to the Danish product register TBHP is used in several products. Only the most important product types and industry groups are listed in descending order according to substance quantity. Product types are paint, lacquer and varnishes, adhesives and binding agents. Industry groups are chemical industry, real estate, renting and other business services (The Danish Product Register, 1997). The numbers of products containing TBHP within a certain concentration interval are summarised in Table 2.2.

Table 2.2. Results from Danish Product Register (1997).

Concentration interval	Number of products	Quantity (tons per annum)
≤ 1 %	38	<1
>1% - <80 %	4	<2
Total	43	<3

Some sources give information about the use of TBHP in bleaching and deodorising operations as an oxidation and sulfonation catalyst (Hawley, 1977) or in cooling systems as an anti-slime agent and as a settling agent in the precipitation of various mineral tailing in aqueous slurries (Brink, 1968 and Hamer, 1977). There is no indication that TBHP is (still) used for these purposes in Europe.

Table 2.3. shows the industrial and use categories of TBHP for the European market in IC/UC terminology being relevant for the environmental exposure assessment. The quantitative distribution for the processing stage tonnage's is around 20% for IC/UC 3-33 and 80% for IC/UC 11-43, based on the data submitted by industry.

Table 2.3. Industrial and use categories of TBHP.

Industrial category	**EC no.**	**Use category**	**EC no.**	**Main category**
Chemical industry: used in synthesis	3	Intermediates	33	I b Intermediates stored on site
Chemical industry: used in synthesis	3	Oxidising agents	37	III Multi-purpose equipment
Polymers industry	11	Process regulators	43	Type III, “Wet”

3 ENVIRONMENT

3.1 GENERAL

TBHP may enter the environment during its production and processing by emission to air and by emission to surface water via effluent from wastewater treatment plants (WWTPs). Furthermore, there may be indirect emission to soil, via deposition from air and/or the use of WWTP sludge on soils.

3.2 ENVIRONMENTAL FATE AND DISTRIBUTION

3.2.1 Abiotic degradation

3.2.1.1 Abiotic degradation in air

Indirect photodegradation

In the atmosphere, photochemical reactions such as the reaction with hydroxyl (OH) radicals are likely pathways for transformations of peroxides (SRI, 1977). For TBHP, because of the stronger C-H bonds than the relatively weak and polar O-H bond, the reaction is expected to proceed mainly via H-atom abstraction from the O-H bond, resulting in the transformation into the $(CH_3)_3COO\bullet$ radical. This radical will react with NO, resulting in the formation of NO_2 and the $(CH_3)_3\ CO\bullet$ radical, the latter reacting further to CH_3COCH_3 (acetone) and the methyl peroxy radical $CH_3COO\bullet$ (SRI, 1977; Atkinson, 1985; 1989; Saunders *et al.*, 1997). In subsequent reactions ozone will be formed. For the gas-phase reaction of TBHP with •OH radicals, a rate constant k_{OH} of $3*10^{-12}$ cm^3 / (molecule*second) was measured at 25 ^0C (Anastasi et al., 1978). At an atmospheric •OH-radical concentration of $5*10^5$ molecules/cm^{-3}, this k_{OH} results in a rate constant for degradation of TBHP in air ($k\text{deg}_{air}$) of 0.13/day (EUSES 1.00 calculation, according to the EU Technical Guidance Document, TGD (EC, 2003) .

In addition to the aforementioned kdeg_{air} of 0.13/day, there is also a reported kdeg_{air} of 0.26/day and a DT50 of 3 days (1993 memo of E. v.d. Plassche (RIVM) to L. Andrews

(ARCO), referring to Atkinson (1980): Chem. Rev. 86, 69-201). The bibliographic data on this reference is not correct and these data can not be found. This report includes a more recent publication of Atkinson (Chem. Rev. 85. 69-201, 1985), but therein only the k_{OH} of $3*10^{-12}$ cm^3 / (molecule*second), measured by (Anastasi et al., 1978) was mentioned. It is noted, however, that the factor of 2 between the two estimates is small regarding the uncertainties in the estimates (of which the results depend on atmospheric temperature and •OH-radical concentration) and that the use of a $kdeg_{air}$ of 0.26/day instead of 0.13/day hardly affects the exposure assessment calculations (concentrations in soil due to atmospheric deposition).

Direct photodegradation

In the atmosphere, direct photodegradation (photolysis by UV-absorption) of TBHP and other peroxides will occur. For TBHP this results in the transformation into $(CH_3)_3CO$**,** followed by the formation of CH_3COCH_3 (acetone) and CH_3OO• (methyl peroxide radical). The highly reactive methyl peroxide will be further oxidised under formation of ozone. There is no quantitative data on the direct photodegradation of TBHP. The rate constant for direct photolysis in air has been estimated to be similar to the rate constant for the indirect photodegradation in air ($k\mathrm{deg}_{air}$; see above section). The occurrence of direct photolysis as a degradation pathway has been confirmed by Atkinson (1990), although not specifically for TBHP, but for hydroperoxides.

Both the indirect and direct photodegradation of TBHP and other peroxides in air result in the formation of ozone. Thus, TBHP may contribute to the build up of photochemical smog. Quantitative data on this potential effect of TBHP (and other peroxides) is lacking. However, because 1) the reactivity of TBHP with OH-radicals is within the same order of magnitude as for e.g. n-pentane and toluene (pers. comm. F. de Leeuw RIVM), and 2) atmospheric TBHP emissions are negligible (< 0.001%) compared to those of n-pentane and toluene, the contribution of TBHP to the build up of photochemical smog is expected to be negligible.

3.2.1.2 Abiotic degradation in water

An abiotic degradation study with TBHP-70 (hydrolysis study, performed essentially in accordance to OECD Guideline 111) did not show an appreciable degradation of TBHP during the 5-d test period at a temperature of 50 ^{0}C and pH values of 4, 7 and 9, respectively (maximal 5% decrease in TBHP concentration, based on a comparison of concentrations measured with a specific method)[2]. The constant and low level of the primary degradation product tertiary butyl alcohol (around 10 mg/l) and the absence of degradation products in the GC determinations also confirmed this stability. The nominal TBHP concentration in the buffer solutions was 630 mg/l; the measured concentrations at day 0 ranged from 650 to 690 mg/l and on day 5 from 620 to 720 mg/l (ARCO, 1992). The differences in measured concentrations mainly depended on the analytical method used. The test report does not contain data on light conditions.

In a recent study the abiotic degradation of TBHP was studied in 10-d tests in ultra-pure water and in sterilised (thus abiotic) activated sludge (Hanstveit and De Bie, 2003)[3]. The tests were performed with 1.5 ml test medium in small (1.6 ml) vials to minimise the possible loss due to evaporation of THBP or degradation products. A combination of un-labelled and ^{14}C-radiolabelled TBHP was used as test substance, at a total TBHP concentration of 25 mg/l test medium (nominal concentration). The total radioactivity was determined by liquid scintillation counting (LSC) and the amount of TBHP and degradation products were determined by HPLC analyses with radiochemical detection (HPLC-Rad) at different intervals during the 10-d tests in which the vials were kept closed and in the dark on a shaking table. The test concentration of TBHP, 25 mg/l, was chosen on the basis of 'realistic worst-case' conditions for one of the production sites at which practically all measured concentrations in the WWTP influent were <25 mg/l (detection limit). The activated sludge was collected from a domestic sewage treatment plant (STP) and contained 3500 mg dry matter per litre. The sludge was sterilised by adding 20 ml mercury chloride solution to 0.5 litre diluted sludge and autoclaving for 15 minutes at 120 ^{0}C. In both media, tests were performed in the absence and presence of a metal-ion (2 or 12 mg Fe^{2+}/l (added as $FeSO_4$), or 12 mg Fe^{3+}/l (added as $FeCl_3$), or 15 mg Al^{3+}/l (added as $AlCl_3$). The metal-ions and concentrations thereof were chosen on

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[2] The study was primarily intended to confirm three analytical methods (titration, polarographic reduction and GC) used by ARCO for the determination of TBHP and its degradation products.

[3] Prior to the start of the study, the test protocol was approved by the Rapporteur.

the basis of a limited survey of actual use conditions as flocculants in domestic STPs in the Netherlands; the results of this survey are included in Hanstveit and De Bie (2003) as Annex B[4]. All test series were carried out in duplicate, with two vials for analysis at each time point. The results show up to around 5% degradation in ultra-pure water and up to around 25% degradation in sterilised sludge, with only a small increase in degradation in the presence of a metal-ion, Fe^{2+} being the most effective metal-ion. The relatively high degradation in the sterilised sludge may be due to incomplete sterilisation (as THBP is degraded rapidly in non-sterilised activated sludge, see section 3.2.2) and to a reaction of the reactive –O-O- group with organic compounds present in the sterilised medium. In the absence of metals the half-life (DT50) of TBHP was 1300 days in ultra-pure water and 45 days in sterilised sludge. In the presence of the highest Fe^{2+} concentration the half-life of TBHP was 170 days in ultra-pure water and 36 days in sterilised sludge (see Table 3.1.b for a summary of the results of all tests in this study). The above data and the recovery of the amount of total radioactivity from the test vials (97% to 104%) show for both media that THBP was not mineralised during the 10 day tests, but mainly degraded to the primary metabolite tertiary butyl alcohol (TBA). In addition, three other, unidentified metabolites were found. In sterilised sludge, one of these metabolites ('unknown 1') represented 6%-8% of the total amount of TBHP plus metabolites after 10 days, with a negligible or small influence of metal-ion added. In ultrapure water, however, the percentage of this metabolite was only 1.5% - 3% in the absence of a metal-ion and in the presence of Fe^{3+} or Al^{3+}, while this percentage increased to 5% and 19% in the presence of 2 mg Fe^{2+}/l and 12 mg Fe^{2+}/l, respectively. This indicates that Fe^{2+} influences the route of degradation (Hanstveit and De Bie, 2003).

The stability of TBHP in water is also confirmed by the results of the aquatic toxicity studies (section 3.4.1 and Annex to Chapter 3). In the 96-h semi-static test (daily renewal) with the fish *Pimephales promelas* and the 48-h static test with the invertebrate *Daphnia magna*, the measured THBP concentrations in the test waters at t = 24-48 hours were $\geq$80% of those at t = 0 hour, showing little loss. In the 72-h static test with the alga *Selenastrum capricornutum*, the measured THBP concentrations in the test waters at t = 72 hours were 70% of those at t = 0

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[4] Metal-ions (added as $FeSO_4$, $FeCl_3$, $FeClSO_4$, or $AlCl_3$) are used in STPs as flocculants in the waterline (for phosphate removal) or in the sludge line (in primary sludge for removal of COD from influent and in secondary sludge for coagualation to improve dewatering characteristics). It is noted that there is a general switch of chemical phosphate removal by metals towards biological phosphate removal, resulting in a strong decrease in metals used in STPs.

hour, showing relatively little loss. The somewhat greater loss in the algae test may be due to adsorption to the algae cells.

There is no quantitative data on photolysis of TBHP in water. The above-mentioned stability of TBHP in the test waters used in the aquatic toxicity studies does not indicate an appreciable degradation due to photolysis (or hydrolysis). Photolysis of TBHP in water yielded high radical concentrations, as did photolysis of its solutions in aliphatic solvents either in the presence or absence of oxygen. In aromatic solvents no radicals were observed unless oxygen was present (Maguire and Pink, 1967). The significance of this latter finding with respect to the aquatic environment is questionable. According to SPI/OPPSD (2001), photolytic and thermal decomposition of TBHP in liquid results in the formation of t-butyl alcohol and the liberation of oxygen gas. In SPI/OPPSD (2001) additional data on the possible reactions of TBHP (viz. homolytic, heterolytic and metallic oxidation-reduction reactions) have been reported, including data on intermediate compounds.

3.2.2 Biodegradation

The biodegradation of TBHP-70 has (among others) been studied in two standardised tests for ready biodegradability (Table 3.1.a). No mineralisation was found, neither in the CO_2 evolution test nor in the closed bottle test (the latter measuring the O_2 uptake), although it is noted that TBHP inhibited the respiration in the inoculum control up to around 40% in both tests, at inoculum concentration (mg/l) to test concentration (mg/l) ratios varying from 0.8:1 to 1.6:1. However, based on the results of the toxicity control in the CO_2 evolution test, the inhibition rate is not high enough to consider TBHP as inhibitory in this test, thus it is concluded that TBHP is not readily biodegradable[5]. On the other hand, both tests showed respiration inhibition of the inoculum control and this effect was confirmed in the activated sludge, respiration inhibition test (section 3.4.1.2) that showed a concentration-related respiration inhibition, increasing from 38% inhibition at the lowest TBHP concentration (inoculum concentration to test concentration ratio is 70:1) to 70% inhibition at the highest TBHP concentration (inoculum concentration to test concentration ratio is 4:1). It is further

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[5] It is noted that there was no toxicity control included in the closed bottle test.

noted that these tests only measure the mineralisation of TBHP and not the biodegradation into the primary metabolite tertiary butyl alcohol (TBA) and further metabolites.

The toxicity of TBHP to micro-organisms was also confirmed in tests for inherent biodegradability (Zahn-Wellens tests, see OECD 302B) of TBA. In these tests, the degradation of TBA (ca. 1500 mg//) was found to be strongly inhibited by TBHP (70 of 140 mg/l), especially at the highest TBHP concentration. At the lowest TBHP concentration, the degradation of TBA was no longer inhibited when TBA was added for the second time (2 weeks after the addition of TBHP and the first load of TBA which was degraded after 2 weeks). This result indicates that the lowest TBHP load (70 mg/l) was degraded after or within 2 weeks). These tests were performed with an inoculum (3000 mg/l) to TBHP concentration (70 or 140 mg/l) ratio of 42:1 and 21:1, respectively (Söllner, 1995). The tests were performed to study the influence of TBHP on the functioning of the WWTP of Peroxid-Chemie (see further below in this section).

Table 3.1.a Biodegradation of TBHP

Test type	**GLP**	**Inoculum Conc.**	**Exp. Time**	**Test compound**	**Test conc., as TBHP** (nominal)	**Readily biodegradable**	**Reference**
CO_2 evolution (modified Sturm test)	Yes	30 mg/l	28 d	TBHP-70 *	19 and 38 mg/l	No	Matla& Blom, 1992 [1]
Closed bottle test	Yes	2 mg/l	96 d	TBHP-70 (Trigonox A-W70)	2 mg/l	No	Van Ginkel, 1990 [2]

1. Test according to EEC Directive 79/831, Annex V Part C, Part III and OECD 301B. Activated sludge from an oxidation ditch used to treat domestic sewage was used as inoculum. No biodegradation was found: the CO_2 production at both test concentrations was 40% and 45% lower (at TBHP-70 concentrations of 54 and 27 mg/l, respectively) than that in the inoculum control, indicating inhibition of the inoculum respiration. In the toxicity control, some inhibition of the biodegradation of the reference substance sodium acetate was found: the maximum inhibition was around 30% (occurring during day 0 to 14) and within 14 days there was 58% biodegradation of sodium acetate in the toxicity controls versus 81% in the inoculum control. According to the guidelines, however, this inhibition is not high enough to consider TBHP as inhibitory (OECD 301: If in the toxicity control less than 35% degradation (based on total DOC) or less than 25% (based on total ThOD or $ThCO_2$) occurred within 14 days, the test substance can be assumed to be inhibitory).
2. Test according to EEC 1984, L251, 1984.09.19, Part C and OECD 301 D. Activated sludge (instead of secondary effluent) from a domestic STP was used as inoculum (according to a draft update of EEC guidelines) and the exposure time was extended from 28 days to 96 days. These minor deviations from the guidelines do not affect the validity of the test. No biodegradation was found: the oxygen consumption in the presence of TBHP was 40% lower than that in the inoculum control, indicating inhibition of the inoculum respiration. However, during the first 28 days of the test, which is the normal test duration for this type of test, the oxygen consumption in the presence of TBHP was only 13% lower than that in the inoculum control. There was no toxicity control (TBHP + reference substance) in this test.

In two recent studies the biodegradation of TBHP was determined in activated sludge, both in 1-h tests (Hanstveit and De Bie, 2003) and in a 6-w activated sludge simulation test (Hanstveit and Cnubben, 2003)[6], see below.

In the 1-h tests, the biodegradation of ^{14}C-radiolabelled TBHP was studied in the absence and presence of a metal-ion (Fe^{2+}, Fe^{3+}, or Al^{3+}), as described in the 10-d abiotic tests that were also performed in this study by Hanstveit and De Bie (2003), see section 3.2.1.2. The activated sludge was taken from the oxidation ditch of a domestic STP, thus the inoculum was not adapted to TBHP. The test concentration of TBHP, 25 mg/l (nominal concentration), was chosen on the basis of 'realistic worst-case' conditions for one of the production sites at which practically all measured concentrations in the WWTP influent were <25 mg/l (detection limit). The inoculum concentration (3700 mg/l) to TBHP concentration (25 mg/l) ratio was 148:1. The results show that around 85% of TBHP was degraded in one hour; the degradation is biodegradation, as negligible or little degradation was found in the abiotic tests. The biodegradation rate was somewhat higher in the presence of a metal-ion, but the differences were small. The half-life (DT50) of TBHP ranged from 18 minutes in the presence of the highest Fe^{2+} concentration to 24 minutes in the absence of a metal-ion (see Table 3.1.b for a summary of the results of all tests in this study), resulting in elimination rate constants of 2.3/hour and 1.7/hour, respectively. THBP was not mineralised during the 1-h tests, but mainly degraded to the primary metabolite tertiary butyl alcohol (TBA); in addition, one unidentified metabolite was found. This second metabolite ('unknown 1'), also found as second major metabolite in the abiotic tests, represented 12%-18% of the total amount of TBHP plus metabolites after 1 hour, with a small influence of metal-ion added (the lowest percentage was found in the absence of a metal-ion and the highest percentage was found at the highest Fe^{2+} concentration (Hanstveit and De Bie, 2003).

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[6] Prior to the start of the study, the test protocol was approved by the Rapporteur.

Table 3.1.b Degradation rate constants and half-lives (DT50) for the abiotic and biotic degradation of THBP in the absence and presence of metal-ions (From Hanstveit and De Bie, 2003)

Medium	**Incubation time**	**Metal-ion concentration**	**Rate Constant (slope)**	**Half-live (DT50)**
ultra-pure water	0-1-3-6-10 days	none	-0.000022/h	1300 days
ultra-pure water	0-1-3-6-10 days	Fe^{3+}: 12 mg/l	-0.000048/h	610 days
ultra-pure water	0-1-3-6-10 days	Al^{3+}: 15 mg/l	-0.000004/h.	6900 days
ultra-pure water	0-1-3-6-10 days	Fe^{2+}: 2 mg/l	-0.000049/h	590 days
ultra-pure water	0-1-3-6-10 days	Fe^{2+}:12 mg/l	-0.000172/h	170 days
sterilized sludge	0-1-3-6-10 days	none	-0.000636/h	45 days
sterilized sludge	0-1-3-6-10 days	Fe^{3+}: 12 mg/l	-0.000701/h	41 days
sterilized sludge	0-1-3-6-10 days	Al^{3+}: 15 mg/l	-0.000780/h	37 days
sterilized sludge	0-1-3-6-10 days	Fe^{2+}: 2 mg/l	-0.000726/h	40 days
sterilized sludge	0-1-3-6-10 days	Fe^{2+}: 12 mg/l	-0.000798/h	36 days
activated sludge [1]	2-12-24-36-48-60 min.	none	-0.02862/min.	24 min.
activated sludge [1]	2-12-24-36-48-60 min.	Fe^{3+}: 12 mg/l	-0.03398/min.	20 min.
activated sludge [1]	2-12-24-36-48-60 min.	Al^{3+}: 15 mg/l	-0.02995/min.	23 min.
activated sludge [1]	2-12-24-36-48-60 min.	Fe^{2+}: 12 mg/l	-0.03762/min.	18 min.

[1] The activated sludge was taken from the oxidation ditch of a domestic STP, thus not adapted to TBHP.

In the 6-w activated sludge simulation test, simulating the aerobic degradation in a WWTP, the removal and biodegradation of THBP was studied. The test was performed largely in accordance to OECD Guideline 303A (Simulation test – aerobic sewage treatment: coupled unit test), with the following major modifications.

- Only one unit, continuously fed with raw sewage and TBHP, was used, thus there was no second unit fed only with raw sewage.
- The test was performed in a ‘closed’ system in which the outlet of the aeration vessel (containing the mixed liquor with activated sludge) was connected with a gas trapping system consisting of two bottles with ethanolamine to trap evolved CO_2, followed by a third bottle with acidified water to trap evolved TBHP, TBA and other volatile metabolites.
- Analyses included total radioactivity measurements by LSC and specific analyses by HPLC-Rad to measure the amount of TBHP and degradation products (TBA and other metabolites) in the different fractions of the system, viz. influent, wasted sludge, gas traps and effluent. This allows for a complete mass balance.

The test consisted of a 1-w stabilisation period (system fed with only raw sewage), followed by a 2-w acclimation period (system fed with raw sewage and un-labelled TBHP) and the final 3-w removal period (system fed with raw sewage and un-labelled plus ^{14}C-radiolabelled TBHP). In the removal period, samples of the different fractions were taken daily for analyses. The total TBHP concentration (un-labelled plus ^{14}C-radiolabelled TBHP) in the influent was 27.7 mg/l (based on the average TBHP concentrations in the stock solutions and the flow rate), corresponding to 19.2 mg/l when corrected for the purity of the unlabelled TBHP. This concentration was chosen on the basis of 'realistic worst-case' conditions for one of the production sites, at which practically all measured concentrations in the WWTP influent were <25 mg/l (detection limit). The activated sludge was taken from the oxidation ditch of one of the production sites, thus the inoculum was already adapted to TBHP (and was further adapted during the acclimation period). The raw sewage was taken from the oxidation ditch of a domestic STP. The 'sludge retention time' (SRT) was 31 days instead of 9 days intended at the start of the test, because the quality of the mixed liquor decreased when THBP was added to the system. Thus it was necessary to adapt the SRT to prevent the sludge from being washed out of the system. The 'hydraulic retention time' (HRT) was 9 hours. The inoculum concentration (2700 mg/l, being the amount of suspended solids in the mixed liquor in the aeration tank) to TBHP concentration (19.2 mg/l) ratio was 141:1.

The results of the activated sludge simulation test, based on the measurements during the last two weeks of the removal period (when the system was stable) are the following.

- No TBHP was found in the effluent.
- The overall removal of radioactivity (based on the radioactivity in influent and effluent) averaged 86%. Of the remaining 14% in effluent, around two-third (9%) was CO_2 and one-third (5%) was the primary degradation product tertiary butyl alcohol (TBA) plus two other, unidentified metabolites ('unknown 1' and 'unknown 2'). When the total amount of the three intermediate metabolites in the effluent is set at 100%, the amount of TBA varied from around 1% to 10%, that of 'unknown 1' from around 10% to 75% and that of 'unknown 2' from around 15% to 85%[7].
- Of the total radioactivity, only 52% was recovered, of which 33% in the gas traps (around 30% CO_2 and 3% TBA), 5% in wasted sludge (almost entirely in the solid fraction, i.e.

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[7] One of the unidentified metabolites of TBHP could be tertiary butyl methyl ether, MTBE ($(CH_3)_3C\text{-}0\text{-}CH_3$) that contains a methyl group instead of the hydroxyl group of TBHP ($(CH_3)_3C\text{-}0\text{-}0H$). No further research had been conducted on this issue. For MTBE (CAS No. 1634-04-4) there is also an EU Risk Assessment Report.

adsorbed to or, more likely, incorporated into the biomass, as THBP has a low sorption potential) and 14% in effluent. The low recovery is most likely related to the formation of the two unidentified metabolites 'unknown 1' and 'unknown 2' that both are most likely very volatile compounds that are not trapped in the gas trapping system (as preliminary tests showed that the gas trapping system was valid for TBHP and TBA). In an additional test it was indeed found that metabolite 'unknown 1' was not trapped in the gas trapping system[8]. Thus, the low recovery is most likely due to the loss of the metabolites 'unknown 1' and 'unknown 2' by evaporation.

The results of this activated sludge simulation test (Hanstveit and Cnubben, 2003) show that TBHP was fully removed from the influent water and that on average 40% was fully mineralised to CO_2.

There are also data on the removal and biodegradation of TBHP in the biological waste water treatment plant (WWTP) of one of the TBHP producers. This WWTP contains activated sludge with micro-organisms that are adapted to TBHP and other peroxides in the waste water. Further conditions in this WWTP are an influent load of total organic carbon (TOC) of around 3000 mg/l (of which maximal 2000 mg/l is TBHP), a temperature of 30-40 ^{0}C and an air stream of 60-100 m^3 air/m^3 waste water. According to the submitted data, TBHP is fully degraded to tertiary butyl alcohol (TBA) which will be further degraded for 80-90% during the residence time of about 90 hours in this WWTP (Peroxide-Chemie GmbH, 1997).

In Söllner (1995) additional data are reported on the functioning of the WWTP of Peroxid-Chemie and on the removal and biodegradation of THBP and TBA in this WWTP. The WWTP consists of two aerobic units with activated sludge, in which TBHP is fully degraded to TBA in the first unit and TBA is largely degraded in the second unit, provided that the TBHP concentration in the influent of the first unit does not exceed 2000 mg/l. Usually no THBP is found in the outlet of the first unit, but several times THBP concentrations of 10-50 mg/l were measured; it is assumed that this remaining part will be degraded in the second unit. In an incident in 1994 the first unit received a bulk load of TBHP, resulting in THBP concentrations up to 1000 mg/l in the outlet of the first unit for up to 10 days. This resulted in an almost complete inhibition of the degradation in the second unit, ascribed to the toxicity of

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[8] In this additional test, Fe_2SO_4 was added to a TBHP solution in water, resulting in a mixture of TBHP, TBA and the metabolite 'unknown 1' in water (see also section 3.2.1.2). Subsequently, air was blown through the

TBHP to the unadapted micro-organisms in the second unit. In this WWTP the emission to air is expected to be negligible, as all basins are covered and the waste air is cleaned by activated carbon (Söllner, 1995).

The results from biodegradation estimation models in the BIOWIN (v4. 00) programme predict that TBHP is biodegradable or even readily biodegradable (EPIWIN, 1997). The results of model calculations with the "Biodegradation Probability Program" (version 3.03, Syracuse Research Corporation, USA) predict that the primary biodegradation of TBHP to metabolites will occur in the aquatic environment between days and weeks and the ultimate mineralization to carbon dioxide and water will occur between weeks and months (Howes et al., 1995). Thus, the results of these model calculations indicate that TBHP is at least inherently biodegradable.

3.2.3 Distribution

The volatility of TBHP from water has been studied in an evaporation study performed under standard biodegradation aeration conditions. The study showed a slight, gradual decline in TBHP concentrations over a 24-h period, with a duplicate mean of 94.1%, 90.0% and 88.6% of the nominal concentration (100 µg/l as TBHP; test compound TBHP-70) at t = 0, 4 and 24 hours, respectively. At t = 0 hour the actual concentrations were within 10% of the nominal concentration. The tests were performed at an ambient temperature of approximate 20 ^{0}C (Howes et al., 1995).

For the volatility of TBHP from water to air a Henry's law constant (H) of 2.43 Pa*m^3/mole was calculated with EUSES (version 1.00) and a value of 1.63 Pa.m^3/mole was calculated by Howes et al. (1995) with the "Henry's Law Constant Programme" (see Table 1, footnote 7 in Chapter 1 for more details on these calculations). These values correspond to a dimensionless Henry's law constant (H$^'$), i.e. the air-water partition coefficient, ($K_{air-water}$), of 10.243E-4 and 6.524E-4, respectively (EUSES calculations). Based on these values, TBHP is considered to be moderately volatile from water (values between 1E-5 and 3E-2; classification according to

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mixture and trapped in the gas trap series. The test solution was analysed by HPLC before and after air was blown through.

Lyman, 1981). The Henry's law constant (H) value of 2.43 Pa*m^3/mole has been used in the environmental exposure assessment in the present report (EUSES calculation).

The distribution/elimination of TBHP in sewage treatment plants (STPs) or waste water treatment plants (WWTPs) has been estimated from the physico-chemical properties using the Simple Treat 3.0 model in accordance with the TGD (EC, 2003); the calculations -for the continental, regional and local scale- were performed with the computer program EUSES 1.00 (ECB, 1996). The rate constant for degradation in activated sludge has been set at 1.7/hour (corresponding to a DT50 of 24 minutes), from section 3.2.2 (1-h degradation test in unadapted activated sludge, no metal-ion added; see also Table 3.1.b). The results of this model calculation show that of the amount of TBHP in the influent, 91.6% is degraded in the STP/WWTP, 7.6% will end up in the effluent, 0.76 % in air and 0.04% in sludge**.**

As indicated above for STP sludge, the adsorption of TBHP to solids is very low. The calculated solids-water partition coefficients (Kp values) for soil, sediment and suspended matter are 0.093, 0.232 and 0.465 l/kg, respectively. Thus, in surface waters nearly all TBHP is in the soluble fraction (less than 0.001% is adsorbed to suspended matter).

3.2.4 Conclusion on environmental fate and distribution

TBHP, a moderately volatile substance, is readily soluble in water (see Table 1 in Chapter 1). The results of an evaporation study performed under standard biodegradation aeration conditions show a low volatility from water, while calculations of the (dimensionless) Henry's law constant indicate a moderate volatility from water. The abiotic degradation rate of TBHP is very low, with a half-life (DT50) of 1300 days in ultra-pure water. The biotic degradation rate of TBHP in activated sludge is rapid, with a half-life of 24 minutes; the primary metabolite is tertiary butyl alcohol (TBA). Both the abiotic and biotic degradation rates were found to increase somewhat in the presence of metal-ions (especially Fe^{2+}), but the effect was small. In an activated sludge simulation test, simulating the fate of TBHP in a WWTP, THBP was fully removed from the water and 40% was fully mineralised.

Based on all data, THBP is considered to be readily biodegradable in WWTPs/STPs and a half-life of 24 minutes (elimination rate constant of 1.7/hour) has been used in the exposure assessments as default value for degradation of TBHP in WWTPs/STPs, resulting in 92%

removal of THBP in WWTPs/STPs, the remaining 8% in effluent discharged into surface water via the effluent. The elimination rate is based on a 1-h degradation test in unadapted activated sludge (see section 3.2.2 and Table 3.1.b). It is noted that the elimination rate constant of 1.7/hour is higher than the maximum TGD default value of 1/hour used for readily biodegradable substances. However, the results of the 1-h tests with unadapted activated sludge show a rapid degradation of TBHP into the primary metabolite TBA and to a limited extent into a further, unidentified metabolite ('unknown 1'), with around 85% of the amount of TBHP degraded in one hour. In addition, the results of the activated sludge simulation test with adapted sludge indicate that TBHP is fully removed from the water, although not fully mineralised. As in the 1-h test with unadapted activated sludge, the metabolites TBA and 'unknown 1' were found in the activated sludge simulation test with adapted sludge. In addition, a third metabolite, 'unknown 2', was found in the latter test. The amount of either of the two unidentified metabolites in the effluent was higher than that of the primary metabolite TBA. For the degradation of TBHP entering surface water and soil, TBHP is considered to be inherently biodegradable, thus for these environmental compartments the TGD default values for the half-lives of inherently biodegradable substances have been used in the exposure assessments for water and soil.

TBHP and other hydroperoxides have a relatively weak and polar O-H bond that makes these compounds susceptible to radical reactions as well as to reactions with metal ions and light. In the atmosphere, reactions with (hydroxyl) radicals appear to be most relevant for the abiotic degradation, while in the aquatic environment reactions with metal ions appears to be most relevant. Both the indirect and direct photodegradation of TBHP and other peroxides in air result in the formation of ozone. Thus, TBHP may contribute to the build up of photochemical smog. The contribution of TBHP to this atmospheric effect is considered to be negligible compared to other relevant industrial chemicals (e.g. pentane and toluene) that have the same potential effect, because of much lower emissions of TBHP.

Based on the low log Kow (0.7), the bioaccumulation and sorption potential of TBHP is considered to be (very) low.

3.3 EXPOSURE ASSESSMENT

3.3.1 General

The environmental exposure assessment of TBHP will be based on the expected releases of the substance during the following life cycle stages:

I. production
II. processing
  IIa. processing chemical intermediate (3/33)
  IIb. processing in polymer industry (11/43)

Based on the submitted data the processing in use category "intermediates" (3/33) and use category "process regulators" (11/43) comprises around 20% and 80%, respectively, of the total processing amount. The total EU processing amount of TBHP is assumed to be covered by these two scenarios (see section 2.2).

Both site-specific and generic scenarios have been used for the exposure assessment of TBHP. Site-specific scenarios are based on actual data from industry on emission patterns etc., whereas generic scenarios are fully based on model calculations for a realistic worst case situation. Generic scenarios are used if no data were obtained from either industry or other references.

The exposure assessment is based on the EU Technical Guidance Document, TGD (EC, 2003) in combination with the European Union System for the Evaluation of Substances, EUSES 1.00 (ECB, 1996), the computer program supporting the assessment according to the TGD.

3.3.2 Local exposure assessment

3.3.2.1 Production

In section 2.1 it is mentioned that there are three major TBHP producers within the EU. A generic scenario for the emissions to air is carried out for scenario I-c, based on the site-specific production volume for the most recent year i.e., 2000. For all other scenarios site-specific emission data were submitted to the Rapporteur. Table 3.2 contains the input data and the initial results for the local exposure assessment at production. For confidentiality reasons not all information is presented in this table.

At sites I-b and I-c both production and processing take place. For both sites the submitted emissions to air and (effluent) water are the summed emissions from both production and processing. The total emission data for production scenario I-b in Table 3.2 and processing scenario II-a1 in Table 3.3 are the same. The processing stage at the other production site, scenario I-c, is treated in the processing scenario II-b2. Also for this site the emissions from processing have been added to those from production. The total emissions for these sites (as mentioned in Table 3.2) finally result in one set of local PEC values per site (Table 3.5).

Table 3.2. Input data for the local exposure assessment for water and air at production (I). Site-specific information is presented ***in bold****.*

	I-a	I-b	I-c
Production tonnage (t/y)	**Conf.**	**Conf.**	**Conf.**
IC/UC	3/33	3/33	3/33
Number of days	Conf.	**Conf.**	Conf.
Release air (%)	n.r.	n.r.	5
Release wastewater (%)	n.r.	n.r.	n.r.
Emission air (kg/d)	**5.5E-3** 2)	**ng.** 7)	117
Emission wastewater (kg/d)	**15.0 (ng.)** 3)	ng.	n.r.
Total emission air (kg/d) 1)	n.r.	**ng.** 7)	135
Total emission wastewater (kg/d) 1)	n.r.	**ng.** 4)	**417** 5)
STP flow (m3/d)	**600**	**1032**	**438**
Receiving water flow (m3/s)	Unknown	Unknown	**Unknown**
Dilution factor	1000 6)	1000 6)	1000 6)

n.r. not relevant
ng. negligible

1) The total emission data (air, water) only apply to site I-b and site I-c; these data include emissions from processing which occurs at the same site (processing scenarios II-a1 and II-b2, respectively; see further the text).
2) Based on a total emission to air of 2 kg/y.
3) Emission to wastewater based on an estimated TBHP concentration of 25 mg/l in influent (worst case estimate, based on the company's statement that practically all measured concentrations in the WWTP influent are below the detection limit of 25 mg/l) and an STP flow of 600 m^3/d. It is noted that the WWTP at this site has a sludge retention time of 110 days, which is much longer than that of 8 hours used in the default WWTP calculations to calculate the TBHP concentrations in effluent and receiving water, respectively. Therefore, a considerably higher degradation/removal rate of TBHP is expected at this site. These data indicate that the TBHP concentrations in the effluent and receiving water will be negligible.

4) Total emission to wastewater is unknown, but the concentrations of TBHP in the wastewater effluent and receiving surface water of this site are below the detection limit (Information provided by the company). No information submitted about the value of this detection limit, but additional data on the WWTP at this site (see Peroxide Chemie GmbH (1997) and Söllner (1995) in section 3.2.2) indicate that concentrations in the effluent and receiving water will be negligible.
5) The total emission to wastewater (417 kg/d) is based on the submitted total tonnage emitted to wastewater. Note that for site 1-c the relatively high default dilution factor of 1000 (*) for category IC/UC 3/33 was used instead of the much lower default dilution factor of 10 for category IC/UC 11/43, although the emission is based on production and processing, the latter having category 11/43 (see also footnote 1 and processing scenario II-b2 in Table 3.4).
   (*) Note that the default dilution factor of 1000 is based on the current (2003) TGD; in a former draft of this risk assessment report a default dilution factor of 2600 was used according to the 1996 TGD.
6) Default value for the dilution factor specifically for category IC/UC 3/33 (set at maximum of 1000, according to the current TGD; see also (*) above) .
7) In the WWTP of this company the emission to air is expected to be negligible, as all basins are covered and the waste air is cleaned by activated carbon (Söllner, 1995, see also section 3.2.2).

3.3.2.2 Processing

IIa. Use category "intermediates" (3/33)

For processing site II-a1 the submitted emissions to air and effluent water (after the WWTP) include production at the same site (see Table 3.2). For the two remaining processing sites a generic scenario (scenarios II-a2 and II-a3) is carried out, based on site-specific processing tonnage's. Table 3.3 contains the input data and the initial results for the local exposure assessment for use category "intermediates" (3/33), used in chemical synthesis. For confidentiality reasons not all information is presented in this table.

Table 3.3. Input data for the local exposure assessment for water and air at processing 3/33 (II-a). Site-specific information is presented ***in bold****.*

	II-a1	II-a2	II-a3
Processing tonnage (t/y)	**Conf.**	**Conf.**	**Conf.**
Number of days	**Conf.**	Conf. 4)	Conf. 4)
Release air (%)	n.r.	2.5	2.5
Release wastewater (%)	n.r.	2	2
Emission air (kg/d)	**ng.**	16.7	100
Emission wastewater (kg/d)	ng.	13.3	80
Total emission air (kg/d) 1)	**ng.**	n.r	n.r.
Total emission wastewater (kg/d) 1)	**ng. 2)**	n.r.	n.r.
STP flow (m3/d)	**1032**	2000	2000
Receiving water flow (m3/s)	Unknown	Unknown	Unknown
Dilution factor	1000 3)	1000 3)	1000 3)

n.r. not relevant

1) The total emission data (air, water) only apply to site II-a1; these data include emissions from production, which occurs at the same site (production scenario I-b in Table 3.2).
2) Total emission to wastewater is unknown, but the concentrations of TBHP in the wastewater effluent and receiving surface water of this site are below the detection limit (Information provided by the company). No information submitted about the value of this detection limit, but additional data on the WWTP at this site (see Peroxide Chemie GmbH (1997) and Söllner (1995) in section 3.2.2) indicate that concentrations in the effluent and receiving water will be negligible.
3) Default value for receiving water flow and dilution factor specifically for category 3/33 (set at maximum of 1000, according to the current TGD). Note that in a former draft of this risk assessment report a default dilution factor of 2600 was used according to the 1996 TGD.
4) The number of production days is based on a (default) fraction, the processing tonnage and the fraction of the main source (TGD, 1996; Appendix 1 B-Tables). Here, the fraction of the main source is 1, because only one local site is considered.

IIb. Use category "process regulators" (11/43)

For fourteen processing sites a generic scenario is carried out based on site-specific processing tonnage's for the most recent years i.e., 2000 and if available the number of processing days. For the seven remaining sites the scenario is based on site-specific emission data for air or wastewater. One company is known to have three processing sites. Only the total sum of the processing tonnage for all three sites was submitted to the Rapporteur. Until further information of the split up of the tonnage between these three sites becomes available, it is assumed that the total tonnage is processed within one site (scenario II-b1). The emissions from scenario II-b2 (processing) have been added to those from scenario I-c (production) as they occur at the same site. Table 3.4 contains the input data and the results for the local exposure assessment for use category "process regulators" (11/43) used in polymers industry. For confidentiality reasons not all information is presented in this table**.**

The European Resin Manufactures Association (ERMA) submitted some general data on the use of TBHP in the resin industry. It is indicated that the chances of TBHP reaching the environment from manufacturing sites are extremely low. This because the peroxide is not only consumed during the process, but also plant washings are treated through flocculation processes using metal ions, offering further opportunity to consume any minuscule peroxide residues. Furthermore, in some cases plant washings are combusted through on-site incinerators into carbon dioxide and water (see also Annex 3). It is emphasised that these general data provide no site-specific evidence that there is no emission to waste water or air. Thus, unless site-specific emission data were provided by industry, a generic scenario has been used to estimate the local emission and the resulting local concentrations (C_{local}) and local PEC values (PEC_{local}) from the site-specific processing tonnage and number of processing days (see Table 3.4 and section 3.3.2.3).

Table 3.4. Input data for the local exposure assessment for water and air at processing 11/43 (II-b). Site-specific information is presented ***in bold.***

	Processing tonnage (t/y) 1)	Number of days	Release air (%)	Release wastewater (%)	Emission air (kg/d)	Emission wastewater (kg/d)	Total emission air (kg/d) 2)	Total emission wastewater (kg/d) 2)	WWTP flow (m^3/d)	Receiving water flow (m^3/d)	Dilution factor
II-b1	**Conf.**	Conf. 3)	0.05	0.5	10	100	n.r.	n.r.	2000	Unknown	10
II-b2	**Conf.**	**Conf.**	0.05	n.r.	18	n.r.	135	**417** 4)	**438**	Unknown	1,000 5)
II-b3	**Conf.**	Conf. 3)	0.05	0.5	2.0	20	n.r.	n.r.	2,000	Unknown	10
II-b4	**Conf.**	Conf. 3)	0.05	0.5	1.3	13	n.r.	n.r.	2,000	Unknown	10
II-b5	**Conf.**	Conf. 3)	0.05	0.5	0.50	5.0	n.r.	n.r.	2,000	Unknown	10
II-b6	**Conf.**	**Conf.**	0.05	n.r.	0.13	**0**	n.r.	n.r.	2,000	Unknown	10
II-b7	**Conf.**	Conf. 3)	0.05	0.5	1.3	13	n.r.	n.r.	**$4.32.10^5$**	**$6.3.10^7$**	**147**
II-b8	**Conf.**	Conf. 3)	n.r.	0.5	**0**	1.2	n.r.	n.r.	2,000	Unknown	10
II-b9	**Conf.**	Conf. 3)	0.05	n.r.	0.033	**0.067**	n.r.	n.r.	2,000	Unknown	10
II-b10 6)	**Conf.**	Conf. 3)	0.05	n.r.	0.067	**0.25**	n.r.	n.r.	**500**	**$5.18.10^6$**	1,000 7)
II-b11	**Conf.**	Conf. 3)	0.05	0.5	0.083	0.83	n.r.	n.r.	2,000	unknown	10
II-b12	**Conf.**	Conf. 3)	0.05	0.5	0.027	0.27	n.r.	n.r.	2,000	unknown	10
II-b13	**Conf.**	Conf. 3)	0.05	0.5	0.0013	0.013	n.r.	n.r.	2,000	unknown	10
II-b14	**Conf.**	**Conf.**	0.05	0.5	0.028	0.28	n.r.	n.r.	2,000	unknown	10
II-b15	**Conf.**	**Conf.**	n.r.	0.5	**0.027**	1.7	n.r.	n.r.	**18,144**	**$4.32.10^6$**	**238**
II-b16	**Conf.**	**Conf.**	n.r.	0.5	**0.014**	0.36	n.r.	n.r.	**13,008**	**$4.32.10^8$**	1,000 8)
II-b17	**Conf.**	Conf. 3)	0.05	0.5	0.083	0.83	n.r.	n.r.	**80,000**	unknown	10
II-b18	**Conf.**	Conf. 3)	0.05	0.5	0.82	8.2	n.r.	n.r.	**$4.32.10^5$**	**$6.34.10^7$**	**147**
II-b19	**Conf.**	**Conf.**	0.05	0.5	0.26	2.6	n.r.	n.r.	**3,456**	unknown	10
II-b0	**Conf.**	Conf. 3)	0.05	0.5	0.12	1.2	n.r.	n.r.	**76,690**	**$8.73.10^6$** 9)	**114**

See next page for footnotes.

n.r. not relevant

1) Data from 1997 for scenario II-b1, II-b3 and IIb5, from 2000 for scenario II-b2, II-b6, II-b7 and II-b14 –II-b16, and from 2001 for scenario II-b12. For the remaining scenarios the year is unknown;
2) The total emission data (air, water) only apply to site II-b2; the total emission for this site includes emissions from production, which occurs at the same site (production scenario I-c, see Table 3.2).
3) The number of processing production days is based on a (default) fraction, the processing tonnage and the fraction of the main source (TGD, 1996; Appendix 1 B-Tables). Here, the fraction of the main source is 1, because only one local site is considered.
4) The total emission to wastewater (417 kg/d) is based on the submitted total tonnage emitted to wastewater.
5) Note that for site II-b the relatively high default dilution factor of 1000 for category IC/UC 3/33 was used instead of the much lower default dilution factor of 10 for category IC/UC 11/43, although the emission is based on production and processing, the latter having category 11/43 (see also footnote 2 and production scenario I-c in Table 3.2).
6) The processing tonnage at site II-b10 covers half of the total amount of TBHP processed by the company involved. The other half of the amount is processed at five other sites within the European Union. The split up of the amount processed at site II-b10 (50%) and that at the other five sites (50%) is based on the amount of emulsions produced. There is no further detailed information on geographic locations and split up of the tonnage processed at these five sites. Therefore only site II-b10 was included in Table 3.4. The estimated emissions of the other five sites are accounted for in the regional emissions. Default emission factors were applied according to the 2003 TGD .
7) The maximum dilution factor of 1000 is used according to the 2003 TGD. Calculated site-specific dilution factor is 10,368.
8) The maximum dilution factor of 1000 is used according to the 2003 TGD. Calculated site-specific dilution factor is 33,210.
9) An average river flow rate of 303 m^3/s for the river Meuse was used to calculate a low river flow rate of 101 m^3/s according to the 2003 TGD.

3.3.2.3 Local PEC values

Predicted Environmental Concentrations (PEC values) in the environmental compartments have been calculated for each production and processing site, using the input data from Tables 3.2, 3.3 and 3.4. The resulting local PEC values are listed in Table 3.5. It is emphasised that the local PEC values are the sum of the local concentrations (C_{local}), calculated from the emissions for each site and the regional background concentration ($PEC_{regional}$).
The regional exposure assessment and the $PEC_{regional}$ values are presented in section 3.3.4.

It is noted that there are no actual (measured) data on TBHP in sediment. The $PEC_{sediment}$, either local or regional, can be calculated by equilibrium partitioning from the PEC_{water}, but according to section 3.4.1.5, there are also no sediment toxicity data to derive a $PNEC_{sediment}$. Consequently, it is not needed to calculate both the $PEC_{sediment}$ and the $PNEC_{sediment}$ by equilibrium partitioning, because this leads to (nearly) the same risk characterisation ratio (PEC/PNEC) as for water.

With respect to possible food chain effects (secondary poisoning), predicted concentrations in fish (PEC_{fish}) and earthworms (PEC_{worm}) could be relevant. However, because the bioaccumulation potential of TBHP is considered to be (very) low, see section 3.4.4, no PEC_{fish} and PEC_{worm} values are presented in this report.

Table 3.5. Local PEC values in the various environmental compartments for production and processing of TBHP.

	STP (µg/l)	Water (µg/l)	Air (µg/m3)	Soil (mg/kg wwt)
Production Cat. 3/33				
I-a [1]	ng.	2.61E-01	3.57E-2	9.33E-6
I-b [1]	ng.	2.61E-01	3.36E-03	1.05E-06
I-c	7.16E+04	7.19E+01	3.08E+01	1.20+00
Processing Cat. 3/33				
II-a1	See production 1-b			
II-a2	5.02E+02	7.63E-01	1.90E+00	8.81E-03
II-a3	3.01E+03	3.28E+00	1.33E+01	5.33E-02
Processing Cat. 11/43				
II-b1	3.76E+03	3.76E+02	2.28E+00	6.32E-02
II-b2	See production I-c			
II-b3	7.52E+02	7.56E+01	4.60E-01	1.26E-02
II-b4	4.70E+02	4.73E+01	2.62E-02	7.83E-03
II-b5	1.88E+02	1.91E+01	1.29E-02	3.13E-03
II-b6	0.00E+00	2.61E-01	9.17E-03	2.47E-06
II-b7	2.18E+00	2.76E-01	2.70E-01	1.07E-04
II-b8	4.61E+01	4.88E+00	5.55E-03	7.68E-04
II-b9	2.52E+00	5.13E-01	1.09E-02	4.49E-05
II-b10	3.09E+01	2.92E-01	1.86E-02	5.19E-04
II-b11	3.14E+01	3.41E+00	2.24E-02	5.27E-04
II-b12	1.01E+01	1.28E+00	9.50E-03	1.70E-04
II-b13	4.70E-01	3.08E-01	3.65E-03	8.94E-06
II-b14	1.05E+01	1.32E+00	8.71E-03	1.78E-04
II-b15	7.16E+00	2.91E-01	1.10E-02	1.23E-04
II-b16	2.11E+00	2.63E-01	7.19E-03	3.72E-05
II-b17	7.84E-01	3.39E-01	2.24E-02	1.91E-05
II-b18	1.42E+00	2.71E-01	1.90E-01	7.38E-5
II-b19	5.60E+01	5.87E+00	7.19E-02	9.50E-04
II-b20	1.15E+00	2.71E-01	3.01E-02	2.72E-5

ng. negligible

[1] For sites I-a and I-b the submitted data indicate that the TBHP concentrations in the WWTP effluent and the receiving water will be negligible, see Table 3.2 (footnotes 3 and 4), thus the local PEC in water (2.61E-01) is equal to the regional PEC, see Table 3.6.
At both sites the WWTP sludge is treated as toxic waste, thus it is assumed that the sludge is not applied to the soil. Thus, the PEC soil is solely due to atmospheric deposition.

3.3.3 Continental exposure assessment (emissions)

Based on the data mentioned in section 3.3.2.1 and 3.3.2.2 it appears that in general the emissions during the production of TBHP are negligible or at least considerably lower compared to those at processing (the latter mainly based now on TGD defaults!), except for one production site (I-c) that has a very high emission to wastewater (due to production and processing at this site, see Table 3.2). Therefore, the continental emissions calculated in this section are largely based on the continental (is total EU) emissions due to processing, i.e. based on the summed emissions due to production at one site, processing as chemical intermediate (3/33, see Table 3.3) and processing as process regulator (11/43, see Table 3.4).

For each processing site the yearly emissions to air and wastewater were calculated from the emission data listed in Table 3.3 and Table 3.4 (emission data expressed as kg/day) and the data on the number of processing days (confidential information). From these data the yearly total continental processing emissions and, subsequently, the daily total continental processing emissions were calculated by summation of the data of all sites. This results in total continental emissions of 165.3 kg/day to air and 511.4 kg/day to waste water. Because TBHP is sold to and used by industrial customers only, there are little or no sales to, or use by small industries or consumers. Hence, it is assumed that most (95%) of the emissions to water can be specified as emissions to waste water. Assuming the split up of 95% to a WWTP and 5% discharge directly to surface water (which deviates from the TGD default of 80% and 20%, respectively); the emissions from industrial sources to waste water and directly to surface water are 485.8 kg/day and 25.6 kg/day, respectively. In section 3.2.3 it is indicated that around 92% of the amount of TBHP in waste water will be degraded in the WWTP and that the remaining 8% will largely end up in the WWTP effluent and thus in surface water.

3.3.4 Regional exposure assessment (emissions and PEC values)

In case there are no specific data on regional emissions, these data are calculated from the continental emissions, normally by applying the “10% rule”. For TBHP, however, it is known that based on the submitted data, about 90% of the total continental air and water emissions are caused by processing companies and one production site in one 200x200 km region in Germany. Thus, for the calculation of the regional emissions from the continental emissions, the 10% rule is not applied here for TBHP: the total regional emissions are now assumed to be equal to the total continental emissions. In the calculations of the regional PEC values this means that these values do not include a continental background concentration.

The regional PEC values resulting from the aforementioned total (continental) emissions of 165.3 kg/day to air and 511.4 kg/day to wastewater are presented in Table 3.6. It is emphasised that the current regional PEC values must be considered as a worst case situation for the EU regions, with exception of the German region, see above.

Table 3.6. Regional PEC values

Compartment	**PEC regional**
PEC air (µg/m^3) (total)	3.36E-03
PEC surface water (µg/l) (total and dissolved)	2.61E-01
PEC sediment (mg/kg$_{wwt}$) (total)	1.80E-04
PEC agricultural soil (mg/kg$_{wwt}$) (total)	3.31E-06
PEC natural soil (mg/kg$_{wwt}$) (total)	1.05E-06

3.3.5 Measured data

There are no measured environmental concentrations of TBHP available, neither local nor regional.

3.4 EFFECTS ASSESSMENT

3.4.1 Aquatic compartment

The aquatic toxicity studies are limited to the required base-set, i.e. short-term tests with freshwater fish (two tests), daphnids (one test), algae (one test) and bacteria (one activated sludge test). The test substance used in the tests was aqueous TBHP-70, a solution containing 70% TBHP and 30% water (w/w).

3.4.1.1 Toxicity to fish, daphnids and algae

The studies on the toxicity of TBHP to fish, daphnids and algae are summarised in Table 3.7; more details are given in Annex 1. The tests were performed according to the appropriate (OECD) guidelines. In the text below the results are expressed as TBHP (100% active ingredient). The results are based on nominal concentrations; the actual concentrations were within 80% (Daphnia and fish test) and 70% (algae test) of the nominal concentrations. The fish tests resulted in 96-h LC50 values of 29 and 57 mg/l for *Pimephales promelas* and *Poecilia reticulata,* respectively. The test with the daphnid *Daphnia magna* resulted in a 48-h EC50 of 14 mg/l (endpoint mobility). The test with the alga *Selenastrum capricornutum* resulted in a 72-h E_rC50 of 1.5 mg/l (endpoint exponential growth rate) and a 72-h E_bC50 of 0.84 mg/l (endpoint biomass); the 72-h NOEC was 0.22 mg/l for both endpoints. The data, although very limited, suggest that algae are considerably more sensitive to TBHP than fish and daphnids. The 72-h E_rC50 of 1.5 mg/l for alga *S. capricornutum* has been used for the derivation of the PNEC for the aquatic environment ($PNEC_{aquatic}$), see section 3.4.1.4.

Table 3.7. Toxicity to fish, invertebrates and algae

Fish

Substance	Species	Method	Duration (h)	Test water	T (^{0}C)	Criterion	Result as TBHP-70 (mg/l)	**Result as TBHP (mg/l)**
TBHP-70	Pimephales promelas	semi-static (daily renewal)	96	DSW, pH 7.7-7.9, hardness 210 mg/l	24.4-24.9	LC50 NOEC	42 32	**29** **22**

Results: nominal concentrations, reported as TBHP-70.

Reference: Hooftman & van Drongelen-Sevenhuisen (1992a): TNO-report R92/068 (study No. IMW-91-0130-04)

Substance	Species	Method	Duration (h)	Test water	T (^{0}C)	Criterion	Result as TBHP-70 (mg/l)	**Result as TBHP (mg/l)**
TBHP-70 (Trigonox A-W70)	Poecilia reticulata	semi-static (renewal at 48 h)	96	DSW, pH 7.9-8.3, hardness 210 mg/l	22-24	LC50 NOEC	- -	**57** **30**

Results: nominal concentrations, reported for TBHP (pure substance).

Reference: Mark & Meuwsen(1989): AKZO-report CRL F89107

Daphnids

Substance	Species	Method	Duration (h)	Test water	T (^{0}C)	Criterion	Result as TBHP-70 (mgl)	**Result as TBHP (mg/l)**
TBHP-70	Daphnia magna	Static	48	DSW, pH 7.4-7.9, hardness 210 mg/l	20.6-20.8	EC50 NOEC	20 10	**14** **7**

Results: nominal concentrations, reported for TBHP-70.

Reference: Hooftman & van Drongelen-Sevenhuisen (1992b): TNO-report R 92/067 (study No. IMW-91-0130-01)

Algae

Substance	Species	Method	Duration (h)	Test water	T (^{0}C)	Criterion	Result as TBHP-70 (mg/l)	**Result as TBHP (mg/l)**
TBHP-70	Selenastrum capricornutum	Static	72	OECD (201) medium, pH 7.9-8.6, hardness 24 mg/l	23	E_rC50 E_bC50 $NOE_{r,b}C$	2.1 1.2 0.32	**1.5** **0.84** **0.22**

Results: nominal concentrations, reported for TBHP-70.

Reference: Hanstveit & Oldersma (1992): TNO-report R92/090 (study IMW-91-0130-02)

3.4.1.2 Toxicity to micro-organisms

The toxicity of TBHP-70 to micro-organisms was tested in an activated sludge (respiration inhibition) test, resulting in a 30-minutes EC50 of 17 mg/l (as TBHP). In addition to this EC50 the study authors also derived an EC10 of 0.2 mg/l (Van Ginkel and Stroo, 1992), which could be used as a NOEC equivalent. However, in this case the EC10 is considered to be very unreliable, as this value is derived by extrapolation far outside the test range: the EC10 (0.2 mg/l) is over 40-times lower than the lowest test concentration (8.6 mg/l). Thus, the EC50 of 17 mg/l has been used for the derivation of the PNEC for STP effluent ($\text{PNEC}_{\text{micro-organisms}}$), see Section 3.4.1.5

Table 3.8. Activated sludge, respiration inhibition test

Test type	GLP	Inoculum Conc.	Exp. Time	Test compound	Test conc., as TBHP (mg/l, nominal)	**Result, as TBHP (mg/l, nominal)**	Reference
Activated sludge, respiration inhibition test	Yes	600 mg/l	30 m	TBHP-70 (Trigonox A-W70)	8.6 17.3 34.5 69.0 138	**EC50: 17**	Van Ginkel & Stroo, 1990

Test according to EEC (1988), L133, Part C and OECD 209. Secondary activated sludge from an STP predominantly treating domestic waste water was used as inoculum. At the test concentrations of 8.6, 17.3, 34.5, 69.0, and 138 mg/l, respiration was inhibited by 38%, 53%, 61%, 64% and 70%. In addition to the EC50 (17 mg/l) the study authors also derived an EC10, EC20 and EC80 of 0.2, 0.9 and 353 mg/l, respectively. It is noted that 2,4,5-trichlorophenol instead of the recommended 3,5-dichlorophenol was used as reference substance to check the validity of the test. Nevertheless the test is considered to be valid, since the EC50 of 2,4,5-trichlorophenol was in the range normally required for 3,5-dichlorophenol and, moreover, a clear effect of TBHP was found.

3.4.1.3 Toxicity to sediment-dwelling organisms

There are no toxicity data on sediment-dwelling organisms (benthic organisms).

3.4.1.4 PNEC for the aquatic compartment ($\text{PNEC}_{\text{aquatic}}$)

The lowest LC50 or EC50 values were found in the algae test with *Selenastrum capricornutum*, resulting in an E_rC50 of 1.5 mg/l (as TBHP) for endpoint exponential growth rate and an E_bC50 of 0.84 mg/l (as TBHP) for endpoint biomass (see section 3.4.1.1). According to the TGD (EC, 2003), the value for growth rate (thus the E_rC50 of 1.5 mg/l) and an assessment factor of 1000 have been used for $PNEC_{aquatic}$ derivation, resulting in a **$PNEC_{aquatic}$ of 1.5 µg/l (as TBHP)**

3.4.1.5 PNEC for STP effluent ($PNEC_{micro\text{-}organisms}$)

The activated sludge (respiration inhibition) test resulted in a EC50 value of 17 mg/l (see section 3.4.1.2). Applying an assessment factor of 100 according to the TGD (EC, 2003) results in a **$PNEC_{micro\text{-}organisms}$ of 0.17 mg/l (as TBHP).**

3.4.1.6 PNEC for sediment ($PNEC_{sediment}$)

There are no data on sediment-dwelling organisms (benthic organisms), so a PNEC for sediment ($PNEC_{sediment}$) cannot be derived directly from sediment toxicity data. A $PNEC_{sediment}$ can be derived from the $PNEC_{aquatic}$ using the equilibrium partitioning (EP) method. However, as already mentioned in section 3.3.2.3, there is in this case no need to calculate the $PNEC_{sediment}$ by equilibrium partitioning.

3.4.2 Terrestrial compartment

3.4.2.1 Toxicity

The effects of TBHP on cell growth (wet weight) and cell membrane integrity (ion leakage) were studied in *in vitro* tests in which cells of tobacco (*Nicotiana tabacum*) were exposed in a growth solution (Koch et al., 1995). The cells were cultured in a medium (LS-medium) containing macro- and micro-elements. For the determination of cell growth, cells were exposed for 7 days in the LS-medium (test concentrations: 0-9-18-45-90-180 mg/l) after which the fresh weight of the cells was determined. For the determination of cell membrane integrity (determined by measuring continuously the conductivity of the medium that was pumped through a flow conductivity cell during a period of 12 hours), cells from the late exponential growth phase (usually 7-d old cultures) were collected, washed 3 times with “electrical conductivity medium” (EC medium, being a 1/100 dilution of the LS-medium), transferred to EC medium and exposed for 12 hours in this medium (test concentrations: 0-18-45-90-135-180 mg/l). Exposure to TBHP resulted in concentrations-related effects on both cell growth (decrease of fresh weight) and cell membrane integrity (increase of conductivity in the medium), with in both cases a LOEC of 45 mg/l (around 70% reduction of cell culture growth and around 50% increase in conductivity; percentages derived from graphs) and a NOEC of 18 mg/l. Maximum conductivity values after treatment with high concentrations of TBHP did not further increase after freeze-thaw treatment of the cultures and were in the same range as those measured after freeze-thawing of untreated cultures. Hence, according to the authors of this study, the observed increase in conductivity during TBHP treatment was due mainly to an efflux of ions caused by membrane damage rather than to a metabolic response of the cells to TBHP or to generation of ions by the reaction of TBHP with cellular components (Koch et al., 1995) [9].

In earlier *in vitro* tests with terrestrial plant tissues, viz. (discs) of egg plant fruit, white gourd, chayote fruit, radish root, potato tuber and red beet, exposure to TBHP in a growth solution also showed membrane damage, as indicated by the leakage of several cellular components, including potassium ions, reducing sugars and UV-absorbing materials. For example, these effects were found in tests with discs of turnip (*Brassica rapa*) and sweet potato (*Ipomoea batatas*) exposed for 8-10 hours to a TBHP concentration of 900 mg/l; in these tests it was found that the leakage of cell components was accompanied by incorporation of TBHP, the formation of lipid hydroperoxides and a decrease in respiratory activity (Matsuo et al., 1989)[10].

The above studies (Koch et al., 1995; Matsuo et al., 1989), *in vitro* tests with terrestrial plant cells or tissues in growth solution, are not suitable for the effects assessment for terrestrial organisms, i.e. not useful for the derivation of a $\text{PNEC}_{\text{terrestrial}}$.

Further data on terrestrial organisms are not available.

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[9] A comparison of the result of this test with terrestrial plant cells (about 70% growth inhibition at a TBHP concentration of 45 mg/l) and that of the aquatic algal growth inhibition test (EC_r50 of 1.5 mg/l for *Selenastrum capricornutum*, see Table 3.7) suggests that terrestrial plants may be less sensitive to TBHP than aquatic unicellular algae. The terrestrial plant cells showed a similar sensitivity as aquatic micro-organisms (EC50 of 17 mg/l derived in the activated sludge, growth inhibition test, see Table 3.8). It is noted, however, that the data are too limited for a sound comparison of the sensitivity of the different taxonomic groups.

[10] The publication by Matsuo et al (1989) only include a detailed description of the tests with discs of turnip and potato tubers. The further data are from earlier publications referred to in Matsuo et al. (1989). These earlier publications were not evaluated by the rapporteur, as the data are not useful fo the derivation of a $\text{PNEC}_{\text{terrestrial}}$.

3.4.2.2 PNEC for the terrestrial compartment ($PNEC_{terrestrial}$)

There are no *in vivo* toxicity data on terrestrial organisms. Therefore the PNEC for the terrestrial compartment was estimated from the $PNEC_{aquatic}$ using the equilibrium partitioning (EP) method according to the TGD (EC, 2003). This results in a **PNEC $_{terrestrial}$ of 0.3 µg/kg wwt (as TBHP).**

3.4.3 Atmosphere

There are no data on the effects of atmospheric TBHP on environmental organisms, so a PNEC for air ($PNEC_{air}$) cannot be derived.

3.4.4 Non compartment specific effects relevant to the food chain

There are no data on bioaccumulation of TBHP in animals and on biomagnification (i.e. accumulation and transfer through the food chain). TBHP has a log Kow of 0.7 (Chapter 1; experimental value), which is well below the value of 3.0 mentioned in the TGD (EC, 2003) for substances that may have a potential for bioaccumulation. Based on this, the bioaccumulation potential of TBHP is considered to be (very) low and food chain effects (secondary poisoning) are not expected.
Tertiary butyl alcohol (TBA), the primary metabolite of TBHP, has a log Kow of 0.35 (see Annex 2). Thus, food chain effects are not expected for TBA either.

3.5 RISK CHARACTERISATION

The risk characterisation ratios (PEC/PNEC) for the environmental compartments on a local and regional scale are shown in table 3.9. The table comprises the data for production (scenarios I-a to I-c) and processing, the latter for two different use categories: 3/33 (scenarios II-a1 to II-a3) and 11/43 (scenarios II-b1 to II-b20). The PEC/PNEC values for sites I-b and I-c are derived from the local PECs from both production and processing (see the earlier explanation in section 3.3).

Table 3.9. Risk characterisation for the various environmental compartments.

	PEC/PNEC water	PEC/PNEC WWTP	PEC/PNEC soil
Production			
I-a	0.2	<1	0.033
I-b	0.2	<1	0.004
I-c	**48**	**420**	**4000**
Processing Cat. 3/33			
II-a1	See production I-b		
II-a2	0.5	**3.0**	**29**
II-a3	2.2	**18**	**180**
Processing Cat. 11/43			
II-b1	**250**	**22**	**210**
II-b2	See production I-c		
II-b3	**51**	**4.4**	**42**
II-b4	**32**	**2.8**	**26**
II-b5	**13**	**1.1**	**10**
II-b6	0.2	0	0.008
II-b7	0.2	0.01	0.4
II-b8	**3.3**	0.3	**2.6**
II-b9	0.3	0.02	0.2
II-b10	0.2	0.2	**1.7**
II-b11	**2.3**	0.2	**1.8**
II-b12	0.9	0.06	0.6
II-b13	0.2	0.003	0.03
II-b14	0.9	0.06	0.6
II-b15	0.2	0.04	0.4
II-b16	0.2	0.01	0.1
II-b17	0.2	0.005	0.06
II-b18	0.2	0.008	0.2
II-b19	**3.9**	0.3	**3.2**
II-b20	0.2	0.01	0.1
Regional	0.2		0.004

3.5.1 Aquatic compartment

3.5.1.1 Local risk characterisation

<u>Production</u>

For the combined production and processing site I-c, a PEC/PNEC water of 48 was calculated from the site-specific emission to wastewater (**conclusion iii**)[11].

For production sites I-a and I-b, the PEC/PNEC water is <1 **(conclusion ii).**

<u>Processing Category 3/33</u>

For processing site II-a3 the PEC/PNEC water is 2.2. The scenario is mainly based on default assumptions, but no site-specific data were submitted by industry that could rebut the followed exposure assessment (**conclusion iii**) [11].

The PEC/PNEC water for processing site II-a2 is <1 **(conclusion ii).**

<u>Processing Category 11/43</u>

The PEC/PNEC water for 7 of the processing sites (Category 11/43) is >1. Most PEC/PNEC water values for these sites were calculated with generic scenarios, but no (further) site-specific data were submitted by industry that may rebut the followed exposure assessment (**conclusion iii**) [11].

For the remaining processing sites of Category 11/43 the PEC/PNEC water is <1 **(conclusion ii).**

It is noted that for production/processing site I-c as well as for most of the processing sites with a PEC/PNEC water >1, there is also a PEC/PNEC WWTP >1. The same situation holds

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[11] Although further, long-term aquatic toxicity testing (towards PNEC refinement) would have been the most consistent and logical way forward in the opinion of the Rapporteur, Industry did not support this additional testing and thereby implicitly accepted a conclusion iii) for this and other surface water scenarios with a PEC/PNEC above 1.

as for water, i.e. no site-specific data were submitted that may rebut the current approach, and therefore a **conclusion iii)** is drawn[12].

For processing site II-a2, which has a PEC/PNEC water <1, the PEC/PNEC WWTP is >1 **(conclusion iii**).

It is further noted that Table 3.9 includes no PEC/PNEC values for sediment, because a $\text{PNEC}_{\text{sediment}}$ could not be derived (no toxicity data, see section 3.4). As explained earlier in section 3.3.2.3 there is no need for toxicity data on sediment organisms.

3.5.1.2 Regional risk characterisation

The regional PEC/PNEC water, calculated from the regional PEC water (0.26 µg/l) and the $\text{PNEC}_{\text{aquatic}}$ (1.5 µg/l), is 0.2. Thus, no risk to aquatic organisms is expected at a regional scale **(conclusion ii**).

3.5.1.3 Metabolites of TBHP

In STPs/WWTPs, TBHP is degraded for around 90% (removal 100% according to the results of an activated sludge simulation test, see section 3.2.2), but not fully mineralised under standard conditions[13]. The primary metabolite of TBHP is tertiary butyl alcohol (TBA), which appears to be an inherently biodegradable compound (see Annex 2). The aquatic toxicity of tertiary butyl alcohol is considerably lower than that of TBHP: for micro-organisms a factor of 40, for daphnids a factor of 66, for fish a factor of 120 and for algae a factor of 670, based on short-term tests (very limited data for TBHP and limited data for tertiary butyl alcohol, see Annex 2). Furthermore, algae (which were considerably more sensitive to TBHP than the other taxonomic groups tested) appear not to be specifically sensitive to tertiary butyl alcohol. Thus, PEC/PNEC values for TBA will be much lower than those currently calculated for TBHP. This statement has been substantiated by a provisional TBA risk characterisation. In

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[12] Additional testing towards TBHP toxicity to industrial, adapted sludge (towards PNEC refinement) would have been the most consistent and logical way forward in the opinion of the Rapporteur. However, Industry did not support this additional testing and thereby implicitly accepted a conclusion iii) for these and other WWTP scenarios with a PEC/PNEC > 1.

this provisional risk characterisation, local PEC values for TBA in water have been calculated for all sites from the TBHP concentration in the influent, using 90% removal of TBHP and 10% degradation to TBA without further degradation of TBA in the WWTP[14]. Based on the aquatic toxicity data in Annex 2, a $\text{PNEC}_{\text{aquatic}}$ of 0.93 mg/l could be derived for TBA, applying an assessment factor of 1000 on the lowest acute LC50 (930 mg/l, for *Daphnia magna*). For all sites, the PEC/PNEC for TBA of water is <1 (**conclusion ii**), with the highest PEC/PNEC value (0.5) for processing site II-b1 and the next highest value (0.1) for production/processing site I-c/II-b2[15]. It is noted that this provisional risk characterisation for TBA is worst-case, as the results of the activated sludge simulation test described in section 3.2.2 indicate that maximal 1% of TBHP in the influent will end up as TBA in the effluent (see also below). Thus, the maximum PEC/PNEC value for TBA in water is rather 0.05 than 0.5.

The results of the activated sludge simulation test show two further metabolites in the effluent, in addition to TBA. These two metabolites, ‘unknown 1’ and ‘unknown 2’ have not been identified. It is assumed that, as TBA, these compounds are tertiary compounds that may be not readily biodegradable. Based on the results of the activated sludge simulation test and an additional test (see section 3.2.2), compound ‘unknown 1’ and (most likely) compound ‘unknown 2’ appear to be highly volatile compounds that will mainly end up in the air from STPs/WWTPs, although in the activated sludge simulation test the amount of either of these two metabolites in the effluent was higher than that of TBA: when the total amount of the three metabolites in the effluent is set at 100%, the amount of TBA varied from around 1% to 10%, that of ‘unknown 1’ from around 10% to 75% and that of ‘unknown 2’ from around 15% to 85%. As the total amount of the three metabolites (other than CO_2) in effluent represented around 10% of the amount of TBHP originally present in the influent, the amount

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[13] Note that in the local exposure assessments for TBHP, 92% removal of TBHP and 8% discharge into surface water was used, see section 3.2.3 and section 3.2.4.

[14] The PEC values for TBA are actually C_{local} values, as a regional background concentration for TBA was not calculated.

[15] Site II-b1: Emission to waste water: 100 kg/d; WWTP flow (2000 m^3/d) → TBHP concentration in influent is 50 E+03 µg/l. TBA concentration in effluent is 10% of TBHP concentration in influent → TBA concentration in effluent is 50 E+02. Site-specific dilution factor 10 → PEC TBA in water is 500 µg/l→ PEC/PNEC is 500 µg/l / 930 µg/l = 0.5.
Site I-c/II-b2: Emission to waste water: 417 kg/d; WWTP flow (438 m^3/d) → TBHP concentration in influent is 95 E+04 µg/l. TBA concentration in effluent is 10% of TBHP concentration in influent → TBA concentration in effluent is 95 E+03 µg/l. Site-specific dilution factor 1000 → PEC TBA in water is 95 µg/l → PEC/PNEC is 95 µg/l / 930 µg/l = 0.1.
(Exposure data from Table 3.2 and Table 3.4).

of metabolite ‘unknown 1’ as well as that of metabolite ‘unknown 2’ represented on average 5% of the amount of THBP in the influent. As for TBA, local PEC values for the total amount of the two metabolites (‘unknown 1’ plus ‘unknown 2’) can be estimated, but a risk characterisation for these two metabolites is not possible because of the lack of toxicity data (unknown identity of these compounds). On top of that, because of the (assumed) high volatility these compounds are expected to have a short residence time in water.

3.5.2 Terrestrial compartment

3.5.2.1 Local risk characterisation

The PEC/PNEC soil at production/processing site 1-c and that of 10 of the processing sites is >1. The high PEC/PNEC values of these sites are mainly related to the emissions to waste water (and the subsequent application of WWTP sludge on agricultural soil)[16]. As stated earlier for water and WWTP no data were received that may have reduced these PEC/PNEC ratios to acceptable levels (e.g. information on fate of sludge) **(conclusion iii)**.[17]

3.5.2.2 Regional risk characterisation

The regional PEC/PNEC soil, calculated from the regional PEC Soil (1.05E-06 mg/kg wwt, for natural soil) and the $\text{PNEC}_{\text{terrestrial}}$ (0.3E-03 mg/kg wwt), is 0.004. Thus, no risk to terrestrial organisms is expected at a regional scale **(conclusion ii)**.

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[16] The calculations used in the exposure assessment indicate that the local concentration in soil is largely determined by the application of sludge. In the majority of the local exposure assessments, sludge application accounts for at least 75% (usually >90%) of the local concentration in soil. This despite the very low adsorption of TBHP to sludge.

[17] Although further soil ecotoxicity testing (towards PNEC refinement) would have been the most consistent and logical way forward in the opinion of the Rapporteur (cf. water and WWTP). Industry did not support this additional testing, however, and thereby implicitly accepted a conclusion iii) for all terrestrial scenarios with a PEC/PNEC above 1.

3.5.3 Atmosphere

Biotic effects

No risk characterisation is possible (see section 3.4.3).

Abiotic effects

TBHP, as a source of free radicals, may contribute to the build up of photochemical smog (see section 3.2.1.1). The contribution of TBHP to this atmospheric effect is considered to be negligible in comparison with other industrial chemicals (e.g. toluene and n-pentane).

3.5.4 Non compartment specific effects relevant to the food chain

Not relevant (see section 3.4.4).

ANNEX 1: AQUATIC TOXICITY OF TBHP (FISH, DAPHNIDS AND ALGAE)

Acute toxicity to fish (study 1)

Substance	Species	Method	Duration (h)	Test water	T (^{0}C)	Criterion	Result as TBHP-70 (mg/l)	**Result as TBHP (mg/l)**
TBHP-70	Pimephales promelas	semi-static (daily renewal)	96	DSW, pH 7.7-7.9, hardness 210 mg/l	24.4-24.9	LC50 NOEC	42 32	**29** **22**

Results: nominal concentrations, reported as TBHP-70.

Reference: Hooftman & van Drongelen-Sevenhuisen (1992a): TNO-report R92/068 (study No. IMW-91-0130-04)

Methods

The acute toxicity of TBHP-70 to the freshwater fish *Pimephales promelas* was determined as described in OECD Guideline 203 and according to the OECD principles of GLP. The test was performed as a 96-h semi-static test, using the following test solutions: 0, 10, 18, 32, 56, and 100 mg/l (nominal TBHP-70 concentrations). The dilution water was ‘Dutch Standard Water’ (DSW; hardness 210 mg/l, as $CaCO_3$; total organic carbon content 2.8 mg/l) prepared from ground water enriched with macro-elements. The solutions were slightly aerated. Ten fish were added to each test solution.

The actual concentrations (using TBHP-70 as a standard because the pure compound was not available) were measured by gas-chromatographic determination in the control and test solutions (with exception of the 56 mg/l concentration), both in newly prepared solutions and in the spent solution after 24 hours of exposure of the fish. In the newly prepared test solutions the actual concentrations were 86% (at 10 mg/l) to 138% (at 100 mg/l) of the nominal concentrations; that in the control was below 3 mg/l (limit of detection). In the spent solutions, the actual concentrations were 70% (at 10 mg/l) to 129% (at 100 mg/l) of the nominal concentrations. The actual concentrations at t = 24 h were 81% (at 10 mg/l) to 93% (at 100 mg/l) of the actual concentrations at t = 0 h, showing little loss.

Results

The lowest three exposure concentrations did not result in mortality or effects on the condition (behaviour; appearance) of the fish, resulting in a 96-h NOEC for TBHP-70 of 32 mg/l (nominal concentration). The 96-h LC50 for TBHP-70 was reported as 42 mg/l, being the geometric mean value of the 32 mg/l and 56 mg/l nominal concentrations. Based on the TBHP content of TBHP-70, the 96-h NOEC and 96-h LC50 are 22 and 29 mg/l, as nominal TBHP concentrations.

Acute toxicity to fish (study 2).

Substance	Species	Method	Duration (h)	Test water	T (^{0}C)	Criterion	Result as TBHP-70 (mg/l)	**Result as TBHP (mg/l)**
TBHP-70 (Trigonox A-W70)	Poecilia reticulata	semi-static (renewal at 48 h)	96	DSW, pH 7.9-8.3, hardness 210 mg/l	22-24	LC50 NOEC	- -	**57** **30**

Results: nominal concentrations, reported for TBHP (pure substance).

Reference: Mark & Meuwsen(1989): AKZO-report CRL F89107

Methods

The acute toxicity of TBHP-70 (Trigonox A-W70) to the freshwater fish *Poecilia reticulata* was determined as described in OECD Guideline 203 and according to the OECD principles of GLP. The test was performed as a 96-h semi-static test, using the following test solutions: 0, 9, 17, 30, 54 and 97 mg/l (nominal TBHP concentrations, as pure TBHP). Actual TBHP concentrations were not determined, as it was assumed that the TBHP concentrations would remain constant during the test. This assumption was based on the negative result for biodegradation found in the study by Van Ginkel (1990), see 3.2.2. Furthermore the test vessels were covered. The dilution water was ‘Dutch Standard Water’ (DSW; hardness 210 mg/l, as $CaCO_3$; total organic carbon content $\leq$2 mg/l). Ten fish were added to each test solution. The LC50 was calculated according to Kooijman (1981).

Results

The lowest three exposure concentrations did not result in mortality of the fish, resulting in a 96-h NOEC for TBHP of 30 mg/l (nominal concentration). The 96-h LC50 for TBHP was 57 mg/l (nominal concentration).

Acute toxicity to aquatic invertebrates

Substance	Species	Method	Duration (h)	Test water	T (^{0}C)	Criterion	Result as TBHP-70 (mgl)	**Result as TBHP (mg/l)**
TBHP-70	Daphnia magna	Static	48	DSW, pH 7.4-7.9, hardness 210 mg/l	20.6-20.8	EC50 NOEC	20 10	**14** **7**

Results: nominal concentrations, reported for TBHP-70.

Reference: Hooftman & van Drongelen-Sevenhuisen (1992b): TNO-report R 92/067 (study No. IMW-91-0130-01)

Methods

The acute toxicity of TBHP-70 to the waterflea *Daphnia magna* was determined as described in OECD Guideline 202 and according to the OECD principles of GLP. The test was performed as a 48- h static test; using the following test solutions: 0, 3.2, 5.6, 10, 18, 32, 56, and 100 mg/l (nominal TBHP-70 concentrations). The dilution water was 'Dutch Standard Water' (DSW; hardness 210 mg/l, as $CaCO_3$; total organic carbon content 2.8 mg/l) prepared from ground water enriched with macro-elements. The test was carried out with 20 (4x5) daphnids for each concentration and the control medium. The EC50 (endpoint: mobility) was calculated according to Kooijman (1981).

The actual concentrations of THBP-70 (using TBHP-70 as a standard because the pure compound was not available) were measured by gas chromatographic determination in the control and the 3.2, 18 and 100 mg/l test solutions, both in the newly prepared solutions and in the spent solution after 48 hours of exposure of the daphnids. In the newly prepared solutions the actual concentrations were 106% (at 3.2 mg/l), 67% (at 18 mg/l) and 160% (at 100 mg/l) of the nominal concentrations; that in the control was below 3 mg/l (limit of detection). After 48 h of exposure, the actual concentrations were 67% (at 18 mg/l) and <94% (at 3.2 mg/l; measured value below 3 mg/l). At 100 mg/l the actual concentration (measured after 24 h because of 100% mortality at that time) was 142% of the nominal concentration. At 18 and 100 mg/l, the actual concentrations at t = 24 h or 48 h were 89% and 100% of the actual concentrations at t = 0 h, showing little loss.

Results

The test resulted in a 48-h NOEC and EC50 for TBHP-70 of 10 and 20 mg/l (nominal concentrations), respectively. Based on the TBHP content of TBHP-70, the 48-h NOEC and EC50 are 7 and 14 mg/l, as nominal TBHP concentrations.

Toxicity to algae

Substance	Species	Method	Duration (h)	Test water	T (^{0}C)	Criterion	Result as TBHP-70 (mg/l)	**Result as TBHP (mg/l)**
TBHP-70	Selenastrum capricornutum	Static	72	OECD (201) medium, pH 7.9-8.6, hardness 24 mg/l	23	E_rC50 E_bC50 $NOE_{r,b}C$	2.1 1.2 0.32	**1.5** **0.84** **0.22**

Results: nominal concentrations, reported for TBHP-70.

Reference: Hanstveit & Oldersma (1992): TNO-report R92/090 (study IMW-91-0130-02)

Methods

The toxicity of TBHP-70 on the growth of freshwater alga *Selenastrum capricornutum* was determined according to OECD Guideline 201 and according to the OECD principles of GLP. The test was performed as a 72-h static test, using the following test solutions: 0, 0.1, 0.32, 0.56, 1.0, 3.2, and 10 mg/l (nominal THBP-70 concentration). The dilution water was algal growth medium according to OECD 201 (but containing a $NaHCO_3$ concentration of 150 mg/l in stead of 50 mg/l, to increase the buffering capacity). The test was carried out in duplicate. The algal growth was determined by electronic particle counting. The EC50 for exponential growth rate (E_rC50) was calculated according to Kooijman et al. (1983); the EC50 for biomass (E_bC50) was calculated according to OECD 201.

The actual concentrations of THBP-70 concentrations (using TBHP-70 as a standard because the pure compound was not available) were measured by gas-chromatographic determination in the control and in the highest test concentration, both in the newly prepared solution and in the spent solution after 72 hours of exposure of the algae. The measurements in the highest test concentration showed that the actual concentrations at the start and at the end of the test were 111% and 77% of the nominal concentration, respectively, showing relatively little loss. In the control the concentration was below 3 mg/l (limit of detection).

Results

The EC50 with respect to the exponential growth rate (E_rC50) was found to be 2.1 mg/l (95% confidence limits 1.9 mg/l and 2.4 mg/l); the E_rC10 was 0.73 mg/l. The EC_{50} with respect to biomass (E_bC50) was found to be 1.2 mg/l (in the range 1.0-3.2 mg/l); the E_bC10 was 0.28 mg/l. The no-observed effect-concentration (NOEC) for both endpoints was reported to be 0.32 mg/l (no statistics applied; the NOEC was estimated from the growth curves).
All above-mentioned values are expressed as nominal TBHP-70 concentrations. Based on the TBHP content of TBHP-70, the E_rC50, E_bC50 and NOEC are 1.5, 0.84 and 0.22 mg/l, as nominal TBHP concentrations, respectively.

Remarks

The measurement of THBP-70 (conducted only at the highest test concentration) showed some loss of the test substance, but this finding (which may be due to adsorption to the algae) does not affect the validity of the test. At the lower concentrations the actual exposure concentrations were not measured, hence the toxicity values could not be calculated from the actual concentrations; the nominal toxicity values are accepted.

ANNEX 2: TERTIARY BUTYL ALCOHOL (CAS NO. 75-65-0)

Data from the IUCLID Dataset (ECB, 2000 – public version). Not evaluated by ECB or Rapporteur. Additional data on biodegradation from Söllner (1995).

Aquatic toxicity data (short-term tests)

Fish (no chronic data available)
96-h LC50 Pimephales promelas: 6400 mg/l
7-d LC50 Poecilia reticulata: 3500 mg/l

Daphnids (no chronic data available)
48-h LC50 Daphnia magna: 5500 mg/l
48-h LC50 Daphnia magna: 930 mg/l

Algae
72-h EC50 Scenedesmus subspicatus: > 1000 mg/l (growth rate and biomass)
8-d NOEC Scenedesmus subspicatus: 1200 mg/l

Micro-organisms (bacteria) (All: Bringmann & Kühn tests ?)
EC10 (NOEC) Escherichia coli: 14000 mg/l
EC50 Escherichia coli: 11000 mg/l
17-h EC10 (NOEC) Pseudomonas putida: >10000 mg/l
17-h EC50 Pseudomonas putida: 6900 mg/l
18-h EC10 (NOEC) Pseudomonas putida: 2000 mg/l

Bioaccumulation

Very low bioaccumulation potential (log Kow: 0.35), thus food chain effects (secondary poisoning) not expected.

Biodegradation

TBA is inherently biodegradable (although variable results were reported, depending on test system and inoculum used: adapted versus non-adapted micro-organisms).

According to Söllner (1995), TBA is poorly degradable because tertiary compounds are not common in the environment. TBA is degraded by adapted micro-organisms when the micro-organisms have no access to compounds that are more easily degradable. Söllner conducted several tests for inherent biodegradability (Zahn-Wellens tests, see OECD 302B) with adapted and un-adapted activated sludge and found that TBA (analysed in the test medium) was fully degraded within about 2 weeks. In unadapted sludge there was a lag time of about 1 week before the micro-organisms were adapted and started to degrade TBA.

In additional Zahn-Wellens tests performed by Söllner (1995), the degradation of TBA (ca. 1500 mg/l) was found to be strongly inhibited by TBHP (70 or 140 mg/l), especially at the highest TBHP concentration. At the lowest TBHP concentration, the degradation of TBA was no longer inhibited when TBA was added for the second time (2 weeks after the addition of TBHP and TBA; this first load of TBA was degraded after 2 weeks). This result indicates that the lowest TBHP load (70 mg/l) was degraded after or within 2 weeks). These tests were performed with an inoculum (3000 mg/l) to TBHP concentration (70 or 140 mg/l) ratio of 42:1 and 21:1, respectively.

ANNEX 3: USE OF TBHP IN THE RESIN INDUSTRY

(Data provided by the European Resin Manufactures Association, ERMA)

Mainly used by manufacturers of synthetic lattices or water borne polymer dispersions. Also used as a component of catalysts systems for unsaturated polyester resins.

Used as a free radical initiator to polymerise unsaturated monomers, usually to high polymers and is consumed virtually completely within the process. Indeed, in this context, TBHP has to be consumed or the fundamental polymerisation process would not be taking place.

In dispersion polymerisation it is most frequently used in conjunction with reducing agents or metal ions to form a ‘redox’ couple, which allows generation of the initiating species at temperatures lower than the decomposition temperature of the peroxide itself.

Typically used at levels in the region of 0.1% active ingredient by weight on the total formulation, sometimes with further trace additions at the conclusion of the polymerisation process to ensure any residual unsaturated monomers are minimised. This mopping up process is essential and virtually eliminates exposure of personnel, downstream users and consumers to the monomers used in producing the latex or dispersion.

The polymer dispersions manufactured in this way are subsequently compounded downstream by the paint, adhesive, textile, printing ink and building industries, to product which are mostly used in other manufacturing processes before they reach professional or domestic users. This further compounding offers still more opportunity for any peroxide residues to be consumed.

The chances of TBHP reaching the environment from manufacturing sites are extremely low since the peroxide is not only consumed during the process but also plant washings are treated though flocculation processes using metal ions, offering further opportunity to consume any minuscule peroxide residues. In some cases plant washings are combusted by on-site incinerators to carbon dioxide and water.

4 HUMAN HEALTH

The draft Human Health Part of the RAR has been discussed at the TCNES II 2006 (Stage I, in depth discussion). In October 2006 the rapporteur will send a Response to Comments Document (RCOM) and a revised draft Human Health Part of the RAR to the EU Member States, for discussion at TCNES IV 2006 or for a Final Written Procedure.

5 RESULTS

CAS No.: 75-91-2
EINECS No.: 200-915-7
IUPAC Name: Tert-butyl hydroperoxide

ENVIRONMENT

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

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

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

Conclusion iii) is reached, because:

- the local PEC/PNEC is >1 for the aquatic environment (including WWTP) and/or terrestrial environment for one production site and a number of processing sites. Although the exposure assessment is based on a number of default assumptions, no additional data were submitted by industry that may rebut the currently followed approach for the PEC calculations.

  It is stressed that from a scientific perspective, a conclusion (**i**) would have been more appropriate, as refinement of both PEC values (now based on a number of default assumptions instead of site-specific data) and the PNEC values (now based on very limited data) may be possible. However, Industry has not supported to provide additional exposure data or to conduct additional ecotoxicological studies (see further Section 3.5) and thereby implicitly accepted a conclusion (**iii**) for a number of sites. Furthermore, it can be questioned if all PEC/PNEC values would be lowered sufficiently by a refinement of PEC and PNEC values, as some of the current PEC/PNEC values are far above 1.

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