Screening Assessment for the Challenge

Peroxide, (1,1,4,4-Tetramethyl-2-butyne-1,4-diyl)bis[(1,1-dimethylethyl)

Chemical Abstracts Service Registry Number
1068-27-5

Environment Canada
Health Canada

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Synopsis

Pursuant to section 74 of the *Canadian Environmental Protection Act, 1999* (CEPA 1999), the Ministers of the Environment and of Health have conducted a screening assessment on Peroxide, (1,1,4,4-tetramethyl-2-butyne-1,4-diyl)bis[(1,1-dimethylethyl)] (DMBP), Chemical Abstracts Service Registry Number 1068-27-5. This substance was identified as a high priority for screening assessment and included in the Ministerial Challenge because it had been found to meet the ecological categorization criteria for persistence, bioaccumulation potential and inherent toxicity to non-human organisms and is believed to be in commerce in Canada.

The substance DMBP was not considered to be a high priority for assessment of potential risks to human health, based upon application of the simple exposure and hazard tools developed by Health Canada for categorization of substances on the Domestic Substances List (i.e., it did not meet the criteria of both being considered to present greatest or intermediate potential for exposure and having been classified by another national or international regulatory agency on the basis of carcinogenicity, genotoxicity, developmental toxicity or reproductive toxicity). Therefore, this assessment focuses on information relevant to the evaluation of ecological risks.

DMBP is an organic substance that is used in Canada and elsewhere in polymer processing. The substance is not naturally produced in the environment. Between 1000 and 10 000 kg of DMBP were manufactured in Canada in 2006 while between 1000 and 10 000 kg of DMBP were imported into Canada during the same period.

Based on certain assumptions and reported use patterns, most of the substance is transformed during the processing phase. Small proportions may be released to water (0.1%). DMBP is not soluble in water and has a tendency to partition to particles because of its hydrophobic nature. For these reasons, DMBP would likely be found almost entirely in sediments and is not expected to be significantly present in other media.

DMBP is not expected to meet the persistence criterion as set out in the *Persistence and Bioaccumulation Regulations*, but it is predicted to have a potential to accumulate in organisms.

Predicted environmental concentrations are a few orders of magnitude lower than the predicted no-effects concentrations for aquatic organisms. This indicates a low probability of risk in the aquatic environment.

This substance will be included in the Domestic Substances List inventory update initiative, to be launched in 2009. In addition and where relevant, research and monitoring will support verification of assumptions used during the screening assessment.

Based on the information available, DMBP does not meet any of the criteria set out in section 64 of the *Canadian Environmental Protection Act, 1999*.

Introduction

The *Canadian Environmental Protection Act, 1999* (CEPA 1999) (Canada 1999) requires the Minister of the Environment and the Minister of Health to conduct screening assessments of substances that have met the categorization criteria set out in the Act to determine whether these substances present or may present a risk to the environment or human health. Based on the results of a screening assessment, the Ministers can propose to take no further action with respect to the substance, to add the substance to the Priority Substances List (PSL) for further assessment, or to recommend that the substance be added to the List of Toxic Substances in Schedule 1 of the Act and, where applicable, the implementation of virtual elimination.

Based on the information obtained through the categorization process, the Ministers identified a number of substances as high priorities for action. These include substances that

- met all of the ecological categorization criteria, including persistence (P), bioaccumulation potential (B) and inherent toxicity to aquatic organisms (iT), and were believed to be in commerce in Canada; and/or
- met the categorization criteria for greatest potential for exposure (GPE) or presented an intermediate potential for exposure (IPE), and had been identified as posing a high hazard to human health based on classifications by other national or international agencies for carcinogenicity, genotoxicity, developmental toxicity or reproductive toxicity.

The Ministers therefore published a notice of intent in the *Canada Gazette*, Part I, on December 9, 2006 (Canada 2006), that challenged industry and other interested stakeholders to submit, within specified timelines, specific information that may be used to inform risk assessment, and to develop and benchmark best practices for the risk management and product stewardship of these substances identified as high priorities.

The substance peroxide, (1,1,4,4-tetramethyl-2-butyne-1,4-diyl)bis[(1,1-dimethylethyl was identified as a high priority for assessment of ecological risk as it was found to be persistent, bioaccumulative and inherently toxic to aquatic organisms and is believed to be in commerce in Canada. The Challenge for peroxide, (1,1,4,4-tetramethyl-2-butyne-1,4-diyl)bis[(1,1-dimethylethyl was published in the *Canada Gazette* on February 3, 2007 (Canada 2007a). A substance profile was released at the same time. The substance profile presented the technical information available prior to December 2005 that formed the basis for categorization of this substance. As a result of the Challenge, submissions of information were received.

Although peroxide, (1,1,4,4-tetramethyl-2-butyne-1,4-diyl)bis[(1,1-dimethylethyl was determined to be a high priority for assessment with respect to the environment, it did not meet the criteria for GPE or IPE and high hazard to human health based on classifications by other national or international agencies for carcinogenicity, genotoxicity,

developmental toxicity or reproductive toxicity. Therefore, this assessment focuses principally on information relevant to the evaluation of ecological risks.

Screening assessments under CEPA 1999 focus on information critical to determining whether a substance meets the criteria for defining a chemical as toxic as set out in section 64 of the Act, where

> "64. [...] a substance is toxic if it is entering or may enter the environment in a quantity or concentration or under conditions that
>
> (*a*) have or may have an immediate or long-term harmful effect on the environment or its biological diversity;
>
> (*b*) constitute or may constitute a danger to the environment on which life depends; or
>
> (*c*) constitute or may constitute a danger in Canada to human life or health."

Screening assessments examine scientific information and develops conclusions by incorporating a weight of evidence approach and precaution.

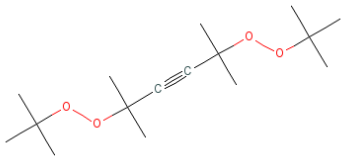
This screening assessment includes consideration of information on chemical properties, hazards, uses and exposure, including the additional information submitted under the Challenge. Data relevant to the screening assessment of this substance were identified in original literature, review and assessment documents, stakeholder research reports and from recent literature searches up to May 2008. Key studies were critically evaluated; modelling results may have been used to reach conclusions. When available and relevant, information presented in hazard assessment from other jurisdictions was considered. The screening assessment does not represent an exhaustive or critical review of all available data. Rather, it presents the most critical studies and lines of evidence pertinent to the conclusion.

This screening assessment was prepared by staff in the Existing Substances Programs at Health Canada and Environment Canada and incorporates input from other programs within these departments. Additionally, the draft of this screening assessment was subject to a 60-day public comment period. The critical information and considerations upon which the assessment is based are summarized below.

Substance Identity

For the purposes of this report, this substance will be referred to as DMBP, which has been derived from the name 2,5-dimethyl-2,5-di-tert-butylperoxyhexyne.

Table 1. Substance Identity

Chemical Abstracts Service Registry Number (CAS RN)	1068-27-5
Name on Domestic Substances List (DSL)	Peroxide, (1,1,4,4-tetramethyl-2-butyne-1,4-diyl)bis[(1,1-dimethylethyl)
Other Inventory Names	Peroxide, 1,1'-(1,1,4,4-tetramethyl-2-butyne-1,4-diyl)bis[2-(1,1-dimethylethyl) (TSCA) Di-tert-butyl 1,1,4,4-tetramethylbut-2-yn-1,4-ylene diperoxide (EINECS)
Other names	2,5-Dimethyl-2,5-di-tert-butylperoxyhexyne; 2,5-Bis(tert-butylperoxy)-2,5-dimethyl-3-hexyne; 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexyne; 2,5-Dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne; 2,5-Dimethyl-2,5-bis(tert-butylperoxy)-3-hexyne; Luperco 130XL; Luperox 130; Lupersol 130; Perhexyne 2.5B, 2.5B40, 25B, 25B40
Chemical group	Discrete organics
Chemical sub-group	Dialkyl peroxides
Chemical formula	$C_{16}H_{30}O_4$
Chemical structure	
SMILES	O(OC(C)(C)C)C(C#CC(OOC(C)(C)C)(C)C)(C)C
Molecular mass	286.42 g/mol

Source: National Chemical Inventories (NCI), 2007: EINECS (European Inventory of Existing Chemical Substances); TSCA (Toxic Substances Control Act Chemical Substance Inventory).

Physical and Chemical Properties

Table 2 contains experimental and modelled physical and chemical properties of DMBP that are relevant to its environmental fate.

Table 2. Physical and chemical properties for DMBP

Property	Type	Value	Temperature (°C)	Reference
Melting point (ºC)	Modelled	92.54		MPBPWIN 2000
Boiling point (ºC)	Experimental	65–67		Milas 1954
	Modelled	290.88 304.8		MPBPWIN 2000 ACD 2007
Vapour pressure (Pa)	Modelled	0.168 0.21	 25	MPBPWIN 2000 ACD 2007
Henry's Law constant ($Pa \cdot m^3/mol$)	Modelled	16.28 (0.0001607 $atm \cdot m^3/mol$)	25	HENRYWIN 2000
Log K_{ow} (Octanol-water partition coefficient) (dimensionless)	Modelled	5.84 5.86	25 25	KOWWIN 2000 ACD 2007
Log K_{oc} (Organic carbon-water partition coefficient) (L/kg)	Modelled	5.208 4.56	 25	PCKOCWIN 2000 ACD 2007
Water solubility (mg/L)	Modelled	0.1518 0.018	25 25	WSKOWWIN 2000 ACD 2007

Most of the physical and chemical properties in the above table were generated using quantitative structure-activity relationship (QSAR) models, and there are uncertainties related to the use of these models. For instance, the applicability domain of a model may not cover the entire structure of a given chemical, thus lowering the reliability of predictions. For DMBP, the comparison of modelled and experimental values for boiling point shows that this property cannot be adequately predicted by the model MPBPWIN. This could also be the case for some of the other physical and chemical properties and associated models.

Manufacture and Import

Organic peroxide initiators were not manufactured in Canada in 2000 and approximately 300 000 kg of dialkyl peroxides were used in the Canadian polymer resin manufacturing process in 2000 (Cheminfo Services Inc. 2002).

Response to a survey notice pursuant to section 71 of CEPA 1999 indicated that one company manufactured DMBP in Canada in 2006 in a quantity meeting the 100 kg reporting threshold. Three companies met the 100 kg reporting threshold and reported importing the substance into Canada in a total quantity, for the three companies, between 1000 and 10 000 kg. One company reported importing the substance at a quantity below 100 kg (Environment Canada 2007a).

It is not known how much DMBP is imported into Canada in finished articles, for example, as residues in polymeric materials.

Elsewhere, DMBP has been identified as a US High Production Volume Chemical, with total use reported under the US Inventory Update Rule within the range of 4.5 to 227 tonnes per year for 1986, 1990, 1994, 1998 and 2002 (US EPA 2002). DMBP is a European Union (EU) Low Production Volume Chemical, indicating that production within the EU is estimated to be in the order of 10 tonnes per year; however the Substances in Preparations in Nordic Countries database has reported that the total use in Sweden in 2002 was 158 tonnes. DMBP was used in Denmark and Sweden from 1999 to 2004 (SPIN Database 2000).

Uses

Information on uses of DMBP in Canada was received in response to the CEPA section 71 Notice for the 2006 calendar year. Uses include use as a polymer and crosslinking agent.

Published literature indicates that DMBP is a dialkyl peroxide that may be used in polymer processing as an initiator for crosslinking of polyolefins. It can be used as a polymerisation initiator for plastics and in rubber processing for the production of window seals and automotive seals, hoses, and soles of shoes. It may also be used for the curing of some resins for applications ranging from boat hulls and swimming pools to bodywork parts (Arkema 2006). In these uses, the peroxide bonds are broken to produce reactive radicals that initiate polymerization.

Releases to the Environment

DMBP is not naturally produced in the environment.

Mass flow tool

To estimate potential release of the substance to the environment at different stages of its life cycle, a mass flow tool was used. Empirical data concerning releases of specific substances to the environment are seldom available. Therefore, for each identified type of use of the substance, the proportion and quantity of release to the different environmental media are estimated, as is the proportion of the substance chemically transformed or sent for waste disposal. Assumptions and input parameters used in making these estimates are based on information obtained from a variety of sources including responses to regulatory surveys, Statistics Canada, manufacturers' websites and technical databases. Of particular relevance are emission factors, which are generally expressed as the fraction of a substance released to the environment, particularly during its manufacture, processing, and use associated with industrial processes. Sources of such information include emission scenario documents, often developed under the auspices of the Organisation for Economic Co-operation and Development (OECD), and default assumptions used by different international chemical regulatory agencies. It is noted that the level of uncertainty in the mass of substance and quantity released to the environment generally increases further down the life cycle. Unless specific information on the rate or potential for release of the substance from landfills and incinerators is available, the Mass Flow Tool does not quantitatively account for releases to the environment from disposal.

Table 3. Estimated releases and losses of DMBP to environmental media,transformation and distribution to management processes, based on the Mass Flow Tool[1]

Fate	Proportion of the mass (%)	Major life cycle stage involved
Releases to receiving media:		
To soil	0.0	
To air	0.0	
To sewer[2]	0.1	Formulation
Chemically transformed	93.5	
Transferred to waste disposal sites (e.g., landfill, incineration)	6.4	Waste management

[1] For DMBP, information from the following OECD emission scenario documents was used to estimate releases to the environment and distribution of the substance, as summarized in this table: OECD 2004; Brooke and Crookes 2007. Values presented for releases to environmental media do not account for possible mitigation measures that may be in place in some locations (e.g., partial removal by sewage treatment plants). Specific assumptions used in derivation of these estimates are summarized in Environment Canada 2007b.

[2] I.e., wastewater before any treatment

The tool results indicate that the substance is mainly (about 94%) lost by transformation mostly during the processing phase at polymer manufacturing facilities, where the peroxide bonds in the substance are broken to form reactive radicals that initiate polymerization. About 6% may end up in waste disposal sites as a result of handling and cleaning processes, manufacture of DMBP and disposal of off-spec product. A small

fraction of solid waste is incinerated, which is expected to result in transformation of the substance. Based largely on information contained in OECD emission scenario documents for processing and uses associated with this substance, it is estimated that 0.1% DMBP may be released to sewers.

Based on the above, the largest release of DMBP to the ambient environment is to sewers during the formulation phase.

Environmental Fate

Based on its physical and chemical properties (Table 2) and the results of Level III fugacity modelling (Table 4), DMBP is expected to reside in sediment, air, soil or water, depending on the compartment of release.

Table 4. Results of the Level III fugacity modelling (EPIWIN 2004)

	Fraction of substance partitioning to each medium (%)			
Substance released to:	**Air**	**Water**	**Soil**	**Sediment**
Air (100%)	23	2.5	11	64
Water (100%)	0.03	3.8	0.01	96
Soil (100%)	0.0002	0.005	99.9	0.1

According to the mass flow tool results presented in Table 3, the largest direct environmental release of DMBP is to sewers during processing and so the 100% release scenario to water seems to be the most relevant for Canada. The fraction of DMBP released to water is expected to strongly adsorb to suspended solids and sediments, according to its very high log K_{ow} value of ~5.8 (Table 2) and Level III fugacity modeling results.

Persistence and Bioaccumulation Potential

Persistence

As mentioned above, the only direct release of DMBP to the environment could be to surface water through sewers (Table 3). Once in water, the fate analysis presented in Table 4 indicates that this substance would partition mainly into sediments (96%), and to a much lower extent to water (3.8%). According to the same analysis, DMBP is not expected to partition to air or soil if released to water. Therefore, the potential for persistence of DMBP will be assessed for the aquatic compartment only.

While peroxides are generally considered to be reactive because of the nature of the peroxide bond, there are differences in the level of reactivity among different categories of organoperoxides, and even among different substances within a category.

Dialkyl peroxides are among the most stable of all the commercially available organoperoxides, with a shelf half-life of at least one year at their recommended storage temperature of < 38°C (ATOFINA 2001). However, storing conditions does not reflect the transformation pathways that can exist in the natural environment, such as hydrolysis, photolysis and biodegradation.

Regarding hydrolysis, DMBP does not contain functional groups expected to react with water. As for photolysis, there are no data on the absorption spectrum of DMBP. Di-tert butyl peroxide (CAS RN 110-05-4), another dialkyl peroxide, has been found to absorb light up to 340 nm and to photolyze to form tert-butoxy radicals (HSDB 1983 –). The rate of this process is not known. Because this substance is structurally similar to DMBP, the latter may also be subject to photolysis when exposed to light.

Biodegradation is often a major transformation pathway in the environment. No standard studies addressing directly the biodegradation potential of DMBP were available. Other types of studies were available, however, and these suggest that DMBP is not persistent. Firstly, in an *in vitro* metabolism study using a trout liver S9 enzyme fraction (OPPSD 2008), DMBP was metabolised rapidly under conditions of incubation and it also degraded rapidly in controls in which the S9 enzyme fraction was denatured. The reported half-life in the controls was 1.89 hours. An expected breakdown product of DMBP, tertiary butanol and a second, more volatile substance, were detected in the controls. These results indicate that DMBP may undergo both biotic and abiotic degradation quite quickly in the environment, and therefore would not be considered persistent.

Secondly, in two laboratory toxicity tests (Table 6), the measured concentration of DMBP in water decreased from 3.76 mg/L to < 0.081 mg/L after 72 hours, and from 5.31 mg/L to 0.375 mg/L after 48 hours (Study Submission 2006a and 2006b). Considering the breakdown of DMBP in the metabolism study cited above, this disappearance may have been the result of degradation of the substance, either through abiotic (e.g. photolysis) or biotic mechanisms. Also, given its high volatility (Table 2), DMBP may have volatilized from the solution since the test containers were not hermetically covered. Finally, the hydrophobic nature of DMBP (estimated log K_{ow} of 5.8; Table 2) could have led to its sorption to test organisms or to the walls of test containers. However, sorption to test organisms would probably not be important enough though to account for the drop seen in the measured concentrations. Similarly, sorption to the walls of the test containers is not likely to be important since these were made of glass. Overall, these laboratory tests show that DMBP is unstable in aqueous solution and dissipates within days.

Studies addressing biodegradation were available for other organic peroxides. The results are presented here even though a lower weight is usually given to data obtained for analogues, in the weight-of-evidence approach. Peroxide (1,1,4,4-tetramethyl-1,4-

butanediyl)bis[(1,1-dimethylethyl) (CAS RN 78-63-7), another dialkyl peroxide, showed only 4% biodegradation over 28 days in a ready-biodegradation test (modified MITI test – OECD 301C) as measured by gas chromatography analysis (NITE 2002). This demonstrates that some dialkyl peroxides can be quite resistant to hydrolysis and ultimate degradation under certain test conditions.

In a risk assessment of tertiary butyl hydroperoxide (CAS RN 75-91-2), a hydroperoxide, the Netherlands Chemical Substances Bureau reported that this substance was not appreciably degraded in abiotic degradation tests. In these tests, half-lives for primary degradation ranged from 170 to 6900 days in 10-day tests in ultra-pure water and from 36 to 45 days in 10-day tests with sterilized sludge (Chemical Substances Bureau 2004). The substance was not readily biodegradable in the modified Sturm test or the closed bottle test, both of which measure ultimate degradation, but the substance was biodegraded in 1-hour activated sludge tests, with primary degradation half-lives of 18–24 minutes (Chemical Substances Bureau 2004). These results show that this hydroperoxide does not undergo hydrolysis and that it has a strong tendency to sorb to organic matter. The results also show that this peroxide can undergo primary degradation within minutes. However, it is resistant to ultimate degradation. It should be noted that in hydroperoxides, the peroxide bond is at the end of the molecule, where it is more accessible to attack than in dialkyl peroxides, where the peroxide bond is closer to the centre of the molecule.

Although experimental data on the degradation of DMBP and analogue substances are available, QSARs were also applied using degradation models. Modeling indicates that DMBP would be persistent in water and sediment. However, the modeled values are considered to be of lower reliability as no chemicals of structural comparability to DMBP are contained in their training sets. Indeed, these fragment-based models do not consider the peroxide bond, which can be reactive in some substances. Given that experimental data are available and given that the modeled values are of lower reliability, the latter are given a very low weight in the assessment of the environmental persistence of DMBP.

The potential for persistence of DMBP in sediment is of particular concern since this substance would partition mainly to this environmental compartment should it be released to surface water (Table 4). Information submitted to Environment Canada states that the reactivity of organic peroxides in the presence of metals such as iron and manganese should prevent their accumulation in soils and sediments (Challenge Submission 2008). These metals are indeed abundant in these matrices. Otherwise, it is generally accepted that the half-life of a substance in sediment is longer than that in water (factor of 1:4, as proposed by Boethling et al. 1995). Considering that the metabolism and toxicity studies conducted with DMBP indicate that its half-life in aqueous solutions is probably of the order of hours, its half-life in sediments should be in the order of days or weeks.

Different lines of evidence were presented above to assess the persistence of DMBP, should it be released in an aquatic environment. It is concluded that the weight of evidence based on the above-described data indicates that DMBP does not meet the

persistence criteria for water (half-life ≥ 182 days) or sediments (half-life ≥ 365 days) as set out in the *Persistence and Bioaccumulation Regulations* (Canada 2000).

Bioaccumulation

No experimental data for BCF or BAF were available for DMBP. Experimental steady-state bioconcentration factor (BCF) values for fish in the NITE database for the close structural analogue CAS# 78-63-7 (DMHBP) were used as suitable information for DMBP. Values of 2250 and 3690 L/kg, (Table 5a) were reported by OPPSD (2008). In this study, fish were exposed under flow-through conditions for 8 weeks. Test water analyses were done twice a week and fish analyses were done every two weeks. Fish were not fed on the days of fish sampling.

Table 5a. Empirical data for bioconcentration

Test organism	Test concentration	Endpoint	Value wet wt	Reference
Fish	40 µg/L	BCF (steady state)	3690 L/kg	NITE Database (2002) reported by OPPSD 2008
Fish	4 µg/L	BCF (steady state)	2250 L/kg	NITE Database (2002) reported by OPPSD 2008

The steady-state BCF values from the NITE database were used to derive an *in vivo*-based metabolic rate constant (k_M) according to the method of Arnot et al. (2008). In this method, k_m is derived according to the following equation:

$$k_M = (k_1\varphi/BCF) - (k_2 + k_E + k_G) \quad (1)$$

where:

k_M = the metabolic rate constant (1/days)
k_1 = the uptake rate constant (Arnot and Gobas 2003)
φ = fraction of freely dissolved chemical in water (Arnot and Gobas 2003)
BCF = the available empirical bioconcentration factor
k_2 = the elimination rate constant (Arnot and Gobas 2003)
k_E = fecal egestion rate constant (Arnot and Gobas 2003)
k_G = growth rate constant (Arnot and Gobas 2003)

The method of Arnot et al. (2008) provides for the estimation of confidence factors (CF) for the k_M to account for error associated with the *in vivo* data (i.e., measurement variability, parameter estimation uncertainty and model error and uncertainty with the predicted log K_{ow}). A CF of ±3.9 was calculated for the available BCF data.

Because metabolic potential can be related to body weight and temperature (e.g., Hu and Layton 2001, Nichols et al. 2006), the k_M was further normalized to 15°C and then corrected for the body weight of the middle trophic level fish in the Arnot-Gobas model (0.184 g). The middle trophic level fish was used to represent overall model output as suggested by the model developer (Arnot *pers. comm.*) and is most representative of fish weight and size likely to be consumed by an avian or terrestrial piscivore. After normalization routines, the k_M ranges from 0.01 to 0.22. Even though similar *in vivo* BCF data were used to derive this metabolic rate constant, this range is not identical to that calculated for analogous CAS# 78-63-7 because of log K_{ow} differences.

An *in vitro* S9 metabolism study was reported by OPPSD (2008). In this study, DMBP was metabolised rapidly under conditions of incubation and also degraded rapidly in controls in which the S9 enzyme fraction was denatured. An expected breakdown product of DMBP, tertiary butanol (10 – 30% of the parent compound on a mass balance basis) and another more volatile compound (with a similar mass balance profile) were detected in the controls but not in the S9 samples. Whole body fish metabolism rate constants, k_{met}, from this study were derived by OPPPSD using the extrapolation methods of Cowan-Ellsberry et al. (2008). The S9 k_{met} for arterial and portal blood flow (most realistic) was reported as 0.16 (Table 3; OPPSD, 2008). Unlike the procedure of Arnot et al. (2008), estimates for k_{met} based on *in vitro* assays do not provide for the calculation of confidence factors. Cowan-Ellsberry et al. (2008) suggests that for acceptance of *in vitro* methods, understanding of uncertainty of these methods and testing on more types of chemicals should be performed to evaluate the various assumptions used in their approach. Han et al. (2007) also indicate that uncertainty of model parameters should be understood for the hepatocyte method. As no bounds of uncertainty could be directly estimated for the *in vitro* data, a one order of magnitude error (CF = ±10) was assumed for potential variability and uncertainty in the parameters used to derive the k_{met}. The S9 and k_{met} value was also normalized to the weight of the middle trophic level fish in the Arnot and Gobas model. The normalized values for k_{met} thus ranged from 0.01 to 0.11.

The *in vivo* and *in vitro* metabolic rate constants were used to adjust the predicted BCF and BAF values from the Arnot and Gobas model's default of zero metabolism. The results are presented along with other QSAR estimates in Table 5b.

Table 5b: BAF and BCF predictions for DMBP using the Arnot-Gobas kinetic model (v1.11).

k_M (1/days)	S9 k_{met} (1/days)	LogK_{ow} Used	Arnot-Gobas BCF	Arnot-Gobas BAF	Half-Life (days)
1.47E-02 (CF -3.9) (2.5%)		5.8	8558	58047	47
5.75E-02 (median)		5.8	2785	8744	12
0.22 (CF +3.9) (97.5%)		5.8	771	1248	3
	1.07E-02 (CF -10)	5.8	10880	87033	65
	1.07E-01	5.8	1549	3443	7
	1.07 (CF +10)	5.8	163	184	<1

Comparing the metabolic rates constants shows that there is approximately a factor of 2 difference between the median values k_M and k_{met} but this factor increase at the extremes of the range. BCF values ranged from 163 to 10880 with an average of ~4117 regardless of which method was used for metabolic correction. BAF values ranged from 184 to 87033 with an average BAF of ~26500 regardless of metabolic correction used. Half-lives ranged from less than 1 day to 65 days. The geometric mean steady-state BCF reported in the NITE database is 2881 (based on CAS# 78-63-7) which is in very good agreement with the corrected BCF of 2785 (factor = 1.03) corresponding to a metabolic rate constant of ~0.06. Greatest confidence is associated with the BAF predicted using this metabolic rate correction. The BAF corresponding to the metabolism corrected BCF of 2785 is 8744.

Table 5c. Additional Modelled data for bioaccumulation.

Test organism	Endpoint	Value wet wt (L/Kg)	Reference
Fish	BCF	16 600	ACD 2007
Fish	BCF	50 119	OASIS Forecast 2005
Fish	BCF	6310	BCFWIN 2000

The modeled values in table 5c however are considered less reliable as no metabolism considerations are taken into account by these models (directly) and no chemicals of structural comparability are contained in their training sets.

According to the *Persistence and Bioaccumulation Regulations* (Canada 2000), measures of BAF are the preferred metric for assessing bioaccumulation potential of substances.

This is because BCF does not adequately account for the bioaccumulation potential of substances via the diet, which predominates for substances with log K_{ow} > ~4.0 (Arnot and Gobas 2003). No empirical BAF were available for DMBP consequently BAF was modelled. Kinetic mass-balance modelling was considered to provide the most reliable prediction method for determining the bioaccumulation potential of DMBP because it allows for metabolism correction and DMBP is within the log K_{ow} domain of the model.

Metabolism corrected BCF and BAF values range from163 to 10 880 and from 184 to 87 033, respectively, depending on the rate of metabolism. Environment Canada has analyzed these values and determined that the most reliable metabolism rate is reached when the metabolism corrected predicted BCF is in close agreement with the empirical BCF. Using this metabolic rate to correct the predicted BAF results in a BAF 8 744. This BAF value is lower than that predicted for the analogous chemical DMHBP (CAS# 78-63-7) because of a lower log K_{ow}. Nevertheless, based on the available empirical and kinetic-based modelled values corrected for metabolism and considering evidence from both *in vivo* and *in vitro* techniques for metabolic potential, DMBP meets the bioaccumulation criterion (BAF ≥ 5 000) as set out in the *Persistence and Bioaccumulation Regulations* (Canada 2000).

Potential to Cause Ecological Harm

A quantitative evaluation based on exposure and ecological effects was conducted for this substance as part of the weight of evidence evaluation of its potential to cause harm.

First, a predicted environmental concentration (PEC) was determined based on an analysis of exposure pathways. A predicted no-effect concentration (PNEC) was derived by selecting a critical toxicity value (CTV) from the available toxicity data and dividing this value by an assessment factor.

Ecological Exposure Assessment

No empirical data have been found regarding levels of DMBP in the environment. The mass flow tool estimated that 0.1% of the quantity used at a polymer manufacturing facility may be released in liquid effluents. A conservative predicted environmental concentration was calculated using the following equation (Environment Canada 2007c):

$$PEC = \frac{I \times L \times (1-R) \times 1000}{D \times (F + S) \times 86\,400}$$

Where:

PEC = Predicted environmental concentration (mg/L)

I	=	Maximum mass imported into (or manufactured in) an industrial complex linked with a discharge point (10 000 kg/year)
L	=	Losses by processing (0.001)
R	=	Removal rate of the sewage treatment plant (0.91) (based on Simple Treat 3.0 model results)
1000	=	Conversion of units (kg/m^3 to mg/L)
D	=	Days of release of the substance from site (250 days/year, OPPSD 2008)
F	=	Flow of the receiving watercourse (0.65 m^3/s) (default value, Environment Canada 2007c)
S	=	Flow of the effluent from the sewage treatment plant (0.04 m^3/s) (default value, Environment Canada 2007c)
86 400	=	Conversion of units (days to seconds)

Based on this equation, the PEC is 0.00006 mg/L.

Ecological Effects Assessment

Two aquatic toxicity studies were conducted with freshwater organisms (Table 6). The interpretation of the results obtained in these studies is complicated by the fact that in both cases, significant losses of the test substance from solution occurred during the test period. Since DMBP has low water solubility, a solvent was used in both studies.

In a study on the effects of DMBP on the freshwater green alga *Pseudokirchneriella subcapitata*, the concentrations measured at the beginning and end of the test in the highest exposure concentration were 3.76 mg/L and <0.081 mg/L (detection limit), respectively. Possible reasons explaining the disappearance of the test substance from test solution have been discussed earlier in this report. The study authors calculated an extrapolated EC_{50} of 6.17 mg/L and a no-observed-effect concentration (NOEC) of 1.88 mg/L, based on the measured concentration at the beginning of the test. Given the major drop in the test concentrations over the duration of the test, Environment Canada used the measured concentrations at each time interval in the test to calculate the geometric mean. This mean is considered to be an appropriate estimator of the concentration to which organisms were exposed during the test, as proposed by the OECD (OECD 2000). Since no inhibitory effects were seen on algal growth for any of the test concentrations, an EC_{50} value of >0.21 mg/L is obtained based on the geometric mean (Table 6).

In a 48-hour toxicity test conducted with *Daphnia magna*, a similar drop in test concentrations occurred. In the highest exposure concentration, a value of 5.31 mg/L was measured at the beginning of the test while it had dropped to 0.375 mg/L by the end.

Again, the study authors reported an endpoint value based on the starting concentration. As for the test with the green alga, Environment Canada calculated the geometric mean of exposure concentration and used it to derive the endpoint value. As no immobile organisms were observed in any of the test concentrations, the EC50 was determined to be >1.41 mg/L (Table 6). However, other effects, specifically floating at the surface, were observed at all concentrations. Such an effect is difficult to interpret in terms of ecological relevance

Table 6 Empirical data for aquatic toxicity for DMBP

Test Organism	Type of test	Endpoint	Value (geometric mean) (mg/L)	Reference
Pseudokirchneriella subcapitata (green algae)	Acute	EC_{50} (72 hr)	>0.21	Study Submission 2006a
Daphnia magna (water flea)	Acute	EC_{50} (48 hr)	>1.41	Study Submission 2006b

EC_{50} – Concentration effecting 50% of the test population

Results for an acute aquatic toxicity study conducted with a closely related dialkyl peroxide, peroxide (1,1,4,4-tetramethyl-1,4-butanediyl)bis[(1,1-dimethylethyl) (CAS RN 78-63-7) were also found. These results reported a 96-hour LC_{50} of 4.5 mg/L for the ricefish, *Oryzias latipes* (NITE 2002). Given that these results were obtained for an analogue, they are given a lower weight in the assessment of the aquatic hazard of DMBP.

A range of aquatic toxicity predictions (0.174 to 2.88 mg/L) were also obtained from various QSAR models. However, the modelled values are considered of low reliability as no chemicals of structural comparability to DMBP are contained in their training sets.

It is important to note that the estimated water solubility of DMBP is <1 mg/L (Table 2), so the substance might not be soluble enough in water to cause acute effects. Based on this low solubility and on the results presented in Table 6, DMBP is probably not highly hazardous to aquatic organisms (i.e., acute $LC/EC_{50} > 1.0$ mg/L).

In order to help characterize the ecological risk of DMBP, a predicted no-effects concentration (PNEC) was derived. To do this a Critical Toxicity Value (CTV) of 0.21 mg/L was first chosen. This value is conservative since it is based on the most sensitive organism and since it could likely be higher as no deleterious effects were observed at that concentration. The CTV was then divided by an assessment factor of 100 to account for interspecies and intraspecies variability in sensitivity, to estimate a long-term no-effects concentration from a short-term EC_{50} and to account for uncertainty in laboratory-to-field extrapolation. It is noted that chronic toxicity levels of this substance may be significantly lower than acute toxicity levels due to bioaccumulation. This gives a PNEC of 0.0021 mg/L.

Characterization of Ecological Risk

The approach taken in this ecological screening assessment was to examine various supporting information and develop conclusions based on a weight-of-evidence approach and using the precautionary principle as required under section 76.1 of CEPA 1999. Particular consideration was given to risk quotient analysis, persistence, bioaccumulation, toxicity, sources and fate in the environment.

A mass flow tool was used to estimate the releases of DMBP to the environment at different stages of its life cycle. The results indicate that DMBP is mainly lost by transformation during its use in industrial operations. A low proportion is expected to end up in waste disposal sites, while an even lower proportion (0.1%) could end up in sewers. Based on this analysis, DMBP could reach the environment through effluents from sewage treatment plants. Once released to aquatic ecosystems, DMBP will partition mainly into sediment, while a minor proportion will stay in the water column. Based primarily on experimental evidence such as its rapid break down in an *in vitro* metabolism study and its rapid disappearance in laboratory toxicity studies, DMBP has been determined not to be persistent in water and sediment. However, DMBP has been determined to be bioaccumulative, based on estimated Bioaccumulation Factors (BAFs). Because it is not expected to persist in water, DMBP should not bioaccumulate substantially in organisms if it is released in aquatic ecosystems. In addition, DMBP is probably not highly hazardous to aquatic organisms.

A risk quotient analysis (PEC/PNEC), integrating conservative estimated potential exposure with conservative levels for potential adverse toxic effects, was performed for the aquatic environment in Canada. A PEC of 0.00006 mg/L was estimated. A PNEC of 0.0021 mg/L was calculated, as described above. The resulting risk quotient is (PEC/PNEC) = 0.00006/0.0021 = 0.03. This value indicates that pelagic organisms would not likely be at risk should DMBP be released in aquatic ecosystems.

If DMBP is released into a water body, it will partition to sediments, where sediment-dwelling organisms would be exposed to the substance. Because no environmental monitoring data or toxicity data specific to sediment-dwelling organisms are available, the equilibrium partitioning approach would be used to calculate a sediment PEC and PNEC based on the aquatic compartment values presented above. The risk quotient (PEC/PNEC) for the sediment compartment would therefore be the same as that for the aquatic compartment, 0.03. Again, this would indicate that benthic organisms would not likely be at risk should DMBP be released in aquatic ecosystems.

Uncertainties in Evaluation of Ecological Risk

There remains uncertainty about the persistence of DMBP in water and sediments under environmental conditions. While some tests, namely metabolism and toxicity studies, indicate that DMBP disappears from water quite quickly, some other tests conducted with other types of organoperoxides suggest that these substances are not readily

biodegradable. The tests conducted with DMBP do not all report the presence of degradation products, so it is unclear if the observed disappearance is due to degradation of the substance or to loss to air through volatilization.

There is also some uncertainty about the potential bioconcentration of DMPB as only a single bioconcentration study was available for an analogous substance (CAS# 78-63-7) with limited detail. There is also uncertainty associated with the estimation of metabolism of DMPB in fish as demonstrated by the range of k_M and k_{met}. The uncertainty bounds were, however, used to determine the most reliable rate of metabolism for correction of BAF predictions for conclusion of bioaccumulation potential.

Conclusion

Based on the information presented in this screening assessment, it is concluded that DMBP is not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute or may constitute a danger to the environment on which life depends. Similarly, it is concluded that DMBP meet the criterion for bioaccumulation but not persistence as set out in the *Persistence and Bioaccumulation Regulations* (Canada 2000).

Therefore it is concluded that DMBP does not meet the definition of toxic as set out in paragraph 64(a) of the Canadian Environmental Protection Act, 1999.

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