

ヘキサブロモビフェニルの危険性の概要

分解性	蓄積性	人健康影響	動植物への影響
<p>【生分解性】 分解度 4% (OECD TG 301C)</p> <p>【光分解性】 大気中における分解及び変化は、OHラジカルによる光酸化と光分解である。OHラジカルとの反応による推定半減期は182日。</p> <p>【半減期】 ・水中:2ヵ月を超える ・土壌及び底質中:6ヵ月を超える</p>	<p>【BCF(経口的生物濃縮係数)】 ・ファットヘッドミノール:BCF=18100(32日間暴露) ・ファットヘッドミノールの身:BCF=10000 ・コイ:BCF=4700-16000(重量ベース。60日間暴露)</p> <p>【BMF(経口的生物濃縮係数)】 ・餌(ニシン)と捕食者(ハルトアザラシ)を較べた食物連鎖:BMF=175(脂質ベース)(PCBと同レベルの値) ・ホッキョクグマ中の濃度がグリーンランド東部のワモンアザラシの約100倍</p>	<p>【反復投与毒性】 ラット(混餌7ヶ月):0.45mg/kg/dayで血清中T4濃度低下</p> <p>ラット(混餌30日):LOEL 0.05mg/kg/day 甲状腺ろ胞数・ろ胞容積増加、血清中T3、T4濃度低下</p> <p>アカゲザル(混餌25~50週):LOEL 0.73mg/kg/day 主な毒性は、体重低下、潰瘍性大腸炎、脱毛、肝臓の変化等</p> <p>【発がん性】 マウス(妊娠0日~生後56日): NOAEL 0.15mg/kg/day 児の肝細胞がん IARCグループ2B(possibly carcinogenic to human)</p> <p>【生殖毒性】 ラット(妊娠0日~14日) 28.6mg/kg/dayで未着床、新生児生存率低値</p> <p>アカゲザル:LOEL 0.012mg/kg/day 主な毒性は、月経周期遅延、流産、死産等</p>	<p>【慢性毒性】 ニジマス <i>Oncorhynchus mykiss</i> :ELS 試験 LD50=3.910 mg/kg</p>

		<p>【その他】 汚染事故で吐き気、腹痛、食欲減退、 関節痛、倦怠感、皮膚障害、 EU-Strategy for Endocrine Disruptors 優先化学物質(無処置動物の少なくとも も一種類において内分泌かく乱活性を 示す科学的根拠がある)に分類</p>	
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**Stockholm Convention on Persistent Organic Pollutants
Persistent Organic Pollutants Review Committee
Second meeting
Geneva, 6–10 November 2006**

Report of the Persistent Organic Pollutants Review Committee on the work of its second meeting

Addendum

Risk profile on hexabromobiphenyl

At its second meeting, the Persistent Organic Pollutants Review Committee adopted the risk profile on hexabromobiphenyl, on the basis of the draft contained in document UNEP/POPS/POPRC.2/9. The text of the risk profile, as amended, is provided below. It has not been formally edited.

HEXABROMOBIPHENYL

RISK PROFILE

Adopted by the Persistent Organic Pollutants Review Committee
at its second meeting

November 2006

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EXECUTIVE SUMMARY

The European Community and its Member States being Parties to the Stockholm Convention have proposed hexabromobiphenyl to be listed in the Convention. The Persistent Organic Pollutants Review Committee concluded in its meeting in November 2005 that the substance comply with the screening criteria set out in Annex D of the Convention and that a draft risk profile should be prepared to review the proposal further.

Hexabromobiphenyl belongs to a wider group of polybrominated biphenyls (PBBs). The term "polybrominated biphenyls" or "polybromobiphenyls" refers to a group of brominated hydrocarbons formed by substituting hydrogen with bromine in biphenyl. The hexabromo congeners exist as 42 possible isomeric forms. According to the available data, production and use of hexabromobiphenyl has ceased in most, if not all, countries. However, it is possible that hexabromobiphenyl is still being produced in some countries.

Hexabromobiphenyl has been used as a fire retardant in acrylonitrile-butadiene-styrene (ABS) thermoplastics for constructing business, machine housings and in industrial and electrical products and in polyurethane foam for auto upholstery. A considerable part of the substance produced will probably reach the environment sooner or later because of the high stability of these compounds.

According to available data, hexabromobiphenyl can be considered to be highly persistent in the environment. There is evidence of low or no degradation in water, soil and sediment, in the laboratory as well as in the field.

Hexabromobiphenyl is less volatile than many of the currently listed POP substances. However, extensive data on monitoring shows that it is found throughout the Arctic wildlife, demonstrating that it does have a high potential for long range environmental transport.

With measured weight-based BCF values in the range 4,700-18,100 and biomagnification factors in the aquatic food chain exceeding 100, hexabromobiphenyl is considered to be highly bioaccumulative and to have a high potential for biomagnification. These properties are demonstrated by several authors to be comparable to those of hexachlorobiphenyl (a PCB compound), for which the bioaccumulative properties are well documented.

Hexabromobiphenyl is readily absorbed into the body and accumulates following prolonged exposure. Although the acute toxicity of hexabromobiphenyl is low, a number of chronic toxic effects including hepatotoxicity have been observed in experimental animals at doses around 1 mg/kg bw/day following long-term exposure, and effects are seen in the rat thyroid at doses as low as 0.05 mg/kg bw/day. The International Agency for Research on Cancer has classified hexabromobiphenyl as a possible human carcinogen (IARC group 2B). The PBBs are endocrine disrupting chemicals, and effects are seen on reproductive capacity in rats, mink and monkeys. There is epidemiological evidence of hypothyroidism in workers exposed to polybrominated biphenyls and of increased incidence of breast cancer in exposed women. Data on toxicity to other species than laboratory mammals is scarce but suggests the environmental toxicity of hexabromobiphenyl is comparable to that of hexachlorobiphenyl.

Based on the available data, hexabromobiphenyl is likely, as result of its long-range environmental transport, to lead to significant adverse human health and environmental effects, such that global action is warranted.

1 INTRODUCTION

The European Community and its Member States being Parties to the Stockholm Convention have proposed hexabromobiphenyl to be listed in Annex A to the Convention. The original proposal is contained in document UNEP/POPS/POPRC.1/7.

The acceptance of the original proposal for further consideration by the Persistent Organic Pollutants Review Committee implies that the properties of the substance comply with the screening criteria set out in Annex D of the Convention. Therefore, the screening criteria are not discussed in this document. This draft risk profile has been prepared following the decision of the Committee, at its first meeting in November 2005, to establish an ad hoc working group to review the proposal further.

In this document all data are presented according to the International System of Units (SI) and, therefore, many have been recalculated from other units in the data sources. Furthermore, all concentrations are presented based on kg or L (*e. g.* µg/kg or mL/L).

1.1 Chemical Identity of the proposed substance

1.1.1 Names and registry numbers

Hexabromobiphenyl belongs to a wider group of polybrominated biphenyls (PBBs). The term “polybrominated biphenyls” or “polybromobiphenyls” refers to a group of brominated hydrocarbons formed by substituting hydrogen with bromine in biphenyl. The hexabromo congeners exist as 42 possible isomeric forms, which are listed with CAS and IUPAC numbers in US ATSDR (2004) and in document INF 2.

CAS chemical name: Hexabromo -1,1'-biphenyl

Synonyms: Hexabromobiphenyl
Biphenyl, hexabromo
1,1'- biphenyl, hexabromo -
HBB

Trade names: FireMaster^(R) BP-6
FireMaster^(R) FF-1

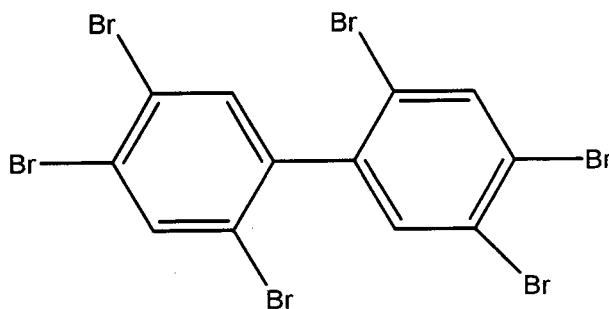
Technical grade PBBs (FireMaster^(R)) contain several PBB compounds, isomers and congeners, hexabromobiphenyl being one of the main components. The composition of FireMaster^(R) BP-6 changes from batch to batch, but its main constituents are 2,2',4,4',5,5'-hexabromobiphenyl (60-80%), and 2,2',3,4,4',5,5'-heptabromobiphenyl (12-25%) together with lower brominated compounds. Mixed bromochlorobiphenyls and polybrominated naphthalenes have also been observed as minor components of FireMaster^(R) (EHC 152 (IPCS, 1994)). FireMaster FF-1 (white powder) is FireMaster BP-6 (brown flakes) to which 2% calcium silicate has been added as an anti-caking agent (EHC 152 (IPCS, 1994)).

Additional data on the composition of identified PBB congeners in FireMaster^(R) BP-6 and FireMaster^(R) FF-1 is given in US ATSDR (2004).

CAS registry number: 36355-01-8¹ (Common CAS number for hexabromobiphenyl isomers)
 59536-65-1 (EHC 192 (IPCS, 1997))²
 67774-32-7 (EHC 192 (IPCS, 1997))³

US ATSDR (2004) provides CAS numbers for a wider number of individual hexabromobiphenyl isomers, as shown in Annex B.

1.1.2 Structure



Structure of 2,2',4,4',5,5'- hexabromobiphenyl (CAS No. 59080-40-9, PBB congener No. 153).
 (Structural formula source: EHC 192 (IPCS, 1997))

1.1.3 Physical chemical properties

The physical and chemical properties of hexabromobiphenyl are listed in Table 1.1.

Table 1.1 Physical and chemical properties of hexabromobiphenyl.

Property	Unit	Value	Reference
Molecular formula'		C ₁₂ H ₄ Br ₆	
Molecular weight'	g/mol	627.58	
Appearance at normal temperature and pressure		White solid	a)
Vapour Pressure	Pa	6.9x10 ⁻⁶ (25° C) 7.5x10 ⁻⁴ (liquid, sub-cooled)	Jacobs <i>et. al.</i> , (1976) ^{a)} Tittlemier <i>et. al.</i> , (2002) ^{a)}
Water solubility	µg/L	11 3	a) Tittlemier <i>et. al.</i> , (2002) ^{a)}
Melting point	°C	72° C	a)
Boiling point		No data	
Log K _{OW}		6.39	Doucette & Andren (1988) ^{a)}
Log K _{OC}		3.33-3.87	Calculated ^{a)}
Henry's Law Constant	Pa m ³ /mol	3.95x10 ⁻¹ 1.40x10 ⁻¹	Waritz <i>et. al.</i> , 1977 ^{a)} Calculated ^{a)}

a): Quoted from US ATSDR, 2004

¹ The CAS registry number 36355-01-8 is given as a generic CAS number for PBBs in the 1988 EU Export-Import Regulation and the UNEP Rotterdam Convention.

² US ATSDR refers to Firemaster^(R) BP-6 as CAS No. 59536-65-1.

³ US ATSDR refers to FireMaster^(R) FF-1 as CAS No. 67774-32-7.

Some of the data for the properties listed in Table 1.1 may not be reliable because products of questionable purity were used by earlier investigators to derive them. Therefore, recent physical and chemical property data that have been reported for hexabromobiphenyl in Tittlemier *et. al.*, (2002) (Quoted from US ATSDR, 2004) are included in Table 1.1.

1.2 Conclusion of the Persistent Organic Pollutants Review Committee on the Annex D information on Hexabromobiphenyl

The POP Review Committee applied at its first meeting on 7–11 November 2005⁴ the screening criteria specified in Annex D to the Stockholm Convention, and decided, in accordance with paragraph 4 (a) of Article 8 of the Convention, that it was satisfied that the screening criteria were fulfilled for hexabromobiphenyl. The Committee decided furthermore, in accordance with paragraph 6 of Article 8 of the Convention and paragraph 29 of decision SC-1/7 of the Conference of the Parties to the Stockholm Convention, to establish an ad hoc working group to review the proposal further and to prepare a draft risk profile in accordance with Annex E to the Convention. It invited, in accordance with paragraph 4 (a) of Article 8 of the Convention, Parties and observers to submit to the Secretariat the information specified in Annex E of the Convention before 27 January 2006.

1.3 Data sources

This Draft Risk Profile is mainly based on information from the following review reports:

- Environmental Health Criteria (EHC) 152: Polybrominated biphenyls. IPCS International Programme on Chemical Safety. United Nations Environment Programme. International Labour Organisation. World Health Organization. Geneva 1994. Available at: <http://www.inchem.org/documents/ehc/ehc/ehc152.htm>.
- Environmental Health Criteria (EHC) 192: Flame Retardants: A General Introduction. IPCS International Programme on Chemical Safety. United Nations Environment Programme. International Labour Organisation. World Health Organization. Geneva 1994. Available at: <http://www.inchem.org/documents/ehc/ehc/ehc192.htm>.
- US ATSDR Toxicological Profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers (PBBs and PBDEs). 2004. Available at: <http://www.atsdr.cdc.gov/toxprofiles/tp68.html>

Where the reviews mentioned above have been cited, the text quoted (or quoted with modifications) includes the references cited in the original review. These references are not shown individually in the reference list.

Following the request of the POP Review Committee for additional information, as specified in Annex E of the Convention, information on hexabromobiphenyl was provided by several Parties and observers. This information was mainly based on the open literature or focused on PBDEs.

A search for more recent information included a literature search via the Danish Technical University Library and the data base FINDit (search terms: HBB, hexabromobiphenyl, brominated biphenyls) as well as a data base search in public data bases. The data bases include “Ecotox” (US-EPA, at <http://www.epa.gov/ecotox/>), “NITE” (Japan, National Institute of Technology and Evaluation at <http://www.safe.nite.go.jp/english/db.html>), BUA Reports at <http://www.gdch.de/taetigkeiten/bua/berichte.htm> and Environmental Fate Data Base at <http://esc.syrres.com/efdb.htm>. This search was based on the search terms: hexabromobiphenyl and CAS numbers 77607091, 36355018, 82865892, 82865905, 59261084, 84303479, 120991482,

⁴ See the meeting report at: www.pops.int/documents/meetings/poprc

82865916, 67888997, 84303480, and 60044260. In addition, the Arctic Monitoring and Assessment Programme⁵ was consulted.

1.4 Status of the chemical under international conventions

Hexabromobiphenyl is listed in Annex A of the Protocol to the Convention on Long-range Transboundary Air Pollution (CLRTAP) on Persistent Organic Pollutants. The provisions of the Protocol oblige Parties (currently 25) to phase out all production and uses of hexabromobiphenyl. Hexabromobiphenyl, together with other PBBs, is also included in the UNEP/FAO Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade.

2 SUMMARY INFORMATION RELEVANT FOR THE RISK PROFILE

2.1 Sources

2.1.1 Production

The commercial production of polybrominated biphenyls (PBBs) generally involves bromination of biphenyl, a process involving a much more specific reaction and producing a smaller number of product mixtures than chlorination (Sundstrom *et al.*, 1976a) (Quoted from US ATSDR, 2004).

The process of manufacturing PBBs consists of a Friedel-Crafts type reaction in which biphenyl is reacted with bromine in the presence of chloride in an organic solvent, using aluminium chloride, aluminium bromide, or iron as catalyst (Brinkman & de Kok, 1980) (Quoted from EHC 152 (IPCS, 1994)).

2.1.2 Trade and stockpiles

The commercial production of PBBs began in 1970. Approximately 6 million kg of PBBs were produced in the United States from 1970 to 1976. Only three commercial PBB products were manufactured (*i. e.* hexabromobiphenyl, octabromobiphenyl, and decabromobiphenyl) and these three products were based on a limited number of congeners (Hardy, 2002b). Hexabromobiphenyl constituted about 5.4 million kg (ca 88%) and octa- and decabromobiphenyl constituted \approx 0.68 million kg together of this total (Neufeld *et al.*, 1977). Michigan Chemical Corporation, St. Louis, Michigan, the sole producer of hexabromobiphenyl in the United States, stopped producing this PBB in 1975. (Quoted from US ATSDR, 2004). Subsequent production of PBBs appears to have been limited to the octa- and decabromobiphenyls.

Production of octa- and decabromobiphenyl continued in the United States until 1979 (IARC 1986; Neufeld *et al.*, 1977). Shortly after the 1973–1974 agriculture contamination accident in Michigan, PBB production in the United States was voluntarily discontinued (Hardy 2000); PBBs are no longer produced in the United States (SRI 2001). Re-initiation of manufacture of PBBs would require approval from the EPA. (Quoted from US ATSDR, 2004)

Two UK companies are reported to have marketed or produced technical-grade decabromobiphenyl in the United Kingdom. In 1977, the production of PBBs in the UK was discontinued. Highly brominated PBBs (Bromkal, 80-9D) were produced in Germany until mid-1985, when the activities concerning bromine-based fire retardants were shifted to the USA. No domestic producer has been identified in the Netherlands. In the early nineties, an Israeli company with two bromine plants in the Netherlands denied the production of PBBs. (Modified from EHC 152 (IPCS, 1994)). There is no information available regarding possible use and production of hexabromobiphenyl in Russia.

⁵ See <http://www.amap.no/>

Until the year 2000, the only PBB in commercial production was decabromobiphenyl, which was manufactured by one company (Atochem) in France (Hardy, 2000). (Modified from US ATSDR, 2004) An author (Darnerud, 2003) has stated that with the closure of the decaBB production in France, the PBB production in the world has ceased.

In the United States, PBBs are not known to be imported or exported anymore except possibly in small quantities for laboratory uses. PBBs have not been imported from other countries into the United States, except in finished products (Neufeld *et al.*, 1977). The two companies that manufactured octa- and decabromobiphenyl in the United States between 1976 (0.805 million pounds) and 1978 exported all of their products to Europe (Neufeld *et al.*, 1977) (Quoted from US ATSDR, 2004).

EXIDIM, the European Database on the Export Import of Dangerous Chemicals under the Rotterdam Convention has registered a total of 6 export applications for PBBs (which do not however include hexabromobiphenyl) in the years 2003–2006 (1 in 2003 and 2004, 2 each in 2005 and 2006). No imports of PBBs to the European Unions are registered in this period.

Information received by 27 January 2006 as a result of the request for information from Stockholm Convention Parties and observers, included response from Brazil, Australia, Japan, Republic of Lebanon and the USA, all stating that there is no production or use of hexabromobiphenyl in these countries.

In summary, according to the information available, production and use of hexabromobiphenyl has ceased in most, if not all, countries. However, it is possible that hexabromobiphenyl is still being produced in some developing countries or in countries with economies in transition.

2.1.3 Uses

In the United States and Canada, hexabromobiphenyl (FireMaster^(R)) was the principal PBB product. It was used as a fire retardant in three main commercial products: acrylonitrile-butadiene-styrene (ABS) thermoplastics for constructing business machine housings and in industrial (e.g. motor housing), and electrical (e.g. radio and TV parts) products: as a fire retardant in coatings and lacquers, and in polyurethane foam for auto upholstery (Neufeld *et al.*, 1977) (Modified from EHC 152 (IPCS, 1994) and US ATSDR, 2004).

Approximately 5 million tonnes of HBB were produced in the USA from 1970 to 1976; 98 per cent was used as FireMaster BP-6 and the rest as FireMaster FF-1 (Hesse and Powers, 1978). Of the estimated 2,200 tonnes hexabromobiphenyl produced in 1974 (IARC, 1978), about 900 tonnes (Mumma & Wallace, 1975; Neufeld *et al.*, 1977; IARC, 1978) were used in ABS plastic products and an even larger amount in cable coatings (Mumma & Wallace, 1975; Neufeld *et al.*, 1977; IARC, 1978). The exact quantity of FireMaster^(R) used in polyurethane foam for automobile upholstery was not published. The two larger consumers ceased using hexabromobiphenyl (one of these in 1972) because PBBs did not decompose in the ultimate incineration of scrapped automobiles (Neufeld *et al.*, 1977) (Quoted from EHC 152 (IPCS, 1994)).

In the EHC 152 (IPCS, 1994), it is stated that at the time, no users of hexabromobiphenyl had been identified (Neufeld *et al.*, 1977; Di Carlo *et al.*, 1978; Brinkman & de Kok, 1980) (Quoted from EHC 152 (IPCS, 1994)).

2.1.4 Releases to the environment

Data for loss into the environment during normal production are published only for the United States. The following information refers to reviews by Neufeld *et al.*, (1977) and Di Carlo *et al.* (1978). Losses of PBBs to the environment at sites of its manufacture can amount to 51 kg/1000 kg of product. These losses occur through:

1) *Emission into the air:*

In 1977, the maximum air losses as particulate matter at production sites were estimated to total 1.1 kg of PBBs/1000 kg manufactured.

2) *Losses in waste waters* resulting from the quenching and washing of the PBBs as they were recovered from the reaction mass. The losses of PBBs to sewers at manufacturing sites were estimated, in 1977, to be 4.6 µg/kg of product.3) *Solid losses to landfills* resulting from drying, handling, shipping and transportation. An estimate of PBB losses as solid waste to landfills was 50 g/kg of product.4) *Losses to the soil*

Soil samples from the bagging and loading areas of the Michigan Chemical Corp. contained PBBs at concentrations of 3500 and 2500 mg/kg, respectively.

(Abbreviated from EHC 152 (IPCS, 1994))

In 1973, an accidental release of PBBs occurred in Michigan (referred to as the "Michigan disaster" in EHC 152), when two products manufactured by the Michigan Chemical Company were inadvertently confused and 250-500 kg (Di Carlo *et al.*, 1978) of FireMaster^(R), instead of NutriMaster^(R), a magnesium oxide-based cattle feed supplement, were added to animal feed and distributed to farms within the state. The compound is believed to have been FireMaster^(R) FF-1 (*e. g.*, Fries, 1985b), even if in some publications the name FireMaster^(R) BP-6 is used (*e. g.*, Neufeld *et al.*, 1977; Di Carlo *et al.*, 1978). This accidental mix up resulted in widespread contamination by PBBs. Chronological reports or reviews of the PBB disaster are given by Carter (1976), Getty *et al.* (1977), Kay (1977), Di Carlo *et al.*, (1978), Damstra *et al.*, (1982), Zabik (1982), and Fries (1985b) (Quoted from EHC 152 (IPCS, 1994)).

Approximately 5350 tonnes of hexabromobiphenyl were used in commercial and consumer products in the United States, most in the production of plastic products with an estimated use life of 5–10 years (Neufeld *et al.*, 1977). Since the cessation of production, all of these products, such as TV cabinet and business machine housings, are expected to have been disposed of by land filling or incineration (Neufeld *et al.*, 1977) (Quoted from US ATSDR, 2004).

Hexabromobiphenyl can enter the environment from the widespread use of flame-retarded products. A considerable part of the substance produced will probably reach the environment sooner or later because of the high stability of these compounds. Furthermore, some of these chemicals may form toxic polybrominated dibenzofurans during combustion processes.

2.2 Environmental fate

2.2.1 Persistence

The EHC review (1994), concludes that polybrominated biphenyls are stable and persistent in the environment. The degradation of PBBs by purely abiotic chemical reactions (excluding photochemical reactions) is considered unlikely.

In air, the two processes that may result in significant degradation or transformation of PBBs are photo-oxidation by hydroxyl (OH) radicals and direct photolysis. Based on a structure-activity relationship for the estimation of half-lives for the gas phase reactions of hydroxyl radicals with organic compounds (Atkinson 1987b), the estimated half-life of hexabromobiphenyl due to reaction with OH radicals is 182 days. The importance of the photochemical reaction under sunlight illumination conditions for the degradation/transformation of PBBs in air cannot be evaluated due to the lack of information. (Abbreviated from US ATSDR, 2004)