ENVIRONMENT
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PRIORITISATION OF FLAME RETARDANTS FOR ENVIRONMENTAL RISK ASSESSMENT

P R Fisk, A E Girling and R J Wildey

Research Contractor:

Peter Fisk Associates

It is not the intention of this report to imply that any particular substance should or should not be used for any particular purpose. It is the aim of this report to evaluate concerns in respect of a wide range of different substances. This report should only be used as a tool to assist in identifying priorities for environmental risk assessment. It should not be used in isolation to assess whether any particular substance should be used for any particular purpose.

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Statement of Use
This report summarises the environmental issues surrounding the use of flame retardant chemicals. It prioritises these on the basis of tonnage, hazardous properties and approximate risk ‘ranking’. The information will help regulatory authorities develop future assessment and monitoring priorities, and guide wider recommendations for policy on flame retardants.

Keywords
Flame retardant, brominated flame retardant, organophosphate, PBDE, polybromodiphenyl ether, PBT, persistence, bioaccumulation, toxicity, substitution, hazard, risk

Research Contractor
Peter Fisk Associates, 9 St Swithin’s Road, Whitstable, Kent CT5 2HT

Fax: +44 (0)1227 779 166

Environment Agency’s Project Manager

S M Dungey
Environment Agency, Chemicals Assessment Section
Isis House, Howbery Park, Wallingford OX10 8BD

Fax: +44 (0)1491 828556
http://www.environment-agency.gov.uk/

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EXECUTIVE SUMMARY

The aim of this study was to present an overview of the use of flame-retardant substances in the UK and, in particular, to identify substances that might require detailed consideration in terms of their possible impact on the environment. We have given particular consideration to brominated flame retardants, because these are currently receiving attention in a number of countries. This report does not consider the human health benefits or risks of such substances.

An earlier report on this topic, produced in 2001, was circulated electronically by the Agency to Industry and regulatory contacts. Industry responded with considerable amounts of new information. This report updates and broadens the scope of that original report. It also includes new information. It is a stand-alone document, and contains most of the technical work performed in the first study. A confidential Project Record provides some further detail.

The researchers have assessed publicly available data and sought information from regulatory authorities and Industry. We approached companies and trade associations at the producer end of the supply chain as well as the users of flame retardants, to get a picture of the whole market. The level of industry input has been fairly high, and a list of industry respondents is included.

We have placed our findings in a broad context, so that the use of these substances is clearly understood. Many flame-retardant substances are available on the market, but the range of substrates is wide, as is the range of applications. We summarise the uses, mechanisms of action and environmental regulation of flame retardants, and we consider the routes by which they may enter the environment. We also summarise issues concerning substitution of flame retardants, since this is not a straightforward activity. We note, too, the current growth in the use of inorganic flame retardants.

As a result of this project, the main resources now available are:

- An Access database of more than 300 substances, summarising all the data (including a large number of predictions to fill gaps) obtained on:
  - physicochemical properties (such as water solubility, vapour pressure and octanol-water partition coefficient, which are used in models of environmental fate and behaviour);
  - toxicity to aquatic and terrestrial organisms (including some mammalian toxicity data);
  - distribution and degradation in the environment;
  - tonnage and information on suppliers and application (some of this is reported only in a confidential version of the database).

  The Project Database is available from the Project Manager on request.
- An overview of the market for flame retardants, with summaries of major industry sectors.

From these data, priority lists of substances for possible further study have been drawn up, based on:

- tonnage on the EU market;
- hazard, including persistence, bioaccumulation and toxicity (PBT) properties;
- risk, based firstly on a simple generic exposure model, and secondly as the tonnage on the market that could give rise to a concern (the ‘critical tonnage’).

Reliable UK tonnage data could not be obtained in many cases, and many data gaps exist. Although a lot of substances were included in the investigations, it is clear that many are no longer used in any significant amounts, although confirmation of this has been difficult.

The experience of European regulatory bodies with assessments carried out under the Existing Substances Regulation (ESR, EC no. 793/93) shows that a detailed investigation of the life cycle and properties of a substance is needed before firm conclusions about it can be drawn. The ESR risk assessments already carried out on flame retardants have reached a variety of conclusions, but it is clear that some of these substances may pose significant risks to the environment. Some flame retardants (as yet not studied in detail) have indications of potential concern at the screening level comparable with substances that are now subject to regulatory controls. These could become priorities for further detailed analysis.

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Appendix 11: Locations of flame retardant production and use in England and Wales contains confidential data, and so access is restricted to government regulatory authorities only. It is available on request from the Project Manager as a separate document.

1. PURPOSE AND BACKGROUND

1.1 Aims and objectives of this project

Flame retardants play an important role in safeguarding life and property. Their application is a growing chemical sector, especially in the UK and Ireland. The properties of some flame retardants (such as persistence) and their diffuse exposure patterns have flagged concern about the possible general environmental effects of this group of substances. The Environment Agency therefore wanted a screen of all flame retardants known to be on the UK market, to help inform future assessment and monitoring priorities and wider recommendations for policy on flame retardants. The chief objectives were to:

1. Identify the substances commercially available for use as flame retardants.
2. Obtain and summarise, for each substance identified, the use pattern (i.e. the scale of supply, typical applications, and trends), and properties affecting environmental fate and ecotoxicity (including data on persistence, bioaccumulation and toxicity (PBT)). Where no measured data have been located, the gap has, where possible, been filled by an estimate.
3. Collate the information obtained in the form of an Access database (referred to hereafter as the Project Database).
4. Assess the information obtained and make recommendations about the general issues affecting the Agency and hazard/risk assessment in particular.

The Project Database is available separately from the Project Manager on request. In addition to substance-specific information, the review also considers general issues surrounding flame retardant substitution and the disposal/recycling of waste containing flame retardant substances.

The overall result is a readily retrievable data set for each substance, and a set of recommendations for future investigation. It is important to note that we have not reviewed original test reports or attempted to validate data. The data set associated with this project must be considered as a screening data set only, though the most reliable sources have been consulted wherever possible. While we have made every effort to make the database as complete as possible, it is inevitable that, in some cases, more detailed information will be found in company archives, which could not be provided during the timescale of the project.

1.2 Background

1.2.1 Why are flame retardants important?

Technological developments during the last century have led to the use of synthetic carbon-based polymers[1] for everyday household and office items (e.g. furniture, fabrics, automotive parts, housings for electronic equipment and surface coatings for other materials) where wood or metal might once have been used. The high fuel values of these materials means that their very presence could pose a danger, particularly in instances where a high risk of ignition is

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[1] In this context ‘polymer’ includes cellulose-derived materials.

associated with the item's use. There is a considerable amount of legislation setting down fire safety requirements for household and electrical equipment, furnishings and vehicles. The achievement of the required fire safety standard (see Box 1) often requires the use of some form of flame retardancy in the components. The term 'flame retardant' is not equivalent to 'fire-proof', and should not be taken to mean that a flame retarded product is non-flammable. The material is likely to char or melt in the presence of flame. It simply indicates that the product has been modified in such a way as to inhibit ignition and reduce the rate of burning, as determined by standard tests.

Box 1 Fire safety standards

A large set of British Standards exist relating to flame retardancy of products. Fire safety standards are also produced by the European Committee for Standardisation (CEN), and the American Society for Testing and Materials (ASTM). Compliance is determined by performance of flame-retarded products in specially designed standard tests to assess factors such as ignition, the rate and temperature of burn, and the by-products released during combustion.

Underwriters Laboratories Inc., an independent product safety testing and certification organisation, has also developed generic standard test methods for plastics (UL94), which are widely applied in this industry. The performance in vertical and horizontal burn tests is assessed and the product classified accordingly (V0-2; if the vertical test is not passed, HB; if the horizontal test is not passed, not classified) and the highest rating is V0.

Types of fire safety standards vary for different applications. One particularly important area is electrical and electronic equipment (EEE), e.g. in equipment housings. The EU fire safety standard for IT appliances, EN 60950, covers different approaches for achieving fire safety in EEE, including the use of flame retardants. Classification V0 in UL94 is typically required for monitor housings, while television sets in the EU often meet only UL94-HB, though some companies are increasing the level of fire safety of such products *(UBA, 2001 and Troitszch, 1998 from DEFRA, 2002b)*.

Criteria for refrigerators and washing machines have been published under the EC eco-labelling scheme, which included a ban on halogenated flame retardants in plastic parts weighing more than 25 grams. These restrictions add to those already established under the same scheme, where criteria limiting use of brominated flame retardants in textile products (including clothing and interior fabrics but not floor coverings), bed mattresses and PC parts have been set.

Motor vehicles are subject to legislative requirements for fire safety through Directive 95/28/EC. Standard methods for assessing horizontal and vertical burn and melting are set out in Annexes IV – VI to the Directive. International Standard ISO 3795 also applies to determination of burning behaviour of materials for road and other vehicles.

Public transport vehicles in the UK are required to conform to the standards set down in BS 6853 "Code of practice for fire precautions in the design and construction of passenger carrying trains".

The German and Nordic national standards organisations have recently set ecolabelling standards whereby equipment (such as household and office electronics housings) cannot be labelled as environmentally friendly if it contains specified chemicals, including certain brominated flame retardants. A Swedish office workers' union scheme (TCO) has also set criteria for labelling office electronic equipment and parts.

For some types of product, the existence of legislative requirements and level of fire safety performance required may vary between countries. For example, the UK requirements for flame retardancy of household furniture is strict[2], while in some parts of the EU, similar fire safety is not necessarily required by law. Legislation has been the driving force behind the use of flame retardants in recent years.

1.2.2 Environmental issues surrounding flame retardants

Flame retardant chemicals are present in various products in homes and businesses throughout Europe (though there are some regional variations in requirements, as noted above). This means they have a very widely dispersed pattern of use. Some types of flame retardant can be lost through abrasion, leaching or volatilisation. While these processes may be very slow, an article's service life can be very long, and so these losses may be significant. A recent Greenpeace study identified a number of flame retardants in household dust (*Santillo et al, 2003*), and so this release route is real. Disposal via landfill or recycling can also lead to further emissions. So flame retardants have a potential for widespread environmental exposure. They are also inherently stable (flame retardants are intended to exist in the treated article for its whole lifetime). Some of them can also accumulate in wildlife. Together, these characteristics mean that there is a high level of concern about some flame retardants, particularly organohalogen compounds. Modelling these processes is not straightforward.

Burning products containing halogenated flame retardants can also release toxic by-products. Particular attention has been drawn to the production of polybrominated dibenzofurans (PBDF) and polybrominated dibenzo-*p*-dioxins (PBDD), which can be formed during high temperature processing (e.g. as part of production or recycling) as well as during combustion.

1.2.3 Summary of relevant international regulatory activity

The Environment Agency is responsible for technical environmental aspects of the notification scheme for new substances[3] in the UK. The regulations apply to substances that are new to the European market. They require the pre-supply submission of a basic data set from the producing or importing company, dependent on the intended supply tonnage. Once successfully notified, the substance can be supplied anywhere in the European Union, though a risk assessment might indicate the need for further data provision. Around 20 new substances have flame retardant uses. While no flame retardant has been subject to formal regulatory controls as a result of the regulations, some have been withdrawn from the market for a number of reasons. Others have been subject to voluntary control measures as a result of the risk assessment. Where notifiers have given permission, we have included details in the project database. There are several substances for which permission was not given.

Several substances used as flame retardants have been identified as priorities for comprehensive risk assessment under the Existing Substances Regulation (ESR, EC no. 793/93). The ESR covers those chemicals that have been on the European market for a long time, and focuses in particular on those with a high supply tonnage. The status of the various assessments is indicated in Table 1.1. To date, environmental risk management has been or is

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[2] Specific British Standard tests must be passed in accordance with The Furniture and Furnishings (Fire) (Safety) Regulations 1988 (SI 1988 no 1324)

[3] Notification of New Substances Regulations 1993 SI 1993 no. 3050

being investigated for the brominated diphenyl ethers and chlorinated paraffins. A large amount of new testing has been required to complete many of the assessments.

Table 1.2 Flame retardants[4] under ESR risk assessment

Substance	CAS No.[5]	Rapporteur	Status	Ref no.
Hexachlorocyclopentadiene*	77-47-4	Netherlands	Draft circulated	
Tetrabromobisphenol-A	79-94-7	UK	Draft circulated	
Decabromodiphenyl ether	1163-19-5	UK/France	Published	13
Pentabromodiphenyl ether	32534-81-9	UK	Published	11
Octabromodiphenyl ether	32536-52-0	UK/France	Published	12
Hexabromocyclododecane	25637-99-4	Sweden	Draft circulated	14
Short-chain chlorinated paraffins	85535-84-8	UK	Published	9
Medium-chain chlorinated paraffins	85535-85-9	UK	Draft circulated	10
Zinc oxide	1314-13-2	Netherlands	Draft circulated	
Zinc chloride	7646-85-7	Netherlands	Draft circulated	
Antimony trioxide	1309-64-4	Sweden	Awaiting first draft	
Tris(2-chloroethyl) phosphate	115-96-8	Germany	Draft circulated	15
Tris(2-chloroisopropyl) phosphate	13674-84-5	Eire/UK	Draft circulated	
Tris(1,3-dichloroisopropyl)phosphate	13674-87-8	Eire/UK	Draft circulated	
2,2-Bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate)	38051-10-4	Eire/UK	Draft circulated	
Boric acid	11113-50-1	Austria	Awaiting first draft	

*May only be an intermediate in the production of flame retardants.

In addition, the Environment Agency is conducting in-depth environmental risk assessments for long-chain chlorinated paraffins (LCCPs) and several aryl phosphates based on a national initiative. Other regulatory authorities have identified flame retardants as particular targets for their own national research work. For example, the Danish Environmental Protection Authority has published a project reviewing the market, uses and properties of brominated flame retardants *(Danish EPA, 1999)*. The Swedish National Chemicals Inspectorate (KemI) has also reported on the flame retardants market *(KemI, 1996)*, including a further report recommending the phase-out of two brominated flame retardants in particular *(KemI, 1999)*. The German Umweltbundesamt has produced a three-volume report setting out data and assessing hazard for a number of flame retardants *(UBA, 2001)*. The Dutch Ministry of Housing, Spatial Planning and the Environment recently proposed a ban on the use of tetrabromobisphenol-A bis(2,3-dibromopropyl ether) (FR-720™). The Australian National Industrial Chemicals Notification and Assessment Scheme (NICNAS) has also produced a review of polybrominated flame retardants.

Various flame-retardant substances and degradation products have been identified as presenting a particular hazard or risk. As a result, their use has been banned or emission controls have been imposed at a European level. For example:

- Penta- and octabromodiphenyl ethers are subject to limitations on their marketing and use in accordance with the outcomes of ESR assessments;

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[4] Some of these substances have uses other than as flame retardants.

[5] Chemical Abstracts Service – the CAS number is a generally recognised identification reference for a chemical. It is possible that a substance can have more than one such number.

- Tris(2,3-dibromopropyl) phosphate (CAS No. 126-72-7), previously used in textiles and garments, was prohibited by Directive 79/663/EEC;

- Council Regulation No. 259/93/EEC on the supervision and control of shipments of waste within, into and out of the European Community contains a 'red list' of wastes. This includes those containing polychlorinated biphenyl (PCB), polychlorinated terphenyl (PCT) and polybrominated biphenyl (PBB), including any other polybrominated analogues of these compounds, at a concentration level of 50 mg/kg or more. In addition, polybrominated biphenyls (PBB) should not be employed in textile articles that come into contact with the skin;

- Implementation of the forthcoming Waste Electrical and Electronic Equipment (WEEE) Directive and its associated Directive on the restrictions of hazardous substances in connection with these products is likely to restrict use of some flame retardants. These are used in applications such as household and office electronics housings (e.g. computer hardware housings, television sets, etc.);

- Some flame-retardant substances have the potential to deplete stratospheric ozone. They are controlled under the Montreal Protocol (implemented in the EU by EC Regulation 3093/94);

- In 2013, the Water Framework Directive (2000/60/EC) will supersede the Water Resources Act 1991. Within its priority list of hazardous substances, the Directive includes two classes of substances that function as flame retardants:
  - Brominated diphenylethers;
  - C_{10-13} chloroalkanes (short-chain chlorinated paraffins).

  Releases of these substances to the environment will be regulated from a water quality perspective.

The UK is committed to the declaration from the Fourth North Sea Conference. This devotes special attention to substituting certain brominated flame retardants with less hazardous substances. Some polybrominated flame retardants have been identified by OSPAR[6] as priority substances in terms of reducing emissions to the North Sea and neighbouring waters.

The International Council of Chemical Associations (ICCA) voluntary programme on high production volume (HPV) chemicals is not a regulatory system as such. It does, though, generate significant information for chemicals in the form of an agreed basic set of hazard data under the auspices of the Organisation for Economic Co-operation and Development (OECD). The Project Database presents the status of relevant flame retardants associated with the various HPV programs, including lead countries or companies as applicable.

Non-regulatory organisations have also been active in research into the use of flame retardants. Greenpeace, for example, has published a monitoring study into levels of hazardous substances in PVC flooring, including various flame retardants *(Greenpeace, 2001).*

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[6] The OSPAR commission for the protection of the marine environment of the north-east Atlantic. The OSPAR Convention (so called because it succeeds the Oslo and Paris Conventions) entered into force in March 1998.

2. GENERAL INFORMATION ON FLAME RETARDANTS

2.1 Additive and reactive flame retardants

A polymer chain can, to a certain extent, be made more stable – and therefore less flammable – by the careful selection of the monomers from which it is constructed. Ring-structures and ionisable side-groups, for example, are relatively resistant to burning *(Wiley, ca. 1991)*. This is not always technically desirable. In general, the base polymer itself must be modified to introduce flame retardant properties. There are three main ways of doing this:

- Use of **additive flame retardants**[7]. Flame-retardant substances are dispersed in the final polymer product, but they do not bind chemically to the polymer chain. These are usually used with thermoplastics. They may be lost during the lifetime of the treated product (when washed, for example). Flame retardancy properties can therefore diminish over time.
- Use of **reactive flame retardants**. These are flame retardant monomers that can be co-polymerised with other monomers. They are chemically bound within the polymer structure, and so losses during the lifetime of the product are limited. Reactive flame retardants are usually used with thermosetting polymers.
- Reaction of the polymer chain, once formed, to render it flame retardant (e.g. perchlorination of a hydrocarbon polymer chain or bromination of polystyrene).

The first two approaches are the more common. To be effective, a significant level of the flame-retardant active substance may need to be present (10-20 per cent by weight is not unusual, though for some systems a far lower loading, e.g. <1 per cent by weight, is effective). The appearance and chemical, physical and mechanical properties of the polymer may be affected. Some flame retardants are more compatible with particular polymer types or applications of the final product than others.

The life cycle of a reactive flame retardant differs from an additive flame retardant in that it will not be as readily released from the polymer. It is therefore less likely to be very widely distributed in the environment. The timescale of release of either type of flame retardant is likely to be long-term.

2.2 Modes of action

A flame retardant may inhibit ignition, prevent combustion by altering the nature of the polymer in the vicinity of the flame, or extinguish the flame. *Vapour-phase* flame retardants act by interfering with free radical mechanisms, or simply reducing the availability of flammable gases and oxygen. *Condensed-phase* flame retardants are active in the molten polymer in the vicinity of the flame, interfering with the thermal degradation processes. *Intumescent* systems, often used in flame retarded coatings, puff up in the presence of flame and produce charrable foams, which have low thermal conductivity *(Wiley, ca. 1991)*.

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[7] Flame retardants may also confer other properties on polymers, such as being plasticisers. Substances which are mainly used for their plasticising properties but which have some flame-retardant properties are included in this project.

Five specific modes of action have been identified:

- gas dilution – use of additives which decompose into non-flammable gases. This reduces both fuel and oxygen levels in the vicinity of the flame (metal hydroxides, metal salts, and some nitrogen compounds);
- thermal quenching – flame retardants which undergo endothermic decomposition, reducing the rate of burning (metal hydroxides, metal salts, and some nitrogen compounds);
- protective coating – additives which promote charring or the formation of a liquid barrier, thus shielding the flammable material from the flame (phosphorus compounds, intumescent systems based on nitrogen or phosphorus compounds);
- physical dilution of the flammable material – introduction of an inert non-flammable component (e.g. glass or minerals);
- chemical interaction – a flame retardant that decomposes into radical species, which compete effectively with the burning process (halogenated compounds).

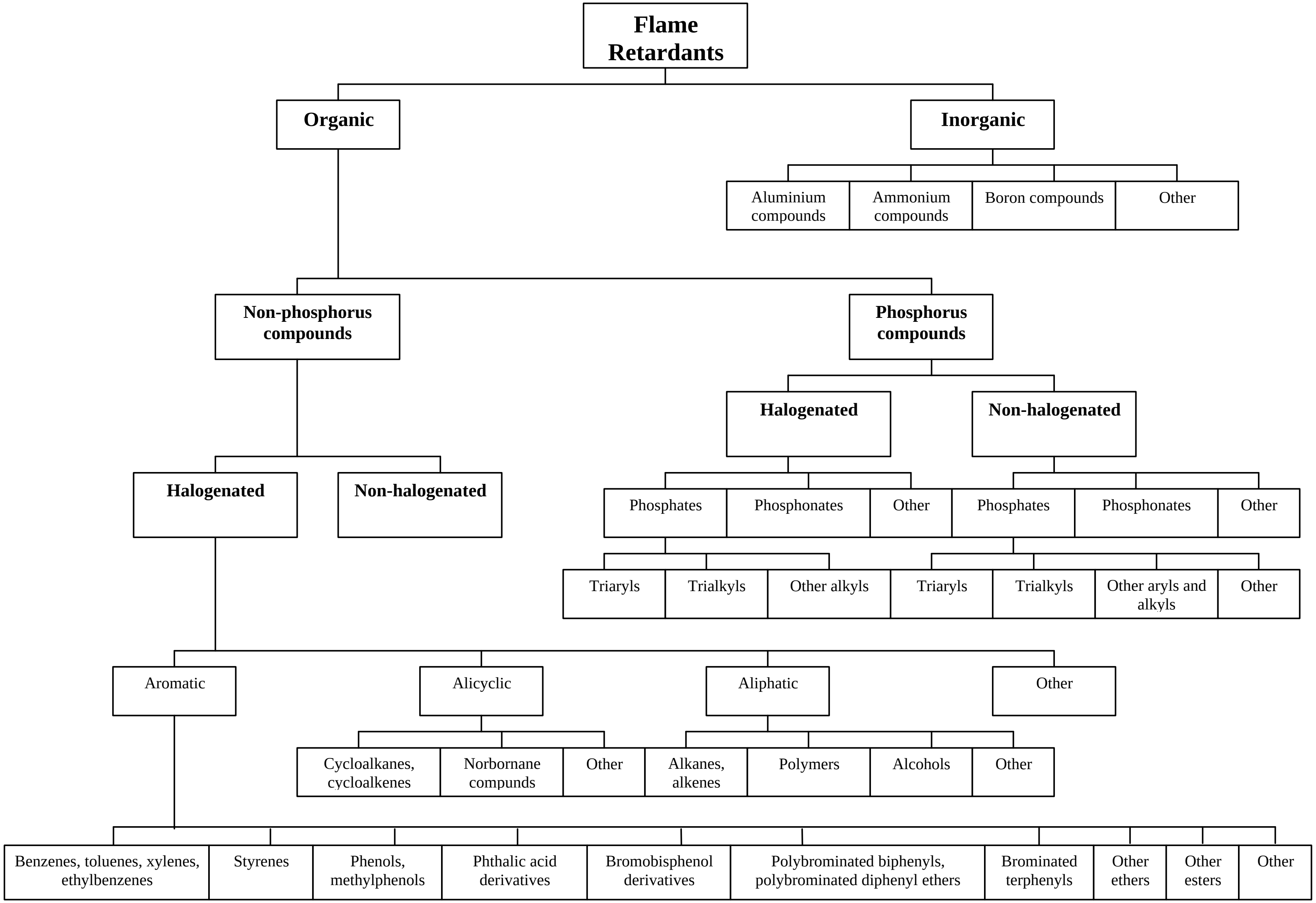
2.3 Chemical categories of flame retardant

Previous reviewers have categorised the chemistry of flame retardant substances in a number of different ways. For the purposes of this project six generic categories have been identified:

1. Inorganic
2. Brominated organic
3. Chlorinated organic
4. Organophosphorus (mainly phosphate esters)
5. Halogenated organophosphorus (chlorinated and brominated, mainly phosphate esters)
6. Nitrogen-based

There are some substances in the Project Database to which none of these categories apply. Figure 2.1 overleaf shows a more comprehensive breakdown of the substance types.

Fig 2.1 Breakdown of flame retardant chemical types (adapted from *KemI, 1996*)



2.3.1 Inorganic flame retardants

Most inorganic flame retardants act in the condensed phase. They do so in various ways. Most decompose endothermically, releasing water of hydration and/or carbon dioxide, both of which inhibit burning. Some flame heat is absorbed in such reactions. The residue conducts heat away from the area, contributing further to the extinction of the flame. Many flame retardants act as smoke suppressants and also promote char. All have a dilution effect.

Metal compounds

Antimony compounds and metal hydroxides have the highest rate of consumption of the inorganics in this sector.

Metal hydroxides, such as aluminium trihydroxide and magnesium hydroxide, decompose in the heat of the flame and release water of hydration. Such substances also act as smoke suppressants. These flame retardants may be used as secondary additives to flame retarded polymer systems in which other flame retardants are present (e.g. antimony trioxide, zinc borate, phosphorus-based).

Antimony oxides and sodium antimonate provide a pigment as well as flame retardancy. Antimony compounds can be used in a variety of plastics. They are particularly effective when used in cellulosic polymers, due to the reaction with the hydroxyl groups present in these polymers. Antimony-silicon compounds are sometimes used, though these are less effective than antimony trioxide. Antimony compounds are not flame retardant in their own right. Instead, they act as synergists with organohalogens. Antimony trioxide is usually used in conjunction with heat-labile halogenated compounds. In the heat of the flame, antimony trihalide is formed. This acts in the flame phase, modifying the reactions of the polymer in the flame such that less energy is released. They create a seal by causing the molten polymer in the vicinity of the flame to char rather than releasing reactive and flammable gases.

Some other metal compounds, particularly zinc and zinc/tin compounds act synergistically with halogenated hydrocarbons. Synergistic action means that a smaller quantity of additives is needed to provide the same level of protection.

Molybdenum oxide is used as a flame retardant, particularly for cellulosics. It probably promotes charring. Ammonium octamolybdate is used as a flame retardant for PVC. Titanium and zirconium compounds are used as flame retardants for textiles, particularly wool.

Boron compounds

Boric acid and sodium borate are frequently used in cellulosics (especially cotton and paper) where the presence of hydroxyl groups contributes to the effectiveness of these flame retardants. In the first instance, the compounds melt in the heat of the flame and form a glasslike coating. Continued exposure to the heat causes water to be released, which cools the flame. Finally, an inorganic char is produced. This dilutes and protects the flammable material.

Zinc borate is frequently used to flame retard PVC; hydrogen chloride released in the presence of flame reacts with the zinc borate producing non-volatile products (which promote char), and water.

Ammonium fluoroborate and zinc borate are frequently used in conjunction with antimony trioxide. Again, flame retardancy is thought to arise through release of water and formation of inorganic char in the presence of a flame.

Other inorganics

Phosphorus-containing compounds act by promoting the dehydration of the polymer in the presence of a flame and increasing the level of charring. Inorganic phosphates are used in cellulosic textiles. Phosphoric acid itself has been used to treat cellulosics. Ammonium polyphosphates of varying chain lengths are used in many applications, particularly in coatings, paints and intumescent applications. Other flame retardants are frequently used in conjunction with them.

Elemental phosphorus exists in several allotropic forms. The red form is used as a flame retardant in plastics, commonly polyamides.

2.3.2 Organohalogens

Three general classes of organohalogen flame retardant may be identified: aromatic, aliphatic and cycloaliphatic. The halogen is either chlorine or bromine. Fluorinated compounds are expensive and generally not effective; iodinated compounds are effective but unstable and are therefore not used. A wide variety of organohalogens are used as additives or reactive flame retardants, and a few can be used as either, depending upon the application.

Incorporation of phosphorus compounds along with halogenated flame retardants further inhibits ignition. This effect is also achieved if the phosphorus and halogen are present in the same molecule. The effect can sometimes be synergistic.

Brominated organics

These are frequently used in ‘brown’ goods such as television sets, computer hardware housings and monitors, etc. Since brominated aromatics have the highest level of thermal stability, these tend to be the most widely used. Typical examples are:

- tetrabromobisphenol-A (TBBPA), used as an additive and reactive flame retardant in various plastics applications;
- decabromodiphenyl ether (DeBDE), used as an additive flame retardant in a range of plastics and textiles.

An example of a brominated cycloaliphatic flame retardant is hexabromocyclododecane (HBCD), used in polystyrene foams and textile applications.

The effectiveness of this category of flame retardants may be connected with the Br· radical. This competes effectively with hydroxyl radical HO· and the oxygen atom ·O· for the substrate in the vapour phase, and extinguishes the flame. An alternative theory is that bromine affects the physical properties of the polymer, including heat capacity.

In recent years, a number of countries and environmental groups have focused their attention on brominated flame retardants. It is appropriate, therefore, to list those substances known or believed to be on the UK market now. These are listed in Table 2.1 (it is not necessarily an exhaustive list). It is immediately apparent that a large variety of chemical structures are involved. Industry representatives (EBFRIP, the European Brominated Flame Retardants

Industry Panel) report that about 75 different brominated flame retardants are currently in significant commercial use. This implies that many of the substances listed in Table 2.1 are either historical or have never really been used as flame retardants. Some substances are considered by Industry to be 'end-cappers', that is, used to terminate polymerisation reactions. We have, however, included them here, since there could be problems of definition, for example compared to reactive flame retardants.

Table 2.1 Brominated flame retardants that could be on the UK market

CAS no.	Name	Used as additive flame retardant	Used as reactive flame retardant
-	1,4-Bis(bromomethyl)-tetrabromobenzene	No information	No information
-	Bis(tetrabromophenoxy) ethane	No information	No information
-	Brominated epoxy – endcapped	No information	Yes
-	Brominated epoxy - partially endcapped	No information	Yes
-	Bromine compound containing LDPE masterbatch	No information	No information
-	Epoxy resin (brominated)	No information	Yes
-	Octabromotriethylphenyl indane	No information	No information
-	Pentabromophenylbenzoate	No information	No information
-	Poly(dibromostyrene) grafted poly(propylene)	No information	No information
-	Proprietary blend pentabromodiphenyl oxide	Yes	No information
-	Tetrabromo-2,3-dimethylbutane	No information	No information
-	Tetrabromobenzoate	No information	No information
-	Tribromochlorobisphenol-A	No information	No information
-	Tetrabromophthalate ester	No information	No information
-	Tribromoneopentyl phenol	No information	Yes
-	Tribromoneopentyl phenyl allyl ether	No information	Yes
-	Tribromoneopentyl phenyl maleimide	No information	Yes
-	Tribromophenol allyl ether (likely to be a misnomer for tribromophenyl allyl ether)	No information	Yes
-	Trichloromethyltetrabromobenzene	No information	No information
-	Tris(tribromophenyl)cyanurate	No information	No information
-	CONFIDENTIAL	No information	No information
-	Tetrabromobisphenol-A epoxy oligomer	No information	No information
-	2,2'-dimethyl-3-bromo-propanoic acid, isopropyl ester	No information	No information
-	Tetrabromophthalic acid, diethylhexyl ester	Yes	No information
75-95-6	Pentabromoethane	Yes	No information
79-27-6	1,1,2,2-Tetrabromoethane	No information	No information
79-28-7	Tetrabromoethylene	Yes	No information
79-94-7	Tetrabromobisphenol-A	Yes	Yes
85-22-3	Pentabromoethylbenzene	Yes	No information
87-82-1	Hexabromobenzene	No information	No information
87-83-2	Pentabromotoluene	No information	No information
87-84-3	Pentabromochlorocyclohexane	No information	No information
93-52-7	Benzene, (1,2-dibromoethyl)-	No information	No information
96-13-9	2,3-Dibromopropanol	No information	Yes
118-79-6	2,4,6-Tribromophenol	No information	Yes
124-73-2	Dibromotetrafluoroethane	No information	No information
126-72-7	Tris(2,3-dibromopropyl)phosphate	Yes	Yes
593-60-2	Vinyl bromide	No information	Yes
598-72-1	2-Bromopropanoic acid	No information	No information
608-71-9	Pentabromophenol	No information	Yes
615-58-7	2,4-Dibromophenol	No information	Yes
632-79-1	Tetrabromophthalic anhydride	No information	Yes

CAS no.	Name	Used as additive flame retardant	Used as reactive flame retardant
1163-19-5	Decabromodiphenyl ether	Yes	No information
1470-82-0	2,4,6-Tribromoaniline	No information	No information
1837-91-8	Hexabromocyclohexane	No information	No information
1960-16-3	Dibromopropyl acrylate	No information	No information
2623-87-2	4-Bromobutanoic acid	No information	No information
3066-70-4	2,3-Dibromopropylmethacrylate	No information	No information
3072-84-2	Epoxy resin, brominated	No information	No information
3194-57-8	Tetrabromocyclooctane	No information	No information
3234-02-4	2,3-Dibromo-2-butene-1,4-diol	No information	Yes
3278-89-5	Tribromophenylallyl ether	No information	Yes
3296-90-0	Dibromoneopentyl glycol	No information	Yes
3322-93-8	1,2-Dibromo-4-(1,1-dibromomethyl)cyclohexane	No information	No information
3555-11-1	1-Pentabromophenoxy-2-propene	No information	No information
4162-45-2	Tetrabromobisphenol-A-bis-(2-hydroxyethylether)	Yes	Yes
5412-25-9	Bis(2,3-dibromopropyl)phosphoric acid	No information	No information
5445-17-0	2-Bromopropanoic acid, methyl ester	No information	No information
5445-19-2	2-Bromohexanoic acid, methyl ester	No information	No information
6519-18-4	Potassium bis(2,3-dibromopropyl)phosphate	No information	No information
6710-97-2	Tetrabromobisphenol-A-bis-(2-ethylether acrylate)	No information	No information
7415-86-3	Bis-(2,3-dibromo-1-propyl)phthalate	No information	No information
20217-01-0	2,4-Dibromophenylglycidyl ether	No information	Yes
20566-35-2	Tetrabromophthalic acid diol	No information	Yes
21850-44-2	Tetrabromobisphenol-A bis(2,3-dibromopropyl) ether	Yes	No information
23488-38-2	Tetrabromoxylene	No information	No information
25327-89-3	Tetrabromobisphenol-A bis(allyl ether)	No information	Yes
25357-79-3	Tetrabromophthalic acid, sodium salt	No information	Yes
25637-99-4	Hexabromocyclododecane	Yes	No information
25713-60-4	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine	No information	No information
26040-51-7	Phthalic acid, tetrabromo-, bis(2-ethylhexyl) ester	No information	No information
31780-26-4	Dibromostyrene	No information	Yes
32534-81-9	Pentabromodiphenyl ether	Yes	No information
32536-52-0	Octabromodiphenyl ether	Yes	No information
32588-76-4	Ethylene-bistetrabromophthalimide	Yes	No information
32844-27-2	Tetrabromobisphenol-A diglycidyl ether - carbonate oligomer	No information	Yes
35109-60-5	2,4,6-Tribromophenoxy-2,3-dibromopropane	No information	No information
36483-57-5	Tribromoneopentyl alcohol (different isomers)	No information	Yes
36711-31-6	Magnesium bis(2,3-dibromopropyl)phosphate	No information	No information
37853-59-1	1,2-Bis(2,4,6-tribromophenoxy)ethane	Yes	No information
37853-61-5	Tetrabromobisphenol-A bis(dimethyl ether)	No information	Yes
38521-51-6	Pentabromobenzyl bromide	No information	Yes
39635-79-5	Tetrabromobisphenol-S	No information	Yes
40088-47-9	Benzene, 1,1 -oxybis-, tetrabromo derivative	No information	No information
40703-79-5	5,6-Dibromohexahydro-2-phenyl-4,7-methano-1H-isoindole-1,3(2H)-dione	No information	No information
41291-34-3	Ethylene-bis(5,6-dibromonorbornane-2,3-dicarboximide)	Yes	No information
52434-59-0	1,3,5-Tris(2,3-dibromopropoxy)-2,4,6-triazine	No information	No information
57137-10-7	Polytribromostyrene	Yes	No information
58965-66-5	Tetradecabromodiphenoxybenzene	Yes	No information
59447-55-1	Pentabromobenzyl acrylate*	Yes	No information
59447-57-3	Poly(pentabromobenzylacrylate)	Yes	No information

CAS no.	Name	Used as additive flame retardant	Used as reactive flame retardant
59789-51-4	Tribromophenyl maleimide	No information	Yes
61262-53-1	Benzene, 1,1'- 1,2-ethanediylbis(oxy) bis 2,3,4,5,6-pentabromo-	No information	No information
61368-34-1	Tribromostyrene	No information	Yes
62354-98-7	Poly(dibromostyrene)	No information	No information
64864-08-0	Sodium bis(2,3-dibromopropyl)phosphate	No information	No information
68441-46-3	1,3-Butadiene homopolymer, brominated	No information	No information
68441-62-3	Brominated polyetherpolyol	No information	Yes
68928-70-1	Tetrabromobisphenol-A diglycidyl ether oligomers	Yes	No information
69882-11-7	Poly(2,6-dibromophenylene oxide)	Yes	No information
71342-77-3	Tetrabromobisphenol-A carbonate oligomer (fully brominated; phenoxy-terminated)	No information	No information
77098-07-8	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, mixed esters with diethylene glycol and propylene glycol	No information	Yes
84852-53-9	1,2-Bis(pentabromophenyl) ethane	Yes	No information
88497-56-7	Brominated polystyrene	Yes	No information
94334-64-2	Tetrabromobisphenol-A – carbonate oligomer	Yes	Yes
109678-33-3	Tetrabromodipentaerythritol	No information	Yes
135229-48-0	Brominated epoxy resin / tribromophenol	Yes	Yes
137370-67-3	Polypropylene/dibromostyrene copolymer	No information	No information
139638-58-7	2-Propanol, 1,1'-[(1-methylethylidene)bis[2,6-dibromo-4,1-phenylene)oxy]]bis[3-(2,4,6-tribromophenoxy)-	Yes	No information
155613-93-7	Brominated trimethylphenylindane	Yes	No information
171091-06-8	Dibromostyrene grafted	No information	No information

* Might not be on the UK market.

Chlorinated organics

Chlorinated flame retardants are much less effective than the equivalent brominated compounds, and are declining in use. The level of chlorination necessary for sufficient flame retardancy often has a detrimental effect on the desired properties of the polymer. Chlorinated paraffins (aliphatics) are used in plastics, textiles and coatings. Chlorinated aromatics are not used as flame retardants.

An ideal reactive flame retardant is a halogenated version of the monomer from which the bulk of the polymer backbone is formed. Polyvinylchloride (PVC) is inherently flame retardant, due to its high levels of chlorine. When plasticisers are added, though, the flammability generally increases.

2.3.3 Organophosphorus compounds

Phosphorus-based flame retardants inhibit further combustion by making use of the catalytic properties of mineral acids in the pyrolysis of cellulose to water and char (as opposed to volatile and combustible organics). The low volatility of phosphoric acid and derivatives makes it the preferred choice. These flame retardants are most effective in polymers that char readily. Some phosphorus compounds, though, are thought also to increase the rate of polymer melt.

Physical or chemical vapour-phase mechanisms can also occur, particularly in non-charring polymers and also when the flame retardant in question is volatilised at the temperature of the flame. There is some evidence that the substances act as free radical scavengers.

Again, there are several compounds within this category; both additives and reactives. Phosphate esters are the most widely used family of organophosphorus flame retardants. Polyols, phosphonium derivatives, and phosphonates are also used. Phosphate esters are widely used in plastics, because as well as their flame retardant properties, they also increase the flexibility of the plastic.

Halogenated organophosphorus compounds

Halogenated phosphate esters are widely used. They combine the properties of both the halogen and the phosphorus components. The presence of the halogen also increases the lifetime of the flame retardant in the end-product by decreasing its mobility in the polymer. Tris(1-chloroisopropyl) phosphate (TCPP), used in polyurethane foams, and tris(2-chloroethyl) phosphate (TCEP), used in several plastics, are examples.

2.3.4 Nitrogen-based flame retardants

These are used mainly in polymers in which nitrogen is present (e.g. polyurethanes, polyamides), and also polyolefins. Melamine and guanidine compounds and their derivatives are the most commonly used, and are relatively cost-effective. Melamine derivatives are also used in intumescent coatings, where they act as blowing agents, catalysing the formation of foam. Some polymers are cross-linked by the internal generation of melamine rings.

Melamine derivatives act synergistically with phosphorus-containing flame retardants. This combination is often used in thermoplastics and intumescent systems. Compounds incorporating both active groups in one molecule (i.e. melamine phosphates) are also used.

Ammonium sulfate and sulfamate and the ammonium halides are used as flame retardants in various cellulosic products (textiles, paper, and wood), and in fighting forest fires.

2.3.5 Developing technologies

New approaches to the provision of flame retardancy are currently being developed, for example by the use of 'nanocomposites' *(Beyer, 2002)* and 'expandable graphite'.

A nanocomposite is a two-phase material comprising a polymer with a dispersed filler phase. Amine-modified silicate fillers incorporated into nanocomposites confer enhanced thermal stability and flame retardant properties. The filler is layered within the structure of the polymer with a layer thickness in the order of nanometres. As a result, the silicates are present at levels of between 2 and 10 per cent, most commonly in the form of montmorillonite, hectorite or saponite organoclays. Three synthesis routes are possible:

- in-situ polymerization;
- solvent method;
- melt-intercalation.

Of these, the first two rely on polymerisation occurring within the layered silicate structure of the clay. The third involves the molten polymer blending with the organoclay.

Flame retardant properties are achieved by the formation of a char layer that insulates the base layer from heat. This layer also acts as a barrier to volatile gases that could maintain combustion.

The manufacturers of nanocomposites claim that these substances have a number of advantages over polymers that are flame retarded using existing methods. These include:

- significantly lower concentrations of fillers are used;
- the properties of the virgin polymer are retained (and in some cases enhanced);
- no halogens are added during production.

Nanocomposites can also be used in combination with other flame retardant filler systems such as aluminium trihydroxide (ATH) to achieve the same, or a higher, level of performance at a lower filler concentration. The reduced filler concentration can have significant benefits in terms of improved mechanical and rheological properties of the polymer.

Expandable graphite exploits a mechanical process whereby, in a fire, a cross-linked carbon char is generated on the surface of the substrate. A wide range of substrates has been investigated *(Wenne, 2002).*

3. RESEARCH METHODS

3.1 Substance identification and use pattern

In the first instance, the researchers determined the possible presence of flame-retardant substances on the EU market from reviews of the Industry in the public domain. Table 3.1 shows the publications and lists consulted. We searched the open literature for references of general relevance (further details are given in the confidential Project Record). Substances on the final list of flame retardants that appear in the Project Database are coded according to the source in which they were mentioned (there is some overlap, since many of the substances were identified in more than one source).

Table 3.1 Sources from which the substance list was developed, and the codes used to identify the substances

Code	Description	Ref no.
IPCS	International Programme on Chemical Safety (IPCS) overview report on flame retardants (source code IPCS *for properties* refers to the IPCS Environmental Health Criteria (EHC) substance summaries)	1
IAL	IAL report	3
DK	Danish EPA report (brominated flame retardants)	4
CIA	CIA Flame Retardant Product Guide	5
IFR	Index of Flame Retardants	6
KO	Kirk-Othmer	7
MSDS	Industry (Material Safety Data Sheets for proprietary substances available on the web – information available by trade name but no chemical identification)	-
Web	Results of open searching on the Internet	-
EA	A large amount of literature, conference proceedings and correspondence provided by the Agency to support this update	
LIT	Results of searching the open literature	
NONS	Some notified new substances in EU are flame retardants. Where notifiers have given permission, data are included in the confidential Project Database (any non-proprietary data are given in the non-confidential version).	

We have checked the list of substances carefully to avoid any duplication. In an attempt to keep the list practical, we did not pursue most ‘product family’-type entries, since we felt that we were unlikely to obtain relevant data. We have also excluded substances that are already subject to comprehensive international controls (polybrominated biphenyls, for example).

The resulting Project Database identifies around 340 discrete substances that appear to have been used as flame retardants at one time or another. Chemical Abstracts Service (CAS) numbers were obtained either from the reference sources, from the Chemical Abstracts Registry file or from Industry. A hyphen is used where we could not identify a CAS number.

The next stage was to liaise with flame retardant producers and ‘downstream’ users. Our aim was to obtain the fullest overview possible of the industry and the life cycle of the substances. Flame retardants can be used in many sectors of industry. We identified consultees from relevant organisations (trade associations, companies, regulatory and other organisations, expert individuals and groups) to gain information on these sectors. We contacted most by telephone, to encourage participation and active data provision.

Published sources and direct contact with industrial consultees furnished us with most of the information on supply tonnage and industrial use pattern. We also held meetings with the Chemical Industries Association, to explain the purpose of our work, and to review progress. The European Flame Retardants Association and the European Brominated Flame Retardants Industry Panel participated in this work. In general, companies were happy to provide information on hazard but were unwilling to supply tonnage data. At the ‘user’ end, some trade associations obtained wide-ranging responses from members. Others were not able to respond in the time scale of the project. We provide comparisons between the EU and UK markets where relevant.

The range of contacts made is extensive and these are listed in Appendix 8. Full details are presented in the Project Record.

Confidentiality

Commercially sensitive substances (i.e. those that are not identifiable at this time for reasons of trade secrecy) are indicated in the Project Database as ‘proprietary’. There are other instances in which certain data must remain confidential. There are, therefore, two versions of the Project Database. The confidential version is available only to official government regulatory bodies.

3.2 Property data

The following publicly available data sources were consulted for each substance in the first instance:

Hazardous substances data bank (HSDB)
IUCLID database (confidential version)
Elsevier ECOTOX database
Syracuse Research Corporation PhysProp and ChemFate databases
Danish brominated flame retardant report *(Danish EPA, 1999)*
Company web site MSDSs
Published ESR reports and drafts
IPCS Environmental Health Criteria series

We also searched the literature and the Internet for relevant recent information. Industry will obviously also hold important data, and so relevant contacts were made with several major producer companies at a very early stage in the study. We are, though, uncertain how much key information rests in company archives that were inaccessible to us.

3.2.1 Physicochemical data

We obtained data for the purpose of conducting simple environmental hazard and risk assessments, as part of this or future work. The properties of most interest for prioritisation and assessment are vapour pressure, water solubility and the octanol-water partition coefficient (K_{ow}, generally expressed as a $\log_{10}$ value).

The sources investigated in respect of these data are set out above. Where two conflicting measurements were available for the same substance, we used expert judgement to select a preferred value, taking the following considerations into account when assessing the validity and quality of the data:

- Evidence from other properties (e.g. the relationship between vapour pressure, melting and boiling points);
- Any possible ionisation effects/variations caused by pH (e.g. does a difference in log K_{ow} imply that the test was conducted at a different pH?);
- Whether values are fully referenced the age of the test, and whether it was conducted using a recognised test method. These criteria are very rarely fulfilled, even in the information received from Industry sources.

3.2.2 Distribution and degradation data

We sought data in relation to biodegradability, hydrolysis and photodegradation (including photo-oxidation). While physicochemical data are useful for modelling the distribution of a substance in the environment, the following data, where available, take precedence:

- Soil adsorption coefficient (K_{oc});
- Fish bioconcentration factor (BCF).

Based on the sources available (see Section 3.1), there is no convincing evidence that more than a few of the organic flame retardant substances are ultimately degradable at a significant rate (excluding acid anhydrides). Data are generally scarce, with almost no photodegradation data or detailed reporting of hydrolysis.

3.2.3 Ecotoxicological data

We searched the literature and contacted potential Environment Agency and Industry sources with a view to accessing ecotoxicity test results (see Project Record). We obtained test results for about 75 substances that could be described by CAS registry numbers. The results mainly covered acute and chronic tests with aquatic organisms (fish, invertebrates, algae and sewage treatment micro-organisms). There were, though, also a limited number of results from tests with terrestrial plants and from dietary studies with birds.

3.2.4 Mammalian toxicity data

We searched the publicly available databases HSDB, IRIS, CCRIS and IUCLID 2000 for mammalian and genetic toxicity data. We also reviewed literature sources provided by the Agency and Industry. We obtained data for approximately 140 substances (mainly acute or long-term toxicity and *in vitro* genetic toxicity data). Of these, carcinogenicity and reproductive toxicity data were obtained for approximately 45 substances. Some *in vivo* genetic toxicity data were also found. We also found entries for nine substances on the Approved Supply List[8] of the CHIP3 Regulations.

This data search cannot be considered exhaustive. It should, though, have retrieved most of the well-established hazard indicator properties.

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[8] This is the UK version of Annex I to the Dangerous Substances Directive (67/548/EEC), which lists substances for which there has been EU-wide agreement on their classification and labelling. The Approved Supply List is an approved document supporting the Chemicals (Hazard information and packaging for Supply) Regulations 2002 (CHIP3).

3.2.5 Endocrine disruption effects

Interference with the endocrine system is recognised as a significant toxic effect. The indication of such effects is one criterion for toxicity according to the EU system for identification of PBT substances (see Section 6.2.2). Certain flame retardants have the potential for such effects. Polybrominated diphenylethers, for example, have been identified as having the potential to interfere with the oestrogen and/or thyroid system *(Meerts et al, 2001)*. Phthalates as a group have also been identified as potential endocrine disruptors. They are common plastics additives, but function chiefly as plasticisers. One brominated phthalate, however, is used as a flame retardant (tetrabromophthalate, diethylhexyl ester). 2,4,6-Tribromophenol has also been identified as a potential endocrine disruptor *(Damstra et al, undated)*.

While no quantitative structure-activity relationship for endocrine disruption exists yet, some experts are likely to consider any phenol or aromatic ether with an octanol-water partition coefficient (log K_{ow}) greater than 3 to be a candidate. Several of the substances identified in this project fall into these groups. Nevertheless, no substance should be considered a candidate on the basis of structure alone, given the current limited state of knowledge.

The European Commission has recently announced its investment in a large-scale research initiative investigating endocrine disruption. Brominated flame retardants in particular will form one area of study. We expect to see significant advances in understanding in this area in the future.

3.3 General analysis of the information collected

The data were added to a Project Database using Microsoft Access. The design and structure of the database is described in Appendix 1. By the end of the research, the Project Database contained records for 334 flame retardant substances. The query tools in Access allow the data set to be analysed with relative simplicity. Table 3.2 indicates the extent of information obtained.

Table 3.2 Analysis of the Project Database

Breakdown by category of flame retardant						
Inorganic (**I**)	Brominated organic (**B**)	Chlorinated organic (**C**)	Organo-phosphorus (**P**)	Halogenated phosphorus (**CP**)	Nitrogen-based (**N**)	Unclear
70	116	17	71	27	12	14

Breakdown by MEASURED property data availability		
Basic physico-chemical data (vapour pressure, Kow and water solubility)	**More detailed environmental fate data** (K_{oc}, BCF)	**Useable ecotoxicological data** (any acute or chronic result)
34	6	89

For about 100 (i.e. around a third) of the substances in the Project Database (i.e. substances identified in at least one source as a flame retardant), no *measured* information on properties whatsoever was found or supplied. For 23 of the substances identified in the CIA Product Guide *(CIA, 2000)* (i.e. a document developed directly by the Industry), no tonnage, ecotoxicological or basic environmental fate data were available. It is possible that some of these substances are misnamed; a few are proprietary.

3.3.1 Data gaps

When all available information had been recorded, many gaps in the data set still remained. Only 170 substances (i.e. around half) have published tonnage data (see section 6.1). Important data were missing for some of the substances that fell into the three lists of substances of concern (see Section 7). These important data gaps break down as follows:

High tonnage, but no details of the use pattern: 29 substances are on the EU market at or above 1,000 tonnes/year with no indication of the materials or end products in which they are used. The Industry (*Great Lakes, 2003*) has indicated that "many of these substances appear not to be flame retardants, but substances that are fire-fighting agents, chemical intermediates or used for other purposes".

Highly toxic, but no details of the tonnage: 35 substances categorised as toxic on the basis of measured or predicted acute, or measured chronic, ecotoxicity (see Section 6.2.1 for details of this approach) have an unknown EU tonnage. Of these, three are acutely toxic with $L(E)C_{50}$s below 1 mg/l based on measured data. In total, there are 182 substances with no tonnage information.

Supply at or above 1,000 tonnes/year in the EU, but missing important physicochemical data: 34 substances are thought to be on the EU market at 1,000 tonnes/year or more, but which lack measured vapour pressure, water solubility and/or octanol-water partition coefficient data.

All of these substances are listed in Appendix 7.

Predicted properties can be useful in the absence of measured data. In this study, we filled as many data gaps as possible by using the quantitative structure-activity relationships (QSARs) (see Appendix 4 for further details about the approaches used to estimate and validate values). Predicted values in the Project Database are indicated by the source code 'EPI' (or 'ECOSAR' in the case of ecotoxicity estimates).

We also used predictive methods (WSKOWWIN software) to obtain water solubility values for nine substances for which ecotoxicity but no measured water solubility data are available. We compared the predicted water solubility values with the ecotoxicity test results. This was to assess whether the toxicity values were likely to reflect exposure concentrations of dissolved test substance.

4. FINDINGS CONCERNING THE USE PATTERNS OF FLAME RETARDANTS

4.1 Applications of flame retardants

The use of flame retardants in different industrial sectors appears in a series of tables in Appendix 5. Each table presents:

- Breakdown by flame retardant type (and overall total where appropriate):
  - Number of substances
  - Number with known tonnage
  - EU tonnage
  - Additive/Reactive flame retardant use
  - Examples of loading rates, and use of synergists
  - Common uses

- Main or typical substance(s) used in that application

The application areas are set out in the following categories:

Carpeting
Coatings
Construction
Electronics
Fluids
Paper
Plastics (various polymer types)
Rubber
Textiles (excl. carpet)
Transport

Detailed descriptions of use pattern for a limited number of flame retardants are available in the risk assessment reports produced under the Existing Substances Regulation. It is not possible to provide the same level of information for the vast majority of substances in this report.

Table 4.1 shows the descriptions of the substrates used in the Project Database and from which the application overviews were developed. Where the database uses an abbreviation for common polymer types, the table gives the full name.

4.2 Key industrial sectors

4.2.1 Plastics

Flame retardants for thermoplastic polymers frequently make use of the plasticity and flow behaviour that occur at high temperatures. They initiate chain scission to promote decomposition of the polymer. This encourages the material to melt and drip, physically removing it from the source of ignition.

The physical properties of thermosetting polymers do not allow scope for this sort of physical flame retardancy. Significantly higher levels of flame retardant substances are therefore necessary.

Table 4.1 Substrates for flame retardants

Acrylic	
Acrylonitrile butadiene styrene	ABS
Alkyd	
Cellulose/cellulosics	
Epoxy	
Ethylene-propylene-diene rubber, ethylene-propylene terpolymer	EPDM
Expanded polystyrene	EPS
Extruded polystyrene	ExPS
High-density polyethene	HDPE
High-impact polystyrene	HIPS
Latex	
Low-density polyethene	LDPE
Neoprene	
Nylon	
Paper	
Phenolic	
Polyamide	
Polybutylene terephthalate	PBT
Polycarbonate	PC
Polychloroprene	
Polyester	
Polyethene	PE
Polyether	
Polyethylene terephthalate	PET
Polyisocyanurate resin	PIR
Polymethyl methacrylate	PMMA
Polyolefin	
Polypropylene	PP
Polyphenylene oxide	PPO
Polystyrene	PS
Polysulfide	
Polyurethane	PU
Polyvinyl	
Polyvinyl acetate	PVA
Polyvinyl chloride	PVC
Rubber	
Silicone	
Styrene	
Styrene-acrylonitrile	SAN
Styrene-butadiene rubber	SBR
Styrene-maleic anhydride	SMA
Textiles	
Triacetate	
Unsaturated polyester	UPE
Wood	

4.2.2 Textiles

The main fabrics for which flame retardants are used are cottons[9] and rayons. They are either treated with a flame-retardant finish, or acquire flame retardancy through chemical modification of the polymer. The latter performs best if the fabric is washed or weathered. Exposure to sunlight can significantly diminish the flame-retardant properties of treated materials. Performance of a flame retardant in such circumstances can be fundamental to its acceptability a specific application, since textiles are much more likely than plastics to be laundered and weathered. Chlorinated paraffins can also confer an element of rainproofing.

Even after a flame is extinguished, the ‘afterglow’ can still consume the fabric. It is important, therefore, that flame retardants used for textiles inhibit this effect. Often, combinations of flame retardant products are used *(Wiley, ca. 1991)*. Most flame-retardant finishes for cellulosic materials contain phosphorus, possibly in addition to brominated and/or nitrogen compounds. These are the most effective at preventing oxidation of the char that forms when flame-retarded cotton burns. Thus the ‘afterglow’ effect is prevented.

Applications include clothing (especially protective clothing), upholstery and furnishings in homes and vehicles, tents, and glass-fibre products. An important application is the back-coating of textiles (especially upholstery fabrics and carpets) with a flame retarded backing layer. Many different substances are used for this purpose. Textiles used in upholstered furniture and mattresses also require flame retardancy, at least in some regions (such as the UK).

Appendix 9 presents relevant information extracted from the IPPC BREF for textiles *(EC, 2002)*, which is an extensive description of the industry sector.

4.2.3 Coatings

It is often useful to make coating materials (paints and varnishes) resistant to flame. Intumescent coatings (which swell in the presence of flame, creating a layer of low-thermal conductivity) are common. They are particularly effective in shielding combustible materials such as wood and plastics.

4.3 End of life and disposal

Approximately three million tonnes of waste plastics are produced in the UK each year *(Environment Agency, 2002a)*. Households are the largest source of plastic wastes - mostly packaging. Various sets of legislation have recently, or will soon, enter into force controlling issues associated with end-of-life plastics in packaging, vehicles, white goods, electrical and electronic equipment, and construction/demolition waste. These may well have direct impacts on the use of certain flame retardants in future, especially if the flame retardants are not easy to retrieve or recycle. The following is a summary of the alternative routes of disposal of flame retarded products at the end of their service lives.

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[9] Cellulose is not inherently flammable, rather in the presence of flame it decomposes into flammable components.

i) Recycling

This broad term covers a range of activities, including re-processing into new articles, re-use of items and incineration for energy recovery. The nature of different types of re-processing varies depending on the form of substrate (e.g. thermoplastic or thermosetting plastic; foamed or solid; polymer type, etc.). For polymers for example, the following processes might take place *(Environment Agency, 2002d)*:

- rebonding,
- adhesive pressing,
- chemolysis, or
- feedstock recycling.

The feasibility of recovering and recycling bromine from plastics containing brominated flame retardants has been demonstrated *(APME, undated a)*. Some additives survive the recycling process such that the recycled product retains the desired performance properties of the original polymer. This is true of certain brominated flame retardants. The change in performance over several recycling cycles has been assessed *(Dawson and Landry, 2001)*. High-impact polystyrene (HIPS) and polybutylene terephthalate flame retarded with ethylene-bistetrabromophthalimide (EBTBP) perform well through several cycles of recycling. Recycled HIPS products contain 5-50 per cent recyclate *(Dawson and Landry, 2002)*. Flame retarded acrylonitrile-butadiene-styrene (ABS) polymers containing brominated epoxy oligomer maintained the original material's performance best.

Around 95 per cent of factory waste plastic around the UK is efficiently recycled. Only around seven per cent of post-consumer waste plastic, though, is recycled. Around three per cent of plastics from end-of-life vehicles were recycled in the UK in 1999, though this proportion is likely to increase significantly due to implementation of the End of Life Vehicles Directive. Another consequence of implementation of this Directive is that the number of different plastics used in cars is likely to reduce. Polypropylene in particular is likely to be used more *(Environment Agency, 2002a)*.

An important factor in successful recycling is the separation of different plastics into polymer types and sorting the plastic components of composite products (e.g. electronic equipment, white goods and cars). These processes tend not to be very cost-effective. They will, though, become more important in the future in order to meet legal targets for various sectors, including the Government’s Waste Strategy. Some organisations have proposed that polymers containing brominated flame retardants be separated from other polymers, but we expect this would be difficult in practice.

ii) Landfill

More than 80 per cent of post-consumer plastic wastes are landfilled *(Environment Agency, 2002a)*. Issues that require consideration are the leaching of the additive out of the substrate into landfill water and thence:

- volatilisation;
- seepage into groundwater;
- degradation;
- adsorption.

Generic models need to be developed for this scenario.

iii) Incineration (with or without energy recovery)

Incineration has its own issues with respect to breakdown products (at high temperatures, polybrominated diphenylether flame retardants, for example, form polybrominated dibenzofurans and dibenzo-p-dioxins). Plastics containing halogenated additives in municipal solid waste can, however, safely be incinerated *(BSEF website)*.

iv) Flytipping and litter

Littering and flytipping are difficult to control and even to evaluate. Nevertheless, they are both potential sources of exposure of flame retardants to the environment.

4.4 Overall trends in the industry

Fire safety regulations mean that flame retardants of some sort will continue to be essential. As a result of international programmes, certain substances are being phased out, and alternatives are being sought. The key question to be addressed by risk managers is whether the benefits – i.e. the protection of human life and property from fire – outweigh the risks, to both the environment and human health. There is, though, clear emphasis on cutting the use of halogenated flame retardants in general, partly driven by pressure from non-governmental organisations. The favoured alternatives appear to be inorganics and organophosphorus compounds.

The issues of substitution (see Section 5) and future technical developments are commercially highly sensitive, and Industry has been understandably unwilling to make much comment on them during this review.

5. SUBSTITUTION

Substitution initiatives are underway in many areas of flame retardant chemistry. The following discussion focuses in particular on the substitution of halogenated (and in particular brominated) substances.

The current status of halogenated flame retardant substitution initiatives in some of the key product areas is summarised in Table 5.1 (as presented by *UBA, 2000* and *Murphy, 2001*).

Table 5.1 Summary of substitution of halogenated flame retardants in key product areas

Product sector	Status of substitution
Computing and TV equipment exterior casings, PU slab-stock and block foams, and components of rail vehicles made of unsaturated polyester resins	Significant substitution has taken place
Duroplastic printed circuit boards and one-component foams	Serious technical obstacles to overcome before alternative flame retardant solutions (such as halogen-free flame retardant substances, halogen-free flame retarding polymers and finished products) can be applied
Sandwich foams	Satisfactory alternatives to existing flame retardant substances that meet technical performance requirements have yet to be identified
Textiles	Substitution of halogen-based flame retardant systems has taken place, but the extent and scope for further activity is unclear at this time

Some of the principal alternatives to halogenated flame retardants in current commercial use are shown in Tables 5.2 and 5.3, alongside the substrates and products in which they are used. The alternatives can be grouped under three main headings:

- substances containing phosphorous (with or without an inorganic synergist);
- compounds containing nitrogen;
- inorganic substances.

It is important to note that performance is a key factor in substitution. For instance, if it is not possible for a ‘substitute’ flame retardant to meet an acceptable level of fire safety, it cannot truly be considered a substitute for a very high-performance, albeit hazardous, flame retardant substance. It is beyond the scope of the present document to consider the cost-effectiveness of different flame retardant approaches.

Table 5.2 Status and trends in halogenated flame retardant substance substitution in selected use sectors (based on UBA *(2000)*, Edenburn *(2001)* and Pandey and Vankar *(2002)*)

Use sector	Substrate	Current or previous flame retardant system	Substitute	Properties of substitute(s) and resulting substrates	Basis for substitution	Factors potentially limiting uptake	Scope for further substitution
Rail travel vehicles and facilities	UP resins	Halogenated or brominated flame retardants (reactive and additive), in combination with antimony trioxide	Aluminium trihydroxide (ATH)	• ATH largely unproblematic from a toxicological and ecotoxicological viewpoint • Favourable effects on the by-products of the fire (fume density; fume toxicity) • Recycling of flame retarded composite materials is possible[10]	• ATH flame retarded resins are cheaper than halogenated resins • Personal safety • Protection of property (corrosion, damage to electronic components by fire gases) • Cleanup and disposal costs associated with the formation of dioxins/furans in the event of fire	Incorporation of ATH increases substrate density and weight	Opportunities for substitution have largely been exhausted
Construction	Poly-urethane insulation and one-component foams	Brominated polyols and halogenated phosphoric acid esters	• Polymer modification through insertion of isocyanurate structures Reduction or complete substitution of halogenated phosphoric acid esters, in the direction of non-halogenated organic phosphorus products • Use of solid flame retardants e.g. ammonium polyphosphate (APP)	• Substrates are halogen-free • Some benefits in terms of environmental hazard properties but also some negatives (e.g. diethyl ethylphosphonate (DEEP) and triphenyl phosphate (TPP) are considered more hazardous compared with tris(2-chloro-1-methylethyl) phosphate (TCPP) • APP is judged to be largely harmless from a toxicological and ecotoxicological standpoint	• Phasing out of the use of halogen-containing components • Reduction in flame retardant content (20–25 per cent cf. 8–11 per cent)	• Technically not achievable with in-situ foams • Higher costs of halogen-free foams • No current alternative to hexabromocyclo-dodecane (HBCD) and dicumyl peroxide exists for polystyrene • Technical reasons prevent adoption into sandwich foams	Potential is high

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[10] Industry have indicated that this is a theoretical possibility. Thermset materials are very difficult to recycle and so it does not generally happen (EFRA, 2003).

Use sector	Substrate	Current or previous flame retardant system	Substitute	Properties of substitute(s) and resulting substrates	Basis for substitution	Factors potentially limiting uptake	Scope for further substitution
Plastics in electrical and electronic appliances	Resin and laminate printed circuit boards	Tetrabromobisphenol-A (TBBPA)	Reactively bound phosphoric and nitrogen compounds	Substrates are halogen-free and may have reduced environmental hazard properties	• Phasing out of the use of halogen-containing components	• Current fire safety standards that are considered inappropriate for some classes of products • Processing difficulties • Higher costs (+30 per cent)	A revision of fire safety standards for certain products could enable a reduction of up to 50 per cent in TBBPA usage
Thermoplastic outer casings for IT and TV appliances	Thermo-plastic casings	Octa- and decabromodiphenyl ethers (Octa- and DecaBDE)	• Organic phosphorus flame retardants • Design-based solutions that obviate the need for flame retardants (e.g. metal casings)	• Substrates are halogen-free and may have reduced environmental hazard properties • Some benefits of OP substances in terms of environmental properties but there are concerns for some (e.g. TPP)	• Phasing out of PBDE usage • Requirement to achieve recycling objectives is made easier	Already being widely adopted	Scope for further substitution and design solutions in all product sectors
Textiles	Materials for upholstered furniture and mattresses	• Chlorinated phosphoric acid esters, melamine, and expandable mineral carbon as a flame retardant in foam • Antimony-halogen compounds, phosphorus-nitrogen compounds and ammonium polyphosphate compounds used for covering fabrics • Decabromodiphenyl ether	• Phosphoric polyols (to replace TCPP (for some applications only) • Silicon-inorganics • Polymer organic char formers • Polymer nanocomposites (incorporating, for example, montmorillonite clay)	Substrates are halogen-free and antimony-free and therefore may have reduced environmental hazard properties	Phasing out of the use of halogen and antimony containing compounds	The need to retain flame retardant properties following repeated use and cleaning of fabrics	Not known

Table 5.3 Halogen-free flame retardants that are in commercial use (based on Danish Environmental Protection Agency *(2001)* and DEFRA *(2002)*)

Substrate(s)	Products in which the substrate is used in flame retardant quality	Halogen-free flame retardant substance(s)
Epoxy	▪ Printed circuit boards ▪ Electronic component encapsulation ▪ Technical laminates	▪ Reactive nitrogen and phosphorous constituents ▪ Ammonium polyphosphate and aluminium trihydroxide
Phenolic resins	▪ Printed circuit boards for consumer electronics ▪ Technical laminates	▪ Nitrogen and phosphorous compounds ▪ Aluminium trihydroxide
Unsaturated polyester	▪ Technical laminates ▪ Plastics components in transportation	▪ Ammonium polyphosphate ▪ Aluminium trihydroxide
PVC	▪ Flooring ▪ Cables	▪ Phosphate esters ▪ Aluminium trihydroxide ▪ Antimony trioxide
ABS	▪ Housings for electronic products	▪ No alternatives
Polystyrene - PPO	▪ Housings for electronic products	▪ Organic phosphorus
Polystyrene	▪ Housings for electronic products ▪ Wiring parts ▪ Construction industry	▪ Organic phosphorous compounds ▪ Magnesium hydroxide
Polybutylene terephthalate / PET	▪ Switches ▪ Sockets ▪ Parts of electrical equipment	▪ No alternatives in commercial use
Polyamide	▪ Parts of electrical and electronic equipment	▪ Magnesium hydroxide ▪ Red phosphorous ▪ Melamine cyanurate ▪ Melamine polyphosphate
Polycarbonate/ABS	▪ Parts of electrical and electronic equipment	▪ Organic phosphorous compounds
Polypropylene and polyethylene	▪ E.g. Roofing foils ▪ Injection moulded parts (electronic equipment)	▪ Ammonium polyphosphate ▪ Magnesium hydroxide (DSBG 2003)
Expanded polystyrene	▪ Insulation of foundations and flooring	▪ No alternatives
Rigid polyurethane foam	▪ Insulation of cold-storage plants/freezing rooms, pipes, etc.	▪ Ammonium polyphosphate ▪ Red phosphorous
Flexible polyurethane foam	▪ Furniture ▪ Components in transportation	▪ Ammonium polyphosphate ▪ Melamine ▪ Reactive phosphorous polyols
Cotton textiles	▪ Furniture, textiles ▪ Components in transportation	▪ Ammonium polyphosphate ▪ Diammonium phosphate
Synthetic textiles	▪ Furniture, textiles ▪ Components in transportation ▪ Protective clothing	▪ Reactive phosphorous constituents

5.1 Availability of information for brominated flame retardant substances

As a group, brominated flame retardants have been subject to regulatory scrutiny within the EU for some time. Of the approximately 75 brominated flame retardants in recent regular use, six (PBBs, HBCD, TBBPA, penta-, octa- and decabromodiphenyl ether (-BDE)) are or have been subject to risk assessment procedures. These have contributed to the development of substantial databases concerning the human health and environmental hazards of these substances. In the case of PBBs and penta- and octaBDE, this has ultimately led to measures being taken to phase-out their use within the EU.

Significant risk management decisions of the type taken in relation to PBBs and pentaBDE could apply to other brominated flame retardants. Each substance, though, has to be considered on its own merits. Risk management requires a risk assessment to be performed as a first step. This typically requires the collection of substantial amounts of information on the properties (health, safety and environmental hazards) of the substance and its predicted concentrations in people and the environment. This process (including international peer review) can take several years to complete and is costly in resource for both regulator and Industry.

The resources required fully to assess all of the brominated flame retardants in current use could therefore be substantial. It is highly unlikely that they could be justified over a short time scale. The question therefore arises whether a strategy could be developed to achieve this goal in a less resource intensive way. The Swedish environment ministry has proposed banning brominated flame retardants in industrial use. This strategy would clearly remove the need for any assessments. We recognise, though, that a ban would require the identification of substitute substances to meet legislated fire safety standards, and that any substitutes would also require assessment. Given the intense lobbying taking place within Europe for the retention of brominated flame retardants on the basis of, among other things, their safety and technical benefits, it seems unlikely that a blanket ban will be forthcoming. A more likely scenario is that substances may be grouped for the purposes of determining their hazards and assessing and managing their risks on a group-by-group basis.

A number of factors will need to be considered for any grouping. A high priority will have to be given to chemical structure, to ensure that data on fate and effect properties can be justifiably used by read-across or QSAR. Grouping does not mean the grouped substances are the same; it means that they share common chemical or use factors. Sub-sets of chemical structure classes might then be developed to cover different use patterns, since this will have a significant bearing on exposure. Tools such as ‘risk profiling’ currently being developed by the Agency may be extremely useful in grouping substances and setting priorities for risk assessment.

We analysed the information on physico-chemical, ecotoxicity and toxicity properties, and on production and use patterns, for 116 brominated flame retardants. This revealed that coverage is incomplete (see Table 5.4). The predicted values have not been included in these totals, but it is noted that for some of these end points, predicted values may be acceptable instead of measurements.

Table 5.4 Key information coverage for 116 brominated flame retardant substances

Type of information	Number of substances with information
Kow	18
Ecotoxicity	25
Mammalian toxicity	47
Production and use pattern	62 (of which 27 are believed to be off the market)

This analysis indicates that information is incomplete. Substituting one brominated substance by another could easily lead to a situation where hazard and risk are less well known for the substitute.

5.2 Grouping of brominated flame retardants for risk assessment

Possible groupings of brominated flame retardant substances based at a primary level on chemical structure, and at a secondary level on use patterns, are:

Polybromodiphenyl ethers
TBBPA derivatives
Polybrominated phenols
Other polybrominated aromatics
Brominated alkanes and alkenes including cycloalkanes
Miscellaneous

Even within these groups, the extent of bromination will have a very large influence on persistence. Grouping is considered further in the recommendations of this report.

Primary application areas include all major flame retardant uses:

- electronics and electrical equipment;
- textiles;
- furniture;
- adhesives/coatings;
- engineering plastics.

5.3 Information on substitutes for brominated flame retardants

The Danish Environmental Protection Agency has qualitatively assessed the availability of physico-chemical, human health and environmental data on potential substitutes for brominated flame retardants *(Danish EPA, 2001)*. That study expressed concern about the paucity of data. Substances covered by the Danish assessment are listed in Table 5.5, but the evaluations have been amended by the results of the research carried out for this project. The term 'good' implies a data set approaching the internationally recognized minimum data set for High Production Volume substances in most areas, and with some long-term ecotoxicity data. 'Poor' implies a significant shortfall. It should be noted that the technical performance of a potential substitute could be significantly different to the substance of concern, and this could mean that larger amounts are needed to achieve the same standard of flame retardancy.

Table 5.5 Perceived availability of data on substitutes for brominated flame retardant substances, modified from a Danish study *(Danish EPA, 2001)*

Substance	Physico-chemical data	Health data	Environmental data
Ammonium polyphosphates	medium	medium	medium
Antimony trioxide	good	good	good
Magnesium hydroxide	medium	good	medium
Melamine	good	good	good
Phosphonic acid (dimethyl ester)	poor	poor	poor
Red phosphorous	medium	medium	medium
Resorcinol bis(diphenyl phosphate)	medium	medium	medium
Tricresyl phosphate	good	good	good
Triphenyl phosphate	good	good	good
Zinc borate	medium	medium	medium

The proposed shift in chemicals policy outlined by the EU White Paper published in February 2001 could result in significant amounts of new data being made available for evaluating the hazards and risks of flame retardant substances.

5.4 What parameters need to be considered in flame retardant substitution?

The increasing use of flame retardant substances is a consequence not only of the growing use of plastics and textiles, but also of developments in fire safety standards across a progressively increasing list of finished consumer goods. The setting of standards for fire retardancy against which product substitution must be viewed is likely to be first and foremost a matter of achieving social aims and preferences in terms of human safety. Environmental objectives are likely to be considered only if human safety is not compromised. For a global chemical industry, this picture can, though, be clouded. For example, different expectations about fire protection exist. Perceptions about the associated social risk also vary. In Europe this is clearly illustrated by the different standards of fire retardancy expected of textile goods and furniture: fire retardancy is a more stringent and regulated requirement in the UK than in Germany. Similar inconsistencies exist in standards applicable to passenger cars, with no EU-wide regulations, though several member countries have set their own.

Having emphasized the key importance of achieving/maintaining fire safety standards in products, it is important to draw attention to other (often conflicting) factors influencing substitution decisions. These include the need to:

- respond to legislation developing in other areas (e.g. waste and recycling – see section 5.3). The proposed EU Directive on Waste Electrical and Electronic Equipment (WEEE), for example, requires plastic electrical and electronic components incorporating brominated flame retardants to be recycled in a separate stream, because of concerns relating to emissions of toxic combustion products (dioxins/furans)[11] *(Soderstrom and Marklund, 2002)*. This could be a stimulus for substitution away from the use of brominated flame retardants. Arguments have also been presented by the brominated flame retardant industry, though, to justify continued use of their products (e.g. 1,2-bis(tetrabromophthalimide) and 1,2-bis(pentabromophenyl)ethane in polybutylene

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[11] It has been demonstrated that decaBDE/high impact polystyrene resins can be recycled without the formation/emission of PBDD/PBDF (Albemarle, 2003).

terephthalate resin and/or HIPS resins) because of the positive benefits they confer on plastics for recycling *(Dawson and Landry, 2001 and 2002)*.
- respond to technical developments in products. For example tris(tribromophenyl) cyanurate (CAS no. 25713-60-4) has been proposed as an alternative to existing brominated flame retardants (decabromodiphenyl ether, tetrabromobisphenol-A, brominated epoxy oligomers and modified congeners used in conjunction with antimony trioxide as a synergist) for use in technical plastics because it confers improvements in properties such as thermal stability, impact properties, UV stability and heat distortion *(Georlette, 2001)*;
- maintain or improve cost competitiveness within product sectors. For example, it is claimed that flame retardants used in "judicious combinations" can "reduce the cost of the compound (substrate), either by making large reductions in the active additive, or by offering multi-functional performance" *(Murphy, 2001)*.

In summary, decisions made in respect of flame retardant substitution cannot be made on the basis of achieving environmental protection objectives in isolation. In practice, they will need to be based on satisfying contrasting, and often conflicting, demands.

5.5 Is there a need for brominated flame retardants?

At a general level, it is clear that there have been concerns over the environmental (and health) hazards posed by halogenated flame retardants. The net result of a variety of initiatives (including voluntary industry phase-outs) has been a decline in the use of some brominated and chlorinated substances, an increase in the use of mineral-based flame retardants, and an increase in the use of organophosphorus compounds and other substitutes.

UBA *(UBA, 2000)* has stated that, for almost all applications, the potential exists for further reductions in the quantity of hazardous flame retardants used without compromising fire safety. This might be achieved by:
- design solutions that completely or partially remove the need for flame retardant use (e.g. metal casings);
- the use of less hazardous substitutes;
- the use of novel formulations that achieve the required level of fire protection at lower loadings of flame retardants in the finished goods;
- the use of synergists (e.g. antimony oxide) that improve the performance of flame retardants, allowing lower loadings of flame retardants in the finished goods.

There are, though, barriers facing the reduction in the quantities of brominated substances in some substrates and applications. This was highlighted earlier in respect of technical barriers to the substitution of flame retardant substances used in in-situ foams, polystyrene, sandwich foams and printed circuit boards. In these and other applications, it is generally not possible simply to substitute one flame retardant for another, because of the substance specific interplay between flame retardant, polymer and properties of the finished product. Likewise, an extensive range of product standards, including EU, national and local regulations, has arisen in response to market pressure and litigation. These have resulted in more stringent flammability standards. Such standards can currently be met only by using flame-retardant systems based on brominated substances. Time-scales for development, testing and commercialisation of a novel flame-retardant system can be more than 10 years. The incorporation of an existing system to a new product can take as long as five years *(UBA,* *2000)*. The process of product substitution can therefore be lengthy – even when there is a commitment to it throughout the supply chain.

Costs can work in favour (e.g. switch from PUR to PIR insulation foams) or against (e.g. use of halogen-free flame protection in one-component foams) environmental goals. The cost of materials normally makes up only a relatively small proportion of the total cost of the substrate. So this alone is unlikely to be a major factor influencing decisions regarding substitution of flame retardants. Material costs can, though, be a decisive obstacle to substitution when added to the associated processing costs. For example, producers of printed circuit boards have claimed that the higher costs (10-30 per cent) of organophosphorus flame retardants and the higher associated processing costs (drying because of higher water absorption; changes in drilling, etc.) have been decisive obstacles to substitution *(UBA, 2000)*. Clearly, where the cost increase is significant, there will be reluctance on the part of Industry to accept substitutes, unless they can be justified on the basis of the:

- need to comply with regulatory or industry-wide voluntary substitution initiatives;
- value added to the product that can be exploited in marketing the substrate to producers of finished goods.

The disposal of used goods is becoming an increasingly important consideration in the assessment of the overall costs of a product throughout its life cycle. EU Directives concerning scrap, waste and incineration are imposing significant additional costs on Industry. These must be taken into account when assessing flame retardant substitution options. These costs arise from legal obligations (taking back products at the end of their service life, recycling, environmentally compatible disposal, for example) that cannot be ignored and apply industry-wide. In this respect, it is interesting to note the advantages of certain brominated flame retardants over alternative polymer/flame retardant solutions in plastics recycling and recovery. These have been highlighted by that sector of the industry *(BSEF, 2002)*.

In summary, the principle barriers to substitution are technical hurdles and cost considerations. There is unlikely to be resistance to change providing that technical developments involving substitute flame retardants achieve the required level of fire safety performance at an acceptable cost to the supply chain. Where the costs are significant, though, the reluctance to change might be overcome only by regulatory imposition or the adoption of industry-wide voluntary agreements. In this regard, we note the findings of a recent survey of retailers conducted by Friends of the Earth (FoE) and reported by ENDS *(ENDS, 2002a)*. The survey asked companies to rate the Government's performance in helping them to substitute hazardous chemicals (including brominated flame retardants) in their products. Of the 10 companies that expressed an opinion, six rated the Government performance as ‘poor’, ‘very poor’ or ’unsatisfactory’, three rated it as ‘adequate’, and only one as ‘good’. Sixteen firms backed FoE's plans to call a meeting with a Department of Trade and Industry Minister to allow companies to express their concerns about the Department's performance in this area. These results would suggest that greater involvement of government (in the form of legislation or rewarding voluntary initiatives) might be required in order to achieve the substitution goals of finished goods suppliers.

6. ENVIRONMENTAL PRIORITISATION

We used three approaches to prioritise substances of concern for the Environment Agency:

- Method 1 deals with the substances that are on the market at the highest tonnage (a crude indication of potential for environmental exposure, at least for additive flame retardants).

- Method 2 deals with hazard potential in two ways:
  i) substances for which aquatic ecotoxicity has been evaluated and found to be high;
  ii) persistent, bioaccumulative and toxic (PBT) substances.

  In general, only data summaries have been reviewed, not full test reports. The ranking is therefore tentative. *In addition, we have not considered terrestrial and food-chain effects*, though these may be addressed in part by the PBT assessment.

- Method 3 deals with a simple risk assessment model using a generic exposure scenario and measured physicochemical and ecotoxicological data. Full details of the method are provided in the Project Record. We also calculated 'critical regional tonnages', following the developments of a separate Agency R&D project (see Section 6.3.2).

6.1 Method 1: Tonnage

Unfortunately, there is not enough information to allow us to rank substances on the basis of UK market size. We therefore sourced total EU supply tonnages from IPCS, IUCLID, Industry data and previous reviews. The year represented is given in the Project Database (some of the data are 10 years' old). Most of the data has not been verified by Industry, and so the information is only indicative. For example, tonnages given in the IPCS overview document are worldwide market figures. Assuming that the world market is split evenly between Europe, North America and Asia, we divided the IPCS figures by three to represent an EU total tonnage. It should be noted that *tonnages are not available for all of the substances of interest.* Some information on EU tonnage is available for 167 substances (i.e. only around half of the total number of substances in the Project Database). These have been placed into tonnage bands, and a breakdown is given in Table 6.1. Substances supplied at tonnages ≥ 1,500 tonnes/year[12] in the EU are listed in Table 6.2.

Table 6.1 Numbers of flame retardants by tonnage bracket, where known

Tonnage Bracket (tonnes/year)	Number of substances
100,000 or above	1
50,000 – 99,999	1
10,000 – 49,999	6
2,000 – 9,999	16
1,500 – 1,999	32
1,000 – 1,499	36
500 – 999	1
<500	25
Off the market	54

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[12] 1,000 tonnes/year is often used as the trigger to identify significant commercial substances. However, in view of the uncertainties in the tonnage data provided for the project, the researchers considered that 1,500 tonnes was more appropriate in this case.

Table 6.2 Substances with a flame retardant market of ^{3} 1,500 tonnes/year in the EU

CAS No.	Name	Type	Total UK tonnage	Source (UK)	Total EU tonnage	Source (EU)
21645-51-2	Aluminium trihydroxide	I	20,000	IAL	136,000	IAL
1309-64-4	Antimony (III) oxide	I	3,500	IAL	23,650	IAL
13674-84-5	Tris (2-chloroisopropyl) phosphate	CP	2,750	IAL	22,950	IAL
108-78-1	Melamine	N	6,250	Industry	15,000	IAL
79-94-7	Tetrabromobisphenol-A (and derivatives)	B	1,200	IAL	13,800	IAL
7631-90-5	Sodium bisulfate	I			10,000	IUCLID (range 5000-10000, 1993)
68937-41-7	Tris(isopropylphenyl) phosphate	P	>0.6	Industry	10,000	Industry; note IUCLID (range 10000-50000, 1993)
25637-99-4	Hexabromocyclododecane	B	750	IAL	9,000	ESR
1309-42-8	Magnesium hydroxide	I			8,500	BCC9
1163-19-5	Decabromodiphenyl ether	B	=>245	Industry	8,210	ESR
-	Ammonium phosphates	I	1,250	IAL	7,750	IAL
-	Bisphosphates	P	1,100	IAL	7,500	IAL
63449-39-8	Paraffin waxes and hydrocarbon waxes, chloro (Long-chain chlorinated paraffins)	Cl			5,000-7,000	Agency report
32588-76-4	Ethylene-bistetrabromophthalimide	B			5,250	IAL
38051-10-4	2,2-Bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate)	CP			5,000	IUCLID (range 1000-5000,1994)
1302-42-7	Sodium aluminate	I			5,000	IUCLID (1992)
16919-27-0	Potassium fluorotitanate	I			5,000	IUCLID (range 1000-5000, 1991/2/3/4)
-	HET acids/others	C	850	IAL	3,600	IAL
32536-52-0	Octabromodiphenyl ether	B			2,550	ESR
84852-53-9	1,2-Bis(pentabromophenyl) ethane				2,500	IAL; further confidential data from industry are available
115-96-8	Tris (2-chloroethyl) phosphate	CP	400	IAL	2,040	ESR
126-73-8	Tri-n-butyl phosphate	P			2,000	Industry
13674-87-8	Tris(1,3-dichloro-2-propyl)phosphate	CP	250	IAL	1,900	IAL

CAS No.	Name	Type	Total UK tonnage	Source (UK)	Total EU tonnage	Source (EU)
-	Dimethyl-3-(hydroxymethylamino)-3-oxopropyl phosphonate	P			>1,500	IPCS
77-47-4	Hexachlorocyclopentadiene	C			>1,500	IPCS
115-86-6	Triphenyl phosphate	P			>1,500	IPCS
115-88-8	Diphenyl octyl phosphate	P			>1,500	IPCS
118-79-6	2,4,6-Tribromophenol	B			>1,500	IPCS
124-64-1	Tetrakis(hydroxymethyl)phosphonium chloride*	P			>1,500	IPCS
608-71-9	Pentabromophenol	B			>1,500	IPCS
615-58-7	2,4-Dibromophenol[13]	B			>1,500	IPCS
632-79-1	Tetrabromophthalic anhydride	B			>1,500	IPCS
1241-94-7	2-Ethylhexyl diphenyl phosphate	P			>1,500	IPCS
1303-96-4	Sodium borate	I			>1,500	IPCS
1330-78-5	Tricresyl phosphate	P			>1,500	IPCS
1344-28-1	Aluminium oxide	I			>1,500	IPCS
1345-04-6	Antimony sulphide	I			>1,500	IPCS
6145-73-9	Tris(2-chloro-1-propyl)phosphate	CP			>1,500	IPCS
7773-06-0	Ammonium sulfamate	I			>1,500	IPCS
7783-20-2	Ammonium sulfate	I			>1,500	IPCS
11113-50-1	Boric acid	I			>1,500	IPCS
12124-97-9	Ammonium bromide	I			>1,500	IPCS
12125-28-9	Magnesium carbonate, basic	I			>1,500	IPCS
13472-45-2	Sodium tungstate	I			>1,500	IPCS
13826-83-0	Ammonium fluoroborate	I			>1,500	IPCS
16923-95-8	Potassium fluorozirconate	I			>1,500	IPCS
19569-21-2	Magnesium calcium carbonate	I			>1,500	IPCS
20120-33-6	Dimethylphosphono-N-hydroxymethyl-3-propionamide	P			>1,500	IPCS

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[13] While IPCS identifies this substance as an flame retardant, it has been indicated by Industry that it is in fact an end-capper. This could still be considered to be a reactive flame retardant application.

CAS No.	Name	Type	Total UK tonnage	Source (UK)	Total EU tonnage	Source (EU)
21850-44-2	Tetrabromobisphenol-A bis(2,3-dibromopropyl) ether	B			1,500	IAL
26444-49-5	Cresyl diphenyl phosphate	P			>1,500	IPCS
29761-21-5	Isodecyl diphenyl phosphate	P			>1,500	IPCS
32844-27-2	Tetrabromobisphenol-A diglycidyl ether - carbonate oligomer	B			>1,500	IPCS
57583-54-7	Resorcinol bis-diphenylphosphate	P			>1,500	IPCS
60763-39-5	Diphenyl isopropyl phosphate	P			>1,500	IPCS
68333-79-9	Ammonium polyphosphate	I			>1,500	IPCS
85535-85-9	Medium chain chlorinated paraffins (C14-17, commercial product ~40 - 60% wt Cl depending on application)	C			>1,500	ESR

*products such as tetrakis-hydroxymethyl phosphonium chloride-based prepolymer (CAS no. 27104-30-9) are now more widely used.

N.B. Only the tonnages used for flame retardant applications are considered. Several of the substances have other uses; therefore the total tonnage on the market may be much higher than indicated here.

Of the 182 substances for which no tonnage data could be obtained (listed in Appendix 7), 90 had no identifiable CAS number. No assumptions can realistically be made regarding the scale of supply of these substances, though it is likely that if the market were very large, a CAS number would probably have been available.

Most UK tonnages are close to 15 per cent of the EU tonnage (with two exceptions). To try to establish whether such substances are being routinely checked for, we asked the Environment Agency's National Centre for Environmental Data and Surveillance whether it held monitoring data for these. Data for only two substances, in one specific location, were retrieved. More details are given in Appendix 3.

6.2 Method 2: Aquatic hazard assessment

6.2.1 Ecotoxicity

Measured ecotoxicity data were available for 76 substances (i.e. only around one quarter of the total number in the Project Database).

i) Chronic effects data

We used the lowest *measured* long-term NOEC[14] values as the basis for categorising 56 of the substances in terms of their ecotoxic hazard to *aquatic organisms* according to the criteria shown in Table 6.3.

Table 6.3 Criteria for allocation of chronic toxicity category

Category	Lowest chronic NOEC (mg/l)	Number of substances in category
C-1	<0.01	15
C-2	0.01-0.1	6
C-3	0.1-1	5
C-4	1-10	7
C-5	>10	6
C-0	See note below	2

Note 1: The 'C-0' category applies to those substances for which all the measured NOECs were limit values (taken as implying no effects) greater than the measured or predicted water solubility. It is assumed that a substance placed in this category would not exert a chronic toxic effect at a higher concentration because of the limitations imposed by its solubility on its bioavailable concentration in the test medium.

Note 2: For two substances, confidentiality does not permit the category to be defined in this report. This also applies in Tables 6.4a and b.

The substances of most concern on the basis of hazard (NOEC < 0.1 mg/l) are listed in Table 6.4. It should be noted that chronic effects data are usually not available, so the absence of data may mean that this list could be much longer. We did not use quantitative structure-activity relationships (QSARs) to fill data gaps since these are generally not well validated for chronic end-points. Some substances for which data are confidential have also not been listed.

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[14] No observed effect concentration. N.B. A NOEC from an algal study is not considered sufficient on its own for the determination of hazard potential. It *can* be considered when a NOEC for a species from another trophic level is also available.

Table 6.4a Category C-1 substances based on measured data only

CAS no.	Name
77-47-4	Hexachlorocyclopentadiene
79-94-7	Tetrabromobisphenol-A
115-86-6	Triphenyl phosphate
1330-78-5	Tricresyl phosphate
2385-85-5	Dodecachlorooctahydrometheno-1H-cyclobutapentalene
25155-23-1	Trixylyl phosphate
25637-99-4	Hexabromocyclododecane
28108-99-8	Isopropylphenyl diphenyl phosphate
29761-21-5	Isodecyl diphenyl phosphate
32534-81-9	Pentabromodiphenyl ether
68937-41-7	Tris(isopropylphenyl) phosphate
85535-84-8	Short-chain chlorinated paraffins (C10 - 13, commercial product 49 - 70% wt Cl depending on application)
85535-85-9	Medium chain chlorinated paraffins (C14-17, commercial product ~40 - 60% wt Cl depending on application)

Table 6.4b Category C-2 substances based on measured data only

CAS no.	Name
124-64-1	Tetrakis(hydroxymethyl) phosphonium chloride
1241-94-7	2-Ethylhexyl diphenyl phosphate
7646-85-7	Zinc chloride
26444-49-5	Cresyl diphenyl phosphate
56803-37-3	tert-Butylphenyl diphenyl phosphate
57583-54-7	Resorcinol bis-diphenylphosphate

ii) Acute effects data

Where no chronic toxicity data were available, we used the lowest acute L(E)C_{50} values as the basis for categorisation in terms of ecotoxic hazard to *aquatic organisms* according to the criteria shown in Table 6.5. Measured and estimated data are included, since QSAR approaches are generally more reliable for acute end-points.

Table 6.5 Criteria for allocation of acute toxicity category

Category	Lowest acute L(E)C_{50} (mg/l)	Number of substances in category
A-1	<1	49
A-2	1-10	24
A-3	10-100	17
A-4	100-1000	11
A-0	See below	44

Note 1: The ‘A-0’ category applies to those substances for which all the measured acute L(E)C_{50} values were limit values (taken as implying no effects) greater than the measured or predicted water solubility. It is assumed that a substance placed in this category would not exert an acute toxic effect at a higher concentration because of the limitations imposed by its solubility on its bioavailable concentration in the test medium. This does not mean that it is non-toxic, since chronic toxicity is a possibility especially for poorly soluble substances.

Note 2: For five substances, confidentiality does not permit the category to be defined in this report. This also applies in Tables 6.6a and b.

The substances of most concern (L(E)C_{50}s < 10 mg/l) are listed in Table 6.6. Some substances for which data are confidential have not been listed.

Table 6.6a Category A-1 substances not listed in C-1 or C-2, based on measured data

CAS no.	Name
118-79-6	2,4,6-Tribromophenol
126-72-7	Tris(2,3-dibromopropyl)phosphate
608-71-9	Pentabromophenol

Table 6.6b Category A-2 substances not listed in C-1 or C-2, based on measured data

CAS no.	Name
78-38-6	Diethylethylphosphonate
78-51-3	Tri-butoxyethyl phosphate
512-56-1	Trimethylphosphate

Table 6.6c Category A-1 and A-2 based on estimated data

Substances already listed in Tables 6.4 and 6.6a/b are not included. The presence of a substance in this table does not preclude the possibility that measured data exist indicating less toxicity than that predicted.

CAS no.	Name
-	2,2'-Dimethyl-3-bromo-propanoic acid, isopropyl ester
-	Tribromochlorobisphenol-A
-	Tetrabromo-2,3-dimethylbutane
-	Tris (isopropyl) phosphate
75-95-6	Pentabromoethane
78-30-8	Tris(o-cresyl)phosphate
78-32-0	Tris(p-cresyl)phosphate
78-43-3	Tris(2,3-dichloro-1-propyl)phosphate
79-95-8	Tetrachlorobisphenol-A
85-22-3	Pentabromoethylbenzene
87-82-1	Hexabromobenzene
87-83-2	Pentabromotoluene
87-84-3	Pentabromochlorocyclohexane
93-52-7	Benzene, (1,2-dibromoethyl)-
101-02-0	Triphenyl phosphite
115-27-5	Chlorendic anhydride
115-88-8	Diphenyl octyl phosphate
115-89-9	Methyl diphenyl phosphate
115-98-0	Bis(2-chloroethyl)vinylphosphonate
117-08-8	Tetrachlorophthalic anhydride
301-13-3	Trioctyl phosphite
563-04-2	Tri (m-cresyl phosphate)
593-85-1	Guanidine carbonate
615-58-7	2,4-Dibromophenol
147-82-0	2,4,6-Tribromoaniline
1770-80-5	Dibutyl chlorendate
1773-89-3	Dimethyl chlorendate
1806-54-8	Trioctyl phosphate
1837-91-8	Hexabromocyclohexane

CAS no.	Name
3066-70-4	2,3-Dibromopropylmethacrylate
3072-84-2	Epoxy resin, brominated
3194-57-8	Tetrabromocyclooctane
3234-02-4	2,3-Dibromo-2-butene-1,4-diol
3278-89-5	Tribromophenylallyl ether
3322-93-8	1,2-Dibromo-4-(1,1-dibromomethyl)cyclohexane
3555-11-1	1-Pentabromophenoxy-2-propene
4162-45-2	Tetrabromobisphenol-A bis(2-hydroxyethylether)
5412-25-9	Bis(2,3-dibromopropyl)phosphoric acid
5445-17-0	2-Bromopropanoic acid, methyl ester
5445-19-2	2-Bromohexanoic acid, methyl ester
6145-73-9	Tris(2-chloro-1-propyl)phosphate
6294-34-4	Bis(2-chloroethyl)-2-chloethylphosphonate based
6749-73-1	Tris(dichloropropyl)phosphite
7415-86-3	Bis-(2,3-dibromo-1-propyl)phthalate
13560-89-9	Dodecachlorodimethan-o-dibenzocyclooctane
18300-04-4	Dibromochlordene
20208-95-1	Melamine phosphate
23488-38-2	Tetrabromoxylene
25327-89-3	Tetrabromobisphenol-A bis(allylether)
26040-51-7	Phthalic acid, tetrabromo-, bis(2-ethylhexyl) ester
30178-92-8	Tetrabromocyclododecane*
31107-44-5	Dodecachlorooctahydrodimethanodibenzofuran
31780-26-4	Dibromostyrene
35109-60-5	2,4,6-tribromophenoxy-2,3-dibromopropane
37853-61-5	Tetrabromobisphenol-A bis(dimethylether)*
38521-51-6	Pentabromobenzyl bromide
39635-79-5	Tetrabromobisphenol-S
52434-59-0	1,3,5-Tris(2,3-dibromopropoxy)-2,4,6-triazine
60763-39-5	Diphenyl isopropyl phosphate
61090-89-9	Bis(1,3-dichloro-2-propyl)-(3-chloro-2,2-dibromomethylpropyl) phosphate
61368-34-1	Tribromostyrene

* Not believed to be currently used as an flame retardant (Industry data)

6.2.2 PBT assessment

Substances that are especially persistent (P), bioaccumulative (B) and toxic (T) are of concern because it is difficult to predict their long-term environmental impact by the traditional risk assessment approach. Due to their high persistence, any impact they might have can be difficult to reverse, since low level exposure will continue even if industrial emissions cease. They also have the potential to impact environments that are remote from their sources of release (e.g. the open ocean). PBT properties are therefore a useful general marker for substances of concern in any strategy for assessment and control of chemicals. A PBT substance is identified by comparing substance-specific property data against a set of criteria in the form of threshold values. Different organisations have set different criteria. Those used in this project (the criteria developed by the EU for the purposes of marine risk assessment[15]) are shown in Table 6.7. The criteria are, by their nature, part of a screening process and can only ever be surrogates for long-term studies. They are, however, a way of setting priorities.

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[15] Included in the revised technical guidance document for risk assessment of industrial chemicals and biocides *(European Commission, 2003)*.

Table 6.7 PBT criteria used for this project

Criterion	PBT criteria	vPvB criteria
P	Half-life > 60 d in marine water or > 40 d in freshwater* or half-life > 180 d in marine sediment or > 120 d in freshwater sediment*	Half-life > 60 d in marine- or freshwater or >180 d in marine or freshwater sediment
B	BCF > 2,000 (log Kow > 4.5 as a screen)	BCF > 5,000 (log Kow > 5 as a screen)
T	Chronic NOEC < 0.01 mg/l (or acute aquatic L(E)C50 < 0.1 mg/l as a screen) or CMR properties or endocrine disrupting effects	Not applicable

* For the purpose of marine environmental risk assessment, half-life data in freshwater and freshwater sediment can be overruled by data obtained under marine conditions

The criteria were developed for organic substances. So inorganic flame retardants are beyond the scope of this review. This assessment focuses on properties related to the aquatic environment.

High production volume (HPV) substances meeting the PBT criteria have already been reviewed in an unpublished Environment Agency PBT screening study *(Environment Agency, 2002c)*. In addition, the EU is reviewing both ‘new’ and ‘existing’[16] substances that meet PBT criteria. The present study fills a gap in that it will pick up flame retardants that are non-HPV existing substances.

We classified each substance for persistence, bioaccumulation potential and toxicity in accordance with the criteria. The data used for assignment of P, B and T can be obtained from the Project Database, apart from those substances that have already been reviewed in the Agency's earlier PBT study.

The substances identified as potential PBT or vPvB candidates on the basis of the EU criteria are listed in Table 6.8. In some cases, we have added a comment for clarity. One ‘new’ substance has been excluded from the list for reasons of confidentiality. Appendix 6 lists the PBT category for all the remaining substances that can be allocated. **N.B. This list acts as a prioritisation tool for further substance-specific review – it is NOT a list of confirmed PBT substances.**

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[16] An ’existing’ substance is one which was listed in the European Inventory of Existing Commercial Chemical Substances (EINECS), and which were therefore on the EU market at some point between 1 January 1971 and 18 September 1981. Substances entering the market since this date are ’new’ substances and must be notified.

Table 6.8 Flame retardants meeting EU PBT screening criteria

CAS no.	Name	In EA PBT screen?
PBT		
-	Tribromochlorobisphenol A	No
79-95-8	Tetrachlorobisphenol-A	No
85-22-3	Pentabromoethylbenzene	No
87-83-2	Pentabromotoluene	No
3555-11-1	1-Pentabromophenoxy-2-propene	No
4162-45-2	Tetrabromobisphenol-A bis(2-hydroxyethylether)	No
23488-38-2	Tetrabromoxylene	No
25637-99-4	Hexabromocyclododecane	Yes
30178-92-8	Tetrabromocyclododecanea	No
32534-81-9	Pentabromodiphenyl ether	Yes
35109-60-5	2,4,6-Tribromophenoxy-2,3-dibromopropane	No
38521-51-6	Pentabromobenzyl bromide	No
52434-59-0	1,3,5-Tris(2,3-dibromopropoxy)-2,4,6-triazine	No
59447-55-1	Pentabromobenzyl acrylate	No
61368-34-1	Tribromostyrene	No
2385-85-5	Dodecachlorooctahydro-metheno-1H-cyclobutapentalene	No
85535-84-8	Short-chain chlorinated paraffins	Yes
vPvB		
-	Tetrabromophthalic acid, diethylhexyl ester	No
-	1,4-Bis(bromomethyl)-tetrabromobenzene	No
-	Bis(tetrabromophenoxy) ethane	No
-	Pentabromophenylbenzoate	No
-	Trichloromethyltetrabromobenzene	No
-	Tris(2,4,6-tribromophenyl)phosphate	No
-	Tris(tribromoneopentyl)phosphate	No
96-69-5	4,4'-Thio-bis(2-t-butyl-5-methylphenol)	No
1770-80-5	Dibutyl chlorendate	No
3194-57-8	Tetrabromocyclooctane	No
3278-89-5	Tribromophenylallyl ether	No
3322-93-8	1,2-Dibromo-4-(1,1-dibromomethyl)cyclohexane	No
13560-89-9	Dodecachlorodimethan-o-dibenzocyclooctane	No
18300-04-4	Dibromochlordene	No
21850-44-2	Tetrabromobisphenol-A bis(2,3-dibromopropyl) ether	No
25327-89-3	Tetrabromobisphenol-A bis(allylether)	No
25713-60-4	2,4,6-Tris(2,4,6-tribromo-phenoxy)-1,3,5-triazine	No
26040-51-7	Phthalic acid, tetrabromo-, bis(2-ethylhexyl) ester	No
31107-44-5	Dodecachlorooctahydro-dimethanodibenzofuran	No
32588-76-4	Ethylene-bistetrabromophthalimide	Yes[17]
37853-61-5	Tetrabromobisphenol-A bis(dimethyl ether)	No
39635-79-5	Tetrabromobisphenol-S	No
49690-63-3	Tris(2,4-dibromophenyl)phosphate	No
51936-55-1	Hexachlorocyclopentadienyl-dibromocyclooctane	No
58965-66-5	Tetradecabromodiphenoxy-benzene	No

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[17] Recent summary information received from Industry suggests that the 8-week fish BCF is < 3.3 at a water concentration of 0.2 ppm (w/v). The water solubility needs checking, but this result suggests that this chemical is not bioaccumulative in aquatic systems.

CAS no.	Name	In EA PBT screen?
61262-53-1	Benzene, 1,1'- 1,2-ethanediylbis(oxy) bis 2,3,4,5,6-pentabromo-	No
63449-39-8	Paraffin waxes and hydrocarbon waxes, chloro (Long-chain chlorinated paraffins)	Yes
139638-58-7	Propanol,1,1'-[(1-methylethylidene)bis[2,6-dibromo-4,1-phenylene)oxy]]bis[3-(2,4,6-tribromophenoxy)-	No

Note: a - Not believed to be currently used as a flame retardant (Industry data).
b - T based on estimated data; non-standard test showed no effects at limit of solubility.
c - These have predicted log Kow > 7.5, and are expected to be persistent. Reliable prediction of toxicity is not possible.

It should be noted that regulatory activity to address the problems posed by ‘PBT’ substances over the next few years is already under way.

6.3 Method 3: Risk-based ranking

6.3.1 Calculation of risk characterisation ratios

A risk characterisation ratio (RCR) is the comparison of an exposure term (PEC – predicted environmental concentration) with a hazard term (PNEC – predicted no effect concentration) as follows:

RCR = PEC/PNEC.

An RCR above 1 suggests a concern (i.e. the environmental exposure is above the level at which no effects are expected).

If RCRs could be estimated for each substance in the Project Database, then they could be compared to indicate the relative threat that each substance might pose. This method of ranking takes both exposure and the exact properties of a substance into account.

Obviously it is beyond the scope of this project to produce a thoroughly researched review of the entire life cycle of each substance, along with an assessment of data validity – these are pre-requisites for a proper risk analysis. We have, though, used a simplified approach for a sub-set of flame retardants from the Project Database. This is described briefly below, and the project record provides more details.

We developed a generic exposure scenario for the two primary industry sectors in which flame retardants are used – plastics and textiles – using the environmental risk assessment tool EUSES (European Union System for the Evaluation of Substances). We applied this to the data held for a number of flame retardants, to assess possible risks to aquatic and terrestrial environments (food chain and human health risks are not considered). We did not consider waste disposal and recycling. Since all the substances have the same (imposed) use pattern using this method, the size of the resulting RCRs should indicate relative concern.

Though this method may seem to be a more sophisticated way of comparing chemicals than taking only tonnage or hazard into account, it is still only a screening tool, because:

- The full life cycle and use pattern of many substances is unknown, and some of those chosen for inclusion might not be used significantly in the plastics or textiles

industries. Even if they are, the generic exposure scenario chosen might not accurately reflect their actual emissions;
- The risk characterisation ratio can only be an indication of relative risk if all PNEC values are derived from the same type of toxicity data, ideally chronic (since assessment factors vary over orders of magnitude depending on the data available). Given the paucity of such data, the ranking is only approximate.

Some substances cannot be assessed in this way due to lack of data. This does not mean that they present no risk, and for these, the other types of prioritisation (tonnage and hazard) are more applicable.

Due to the screening nature of this type of assessment, descriptive terms have been used rather than a numerical value for the RCR. These are 'low', 'medium', 'high' and 'very high', and are merely relative terms. Substances that give RCRs that are not 'low' for the processing and 'regional' (linked to losses from 'in service' use) scenarios are of most interest, since supplier controls or advice are least likely to be effective for these parts of the life-cycle. Table 6.9 lists the substances that have been assessed, grouped into sub-sets to compare like with like. A 'less than' symbol implies that a limit value has been used. **In any interpretation of these data it is essential to bear in mind that this is a screening exercise and not a definitive statement of risk.**

Table 6.9 Risk characterisation ratios for selected flame retardant substances

a. Chronic ecotoxicity data available L = low; M = medium; H = high; V = very high

CAS No.	Name	Textile processing		Polymer processing		Regional
		Water	Soil	Water	Soil	Water
79-94-7	Tetrabromobisphenol-A	-	-	V	V	V
115-28-6	Chlorendic acid	M	M	L	L	L
115-86-6	Triphenyl phosphate	M	L	H	V	M
115-96-8	Tris (2-chloroethyl) phosphate	V	V	M	L	L
1330-78-5	Tricresyl phosphate	L	L	M	H	L
13674-84-5	Tris(2-chloroisopropyl) phosphate	L	L	L	L	L
13674-87-8	Tris(1,3-dichloro-2-propyl)-phosphate	H	H	L	L	L
25637-99-4	Hexabromocyclododecane	<V	<V	<V	<V	<H
29761-21-5	Isodecyl diphenyl phosphate	<L	<L	<M	<H	<L
85535-84-8	Short-chain chlorinated paraffins	-	-	L	M	L
85535-85-9	Medium-chain chlorinated paraffins	-	-	M	H	M

b. Based on acute data only L = low; M = medium; H = high; V = very high

CAS No.	Name	Textile processing		Polymer processing		Regional
		Water	Soil	Water	Soil	Water
78-38-6	Diethylethylphosphonate	L	M	L	L	L
78-40-0	Triethyl phosphate	M	L	L	L	L
78-42-2	Tris(2-ethylhexyl) phosphate	<H	<H	<L	<L	<L
78-51-3	Tri-butoxyethyl phosphate	L	L	L	L	L
79-95-8	Tetrachlorobisphenol-A	<V	<V	<M	<H	<L
115-88-8	Diphenyl octyl phosphate	V	V	M	H	L
118-79-6	2,4,6-Tribromophenol[a]	V	V	M	H	L
124-64-1	Tetrakis(hydroxy-methyl)phosphonium chloride (and derivatives)	V	M	M	M	L
608-71-9	Pentabromophenol[a]	V	V	H	H	M
615-58-7	2,4-Dibromophenol[a]	H	H	L	L	L
756-79-6	Dimethylmethyl phosphonate	<L	<L	<L	<L	<L
868-85-9	Dimethyl phosphonate	L	L	L	L	L
1241-94-7	2-Ethylhexyl diphenyl phosphate	H	V	L	H	L
3234-02-4	2,3-Dibromo-2-butene-1,4-diol	H	M	M	L	L
3278-89-5	Tribromophenylallyl ether	H	V	M	H	L
3296-90-0	Dibromoneopentyl glycol	<L	<L	<L	<L	<L
6145-73-9	Tris(2-chloro-1-propyl)phosphate	H	H	L	L	L
20120-33-6	Dimethylphosphono-N-hydroxymethyl-3-propionamide	<M	<L	<L	<L	<L
20566-35-2	Tetrabromophthalic acid diol	-	-	<H	<H	<M
25357-79-3	Tetrabromophthalic acid, sodium salt	-	-	<L	<L	<L
26444-49-5	Cresyl diphenyl phosphate	<V	<V	<M	<H	<L
31780-26-4	Dibromostyrene	H	H	L	M	L
32588-76-4	Ethylene-bistetrabromo-phthalimide	-	-	<L	<L	<L
36483-57-5	Tribromoneopentyl alcohol (different isomers)	M	M	L	L	L
38051-10-4	2,2-bis(chloromethyl) trimethylene bis (bis(2-chloroethyl)-phosphate)	<H	<V	<M	<M	<L
39635-79-5	Tetrabromobisphenol-S	-	-	<H	<VH	<M
41291-34-3	Ethylene-bis(5,6-dibromo-norbornane-2,3-dicarboximide)	-	-	<M	<M	<L
60763-39-5	Diphenyl isopropyl phosphate	H	H	L	L	L

Note: a – Industry has indicated that these substances are end-cappers and should be considered intermediates. The scenarios may therefore be inappropriate.

Eight of these substances (four chlorinated phosphate esters, short- and medium-chain chlorinated paraffins, hexabromocyclododecane and tetrabromobisphenol-A) are already being reviewed under the Existing Substances Regulation (ESR). In addition, the Agency is currently assessing aryl phosphates under a national initiative. These assessments will inevitably be much more detailed and realistic, but it is interesting to note that, using this method, most of these substances would flag as a concern, and the ESR assessments seem to be bearing this out.

Most substances for which only acute toxicity test results are available have high RCRs, mainly since the assessment factor used to derive the PNEC is very large (1,000).

Conclusions based on predicted properties must be treated with caution. Some of the high RCRs, though, suggest that toxicity testing, or further use data, is necessary for some substances. These are: tribromophenylallyl ether; tetrachlorobisphenol-A; tetrabromobisphenol-S (indicated by Industry to be mainly used in Asian markets); and tetrabromophthalic acid diol.

This approach therefore tends to highlight the high tonnage, highly toxic substances. It is validated to some extent validated since it picks out several substances that have already been identified as representing a risk by the ESR process. The table does suggest a number of other substances could also be prioritised for a detailed assessment.

6.3.2 Calculation of 'critical tonnage'

As part of a further project being conducted by the Environment Agency (*Risk profiles for substances used in specific industry sectors*, R&D Project P6-012/7), we examined another *screening* approach to the consideration of risk. We set up a spreadsheet to calculate the amount of a substance that would have to be on the market in a large industrial ‘region’ to produce a corresponding aquatic or terrestrial RCR equal to 1 (i.e. a ‘critical’ tonnage). The scenario chosen was the default exposure model for polymer processing, derived from the Plastics Additives Emission Scenario Document *(Environment Agency, 2001)*. All substances in the Project Database have been considered under this approach (as long as sufficient data were available), even if they are not used in plastics in any significant quantities.

The PNEC value was, in most cases, derived from measured or estimated acute L(E)C_{50} values using an assessment factor of 1,000. For 13 substances, measured long-term NOEC data were available. These were used with an assessment factor of 50 to obtain the PNEC. We have not reviewed test reports, so the choice of assessment factor might change for the purposes of a more detailed investigation. In respect of the acute data, there were very few complete ‘base sets’ (i.e. fish, invertebrate and algal studies) available. The most sensitive trophic level cannot be identified with certainty, which is a drawback.

While it is frequently accepted that substances of molecular weight greater than 700 are unlikely to express biological effects due to a lack of bioavailability, that expectation does not necessarily apply to brominated compounds. Thus, even though some substances show no effects in acute tests, and even though they have a molecular weight greater than 700, the possibility of chronic effects cannot be ruled out. We have therefore kept them in the data set, albeit with very uncertain effects values.

The critical tonnage can be calculated explicitly for the aquatic compartment. The lower the critical tonnage, the lower the amount of substance that can be on the market before a concern is triggered. Substances listed in Table 6.10 have a critical tonnage below 400 tonnes/year. This has been chosen somewhat arbitrarily as representing 40 per cent of a substance if used at 1,000 tonnes/year in the EU. Many of the substances screened had critical tonnages far higher than this value, and these are listed in Table 6.11. Substances of highest concern from a screening point of view are those with critical regional tonnage of less than 40 tonnes/year. We must emphasise that this is only a screening exercise and not a definitive statement of risk at a particular tonnage. A true risk assessment would, for example, take into account actual loss levels, daily use rate for the largest sites, and the full range of uses. To avoid over-interpretation of the values, relative terms have been used to describe the critical tonnage in each case. We have, however, listed the substances in order of their estimated critical tonnage – i.e. the substances decrease in order of concern.

Critical tonnages represent a useful guide to producers of flame retardants, because if the actual tonnage on the market exceeds the critical tonnage in any one region, a review of use pattern should be undertaken since a potential risk is implied. A full consultation on this method is envisaged as part of the R&D 'Risk profiles' project.

Should any substance not be found in Tables 6.10 or Table 6.11 it is implied that it has not been considered by this method.

Table 6.10 Priority substances based on the critical tonnage method

a. Based on aquatic PNEC from long-term studies

CAS No.	Name	Critical annual regional tonnage	Concern
2385-85-5	Dodecachlorooctahydrometheno-1H-cyclobutapentalene	Small	High
115-86-6	Triphenyl phosphate	Small	High
25637-99-4	Hexabromocyclododecane	Small	High
32536-52-0	Octabromodiphenyl ether	Medium	Medium
85535-84-8	Short-chain chlorinated paraffins (C10 - 13, commercial product 49 - 70% wt Cl)	Medium	Medium
36355-01-8	Hexabromobiphenyl	Medium	Medium
32534-81-9	Pentabromodiphenyl ether	Medium	Medium
124-64-1	Tetrakis(hydroxymethyl) phosphonium chloride	Medium	Medium
29761-21-5	Isodecyl diphenyl phosphate	Medium	Medium
85535-85-9	Medium chain chlorinated paraffins (C14-17, commercial product ~40 - 60% wt Cl	Medium	Medium

b. Based on aquatic PNEC from short-term studies (estimated data)

CAS No.	Name	Critical annual regional tonnage	Concern
40703-79-5	5,6-Dibromohexahydro-2-phenyl-4,7-methano-1H-isoindole-1,3(2H)-dione	Small	High
1837-91-8	Hexabromocyclohexane	Small	High
3194-57-8	Tetrabromocyclooctane	Small	High
3322-93-8	1,2-Dibromo-4-(1,1-dibromomethyl)cyclohexane	Small	High
32588-76-4	Ethylene-bistetrabromophthalimide	Small	High
4351-70-6	Oligomeric chloroalkyl phosphate	Small	High
53461-82-8	Tetrakis(2-chloroethyl)diethylene-oxy diphosphate	Small	High
18300-04-4	Dibromochlordene	Small	High
60763-39-5	Diphenyl isopropyl phosphate	Small	High
61090-89-9	Bis(1,3-dichloro-2-propyl)-(3-chloro-2,2-dibromomethylpropyl) phosphate	Small	High
6294-34-4	Bis(2-chloroethyl)-2-chloethylphosphonate based	Small	High
Unknown	Xylyl diphenyl phosphate	Small	High
140-08-9	Tris-(2-chloroethyl)phosphite	Small	High
3072-84-2	Epoxy resin, brominated	Small	High
87-82-1	Hexabromobenzene	Small	High
93-52-7	Benzene, (1,2-dibromoethyl)-	Small	High
37853-59-1	1,2-Bis(2,4,6-tribromophenoxy)ethane	Small	High
1806-54-8	Trioctyl phosphate	Small	High
Unknown	Tribromochlorobisphenol A	Small	High
101-02-0	Triphenyl phosphite	Small	High
78-32-0	Tri (p-cresyl phosphate)	Small	High
13560-89-9	Dodecachlorodimethan-o-dibenzocyclooctane	Small	High
301-13-3	Trioctyl phosphite	Small	High
26040-51-7	Phthalic acid, tetrabromo-, bis(2-ethylhexyl) ester	Small	High
115-88-8	Diphenyl octyl phosphate	Small	High
58965-66-5	Tetradecabromodiphenoxybenzene	Small	High
79-27-6	1,1,2,2-Tetrabromoethane	Small	High
85-22-3	Pentabromoethylbenzene	Small	High
36483-60-0	Hexabromodiphenyl ether	Medium	Medium
87-84-3	Pentabromochlorocyclohexane	Medium	Medium
23488-38-2	Tetrabromoxylene	Medium	Medium
75-95-6	Pentabromoethane	Medium	Medium
61262-53-1	Decabromodiphenylethane	Medium	Medium
35109-60-5	2,4,6-tribromophenoxy-2,3-dibromopropane	Medium	Medium
6145-73-9	Tris(2-chloro-1-propyl)phosphate	Medium	Medium
33125-86-9	Tetrakis(2-chloroethyl)ethylene diphosphate	Medium	Medium
2781-11-5	O,O-diethyl-N,N-bis(2-hydroxyethyl)aminomethylphosphonate	Medium	Medium
563-04-2	Tri (m-cresyl phosphate)	Medium	Medium
96-32-2	2-Bromoacetic acid, methyl ester	Medium	Medium
6749-73-1	Tris(dichloropropyl)phosphite	Medium	Medium
115-89-9	Methyl diphenyl phosphate	Medium	Medium

c. Based on aquatic PNEC from short-term studies (measured data)

CAS No.	Name	Critical annual regional tonnage	Concern
26444-49-5	Cresyl diphenyl phosphate	Small	High
25155-23-1	Trixylyl phosphate	Small	High
78-40-0	Triethyl phosphate	Medium	Medium
78-38-6	Diethylethylphosphonate	Medium	Medium
79-08-3	Bromoacetic acid	Medium	Medium
115-96-8	Tris (2-chloroethyl) phosphate	Medium	Medium
125997-20-8	Phosphoric acid, mixed 3-bromo-2,2-dimethylpropyl and 2-bromoethyl and 2-chloroethyl esters	Medium	Medium
19186-97-1	Tris(3-bromo-2,2(bromomethyl)propyl)phosphate	Medium	Medium
756-79-6	Dimethylmethyl phosphonate	Medium	Medium

d. Based on terrestrial PNEC

We recognise that the aquatic compartment might not necessarily be the cause of the greatest concerns. Substances that have a potentially higher risk to the terrestrial compartment than to the aquatic compartment are listed in decreasing order of concern for the terrestrial compartment in the following table.

CAS No.	Name
32588-76-4	Ethylene-bistetrabromophthalimide
31107-44-5	Dodecachlorooctahydrodimethanodibenzofuran
37853-59-1	1,2-Bis(2,4,6-tribromophenoxy)ethane
26040-51-7	Phthalic acid, tetrabromo-, bis(2-ethylhexyl) ester
49690-63-3	tris(2,4-Dibromophenyl)phosphate
1806-54-8	Trioctyl phosphate
3072-84-2	Epoxy resin, brominated
58965-66-5	Tetradecabromodiphenoxybenzene
59536-65-1	Hexabromobiphenyl (mainly 2,2',4,4',5,5'-hexabromo-)
61262-53-1	Decabromodiphenylethane
13560-89-9	Dodecachlorodimethan-o-dibenzocyclooctane
301-13-3	Trioctyl phosphite
Unknown	Xylyl diphenyl phosphate
18300-04-4	Dibromochlordene
85-22-3	Pentabromoethylbenzene
2385-85-5	Dodecachlorooctahydrometheno-1H-cyclobutapentalene
87-83-2	Pentabromotoluene
1770-80-5	Dibutyl chlorendate
3555-11-1	1-Pentabromophenoxy-2-propene
77-47-4	Hexachlorocyclopentadiene
Unknown	Tribromochlorobisphenol A
101-02-0	Triphenyl phosphite
25713-60-4	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine {Tris (tribromophenyl) cyanurate}
23488-38-2	Tetrabromoxylene
56803-37-3	tert-Butylphenyl diphenyl phosphate
115-88-8	Diphenyl octyl phosphate
35109-60-5	2,4,6-tribromophenoxy-2,3-dibromopropane
79-95-8	Tetrachlorobisphenol-A

CAS No.	Name
78-32-0	Tri (p-cresyl phosphate)
78-30-8	Tris(o-cresyl)phosphate
28108-99-8	Isopropylphenyl diphenyl phosphate
21850-44-2	Tetrabromobisphenol A bis(2,3-dibromopropyl) ether
25637-99-4	Hexabromocyclododecane
32536-52-0	Octabromodiphenyl ether
87-82-1	Hexabromobenzene
29761-21-5	Isodecyl diphenyl phosphate
85535-84-8	Short-chain chlorinated paraffins (C10 - 13, commercial product 49 - 70% wt Cl depending on application)
32534-81-9	Pentabromodiphenyl ether
36355-01-8	Hexabromobiphenyl
85535-85-9	Medium chain chlorinated paraffins (C14-17, commercial product ~40 - 60% wt Cl depending on application)
1330-78-5	Tricresyl phosphate
3322-93-8	1,2-Dibromo-4-(1,1-dibromomethyl)cyclohexane
3194-57-8	Tetrabromocyclooctane
115-86-6	Triphenyl phosphate
57583-54-7	Resorcinol bis-diphenylphosphate
298-07-7	Phosphoric acid, bis(2-ethylhexyl) ester
1241-94-7	2-Ethylhexyl diphenyl phosphate
68937-41-7	Tris(isopropylphenyl) phosphate
25155-23-1	Trixylyl phosphate
7415-86-3	Bis-(2,3-dibromo-1-propyl)phthalate
61090-89-9	Bis(1,3-dichloro-2-propyl)-(3-chloro-2,2-dibromomethylpropyl) phosphate
26444-49-5	Cresyl diphenyl phosphate
60763-39-5	Diphenyl isopropyl phosphate
1837-91-8	Hexabromocyclohexane
87-84-3	Pentabromochlorocyclohexane
Unknown	Tetrabromo-2,3-dimethylbutane
126-73-8	Tri-n-butyl phosphate
124-73-2	Dibromotetrafluoroethane
563-04-2	Tri (m-cresyl phosphate)

Table 6.11 Substances considered of low concern for the aquatic compartment

CAS No.	Name	Critical annual regional tonnage	Concern
Unknown	4-Bromobutanoic acid	Large	Low
Unknown	2-Bromohexanoic acid, methyl ester	Large	Low
Unknown	2,2'-dimethyl-3-bromo-propanoic acid, isopropyl ester	Large	Low
Unknown	Tris (isopropyl) phosphate	Large	Low
Unknown	Tetrabromo-2,3-dimethylbutane	Large	Low
Unknown	2-Bromopropanoic acid	Large	Low
Unknown	Dimethyl-3-(hydroxymethylamino)-3-oxopropyl phosphonate	Large	Low
Unknown	Tris(hydroxymethyl)phosphine oxide	Large	Low
77-47-4	Hexachlorocyclopentadiene	Large	Low
78-30-8	Tris(o-cresyl)phosphate	Large	Low
78-43-3	Tris(2,3-dichloro-1-propyl)phosphate	Large	Low

CAS No.	Name	Critical annual regional tonnage	Concern
78-51-3	Tri-butoxyethyl phosphate	Large	Low
79-95-8	Tetrachlorobisphenol-A	Large	Low
87-83-2	Pentabromotoluene	Large	Low
105-36-2	2-Bromoacetic acid, ethyl ester	Large	Low
108-78-1	Melamine	Large	Low
124-73-2	Dibromotetrafluoroethane	Large	Low
126-73-8	Tri-n-butyl phosphate	Large	Low
141-83-3	Guanyl Urea	Large	Low
147-82-0	2,4,6-tribromoaniline	Large	Low
298-07-7	Phosphoric acid, bis(2-ethylhexyl) ester	Large	Low
512-56-1	Trimethylphosphate	Large	Low
545-55-1	Tris(1-aziridinyl)phosphine	Large	Low
762-04-9	Phosphinic acid, diethyl ester	Large	Low
791-28-6	n-Triphenylphosphine oxide	Large	Low
868-85-9	Dimethyl phosphonate	Large	Low
1241-94-7	2-Ethylhexyl diphenyl phosphate	Large	Low
1330-78-5	Tricresyl phosphate	Large	Low
1502-47-2	2,5,8-Triamino-1,3,4,6,7,9,9b-heptaaza-phenalene (Cyamelurotriamide)	Large	Low
1770-80-5	Dibutyl chlorendate	Large	Low
3066-70-4	2,3-Dibromopropylmethacrylate	Large	Low
3555-11-1	1-Pentabromophenoxy-2-propene	Large	Low
5205-93-6	Dimethylamino propyl methacrylamide	Large	Low
5412-25-9	Bis(2,3-dibromopropyl)phosphoric acid	Large	Low
5445-17-0	2-Bromopropanoic acid, methyl ester	Large	Low
7415-86-3	Bis-(2,3-dibromo-1-propyl)phthalate	Large	Low
10310-38-0	Ethylene bis(tris(2-cyanoethyl)-phophonium)bromide	Large	Low
13674-84-5	Tris (2-chloroisopropyl) phosphate	Large	Low
13674-87-8	Tris(1,3-dichloro-2-propyl)phosphate	Large	Low
18755-43-6	Phosphonic acid, propyl-, dimethyl ester	Large	Low
21850-44-2	Tetrabromobisphenol-A bis(2,3-dibromopropyl) ether	Large	Low
25713-60-4	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine {Tris(tribromophenyl) cyanurate}	Large	Low
28108-99-8	Isopropylphenyl diphenyl phosphate	Large	Low
31107-44-5	Dodecachlorooctahydrodimethanodibenzofuran	Large	Low
34432-82-1	Ammonium bis(2,3-dibromopropyl)phosphate	Large	Low
38051-10-4	2,2-Bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate)	Large	Low
49690-63-3	tris(2,4-Dibromophenyl)phosphate	Large	Low
53506-00-6	1,4-di(cyanoethylphospine oxide)-2,3,5,6-tetramethylbenzene	Large	Low
55566-30-8	Tetrakis(hydroxymethyl) phosphonium sulfate (2:1)	Large	Low
56803-37-3	tert-Butylphenyl diphenyl phosphate	Large	Low
57583-54-7	Resorcinol bis-diphenylphosphate	Large	Low
59536-65-1	Hexabromobiphenyl (mainly 2,2',4,4',5,5'-hexabromo-)	Large	Low
68937-41-7	Tris(isopropylphenyl) phosphate	Large	Low

6.3 Conclusions

The experience of European regulatory bodies shows that detailed investigation of the life cycle and properties of a substance is needed before firm conclusions can be drawn about its potential risks. For example, those ESR risk assessments carried out on flame retardants have a wide range of conclusions. For some there is little concern, for others data gathering is underway, and for a few risk management has been required. The screening methods used in this section can therefore be considered only as an indicator of concern, or lack of it. We have, nevertheless, highlighted some substances (as yet not studied in detail) that, at a screening level, have indications of concerns that may be comparable with substances that have needed controls. This should be useful information for both regulatory agencies and Industry alike. It is interesting to note that these are not all brominated flame retardants.

Finally, we emphasise again that we have not attempted to judge the value of substances in terms of the protection of life and property.

7. RECOMMENDATIONS

1. More detailed reviews could be carried out on those substances that are either:
   - high tonnage (e.g. >1,500 tonnes/year supplied in the EU);
   - hazardous to the aquatic environment (i.e. chronic NOEC < 0.1 mg/l or acute $L(E)C_{50}$s < 10 mg/l), or potentially PBT/vPvB; or
   - have indications of risk from the screening assessments (i.e. either giving RCRs that are not 'low' for the processing and regional scenarios, or a critical regional tonnage of less than 40 tonnes/year).

   Substances that meet these criteria and that are not known to be already under investigation by regulatory authorities are listed in Table 7.1 overleaf. Substances already under investigation are listed in Appendix 10. Where possible, dealing with substances as groups might be more efficient both in terms of assessment time and Industry consultation. We have therefore split the table into a number of groupings, based around chemical similarity (rather than, say, use pattern). **The groups are not in any order of priority.**

   Substances flagging positively under more than one criterion might warrant further investigation as a priority. Particular attention could be given to those that could be proposed as substitutes for any substance currently considered a serious risk under any ongoing risk assessment regimes. Similarly, any substance flagging as a potential PBT/vPvB could be a priority if supplied in any significant quantities.

   N.B. It is very important to remember that very little is known about many of the substances identified in Table 7.1. In several cases, they have been identified based on predicted rather than measured data. In addition, the assumptions made about tonnage and use pattern may not be appropriate[18]. This sort of detail can be obtained only by a thorough consultation with the relevant suppliers and users for specific substances or groups. It has not been possible to do this in the time available for this project. **THIS TABLE SHOULD THEREFORE NOT BE USED TO INFER THAT THESE SUBSTANCES ARE 'PROBLEM' CHEMICALS.** It is merely a starting point for the collection of additional information. It should also be remembered that any group assessment could benefit from the inclusion of other related chemicals not specifically highlighted in this table.

   A number of inorganic substances have also flagged as being of high tonnage. These are: aluminium trihydroxide (CAS No. 21645-51-2); sodium bisulfate (CAS no. 7631-90-5); magnesium hydroxide (CAS no. 1309-42-8); ammonium phosphates (no CAS number); ammonium chloride (CAS No. 12125-02-9); sodium aluminate (CAS No. 1302-42-7) and potassium fluorotitanate (CAS No. 16919-27-0)). These are less straightforward to assess because inorganic ions can have numerous sources (including the earth's crust) and their toxicity is strongly influenced by environmental conditions and their essentiality. However, they *generally* tend to have fewer serious environmental concerns compared to organic substances. They have not been prioritised because of this.

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[18] For example, it is recognised that the risk-based criteria could be misleading if a substance is not used in the plastics industry as an additive flame retardant (e.g. Industry does not consider the brominated phenols to be true flame-retardant substances, although they still flag as a concern under hazard).

Table 7.1. Substances requiring further investigation, that are not already being studied in detail

Group	CAS No.	Substance name	High tonnage	Aquatic hazard	Potential PBT/ vPvB	Possible risk	Low critical tonnage
TBBPA derivatives and related substances	79-95-8	Tetrachlorobisphenol-A		v	v	v	
	4162-45-2	Tetrabromobisphenol-A bis(2-hydroxyethyl ether)		v	v		
	21850-44-2	Tetrabromobisphenol-A bis(2,3-dibromopropyl) ether[19]	v		v		
	25327-89-3	Tetrabromobisphenol-A bis(allyl ether)		v	v		
	37853-61-5	Tetrabromobisphenol-A bis(dimethyl ether)[20]		v	v		
	39635-79-5	Tetrabromobisphenol-S		v	v	v	
	32844-27-2	Tetrabromobisphenol-A diglycidyl ether - carbonate oligomer	v				
	-	Tribromochlorobisphenol-A		v	v		v
Brominated phthalates and related substances	117-08-8	Tetrachlorophthalic anhydride		v			
	632-79-1	Tetrabromophthalic anhydride	v				
	7415-86-3	Bis-(2,3-dibromo-1-propyl)phthalate		v			
	32588-76-4	Ethylene-bistetrabromophthalimide	v		v?		v
	20566-35-2	Tetrabromophthalic acid diol				v	
	26040-51-7	Phthalic acid, tetrabromo-, bis(2-ethylhexyl) ester (also known asTetrabromophthalic acid, diethylhexyl ester)		v	v		v
Brominated phenols and derivatives	118-79-6	2,4,6-Tribromophenol	v	v		v	
	608-71-9	Pentabromophenol	v	v	v	v	
	615-58-7	2,4-Dibromophenol	v	v		v	
	3278-89-5	Tribromophenylallyl ether		v	v	v	
	3555-11-1	1-Pentabromophenoxy-2-propene		v	v		
	25713-60-4	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine			v		
	35109-60-5	2,4,6-Tribromophenoxy-2,3-dibromopropane		v	v		
	37853-59-1	1,2-Bis(2,4,6-tribromophenoxy)ethane					v

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[19] The Netherlands are conducting an assessment of this substance, although the status of the work is unknown. It is therefore left in this table rather than Appendix 10.

[20] This substance is not used itself as a flame retardant but has been found in the environment. This can be explained by the O-methylation of tetrabromobisphenol-A by certain biological processes.

Group	CAS No.	Substance name	High tonnage	Aquatic hazard	Potential PBT/ vPvB	Possible risk	Low critical tonnage
	52434-59-0	1,3,5-Tris(2,3-dibromopropoxy)-2,4,6-triazine		v	v		
	58965-66-5	Tetradecabromodiphenoxybenzene					v
	61262-53-1	Benzene, 1,1'- 1,2-ethanediylbis(oxy) bis 2,3,4,5,6-pentabromo-			v		
	139638-58-7	Propanol, 1,1'-[(1-methylethylidene)bis[2,6-dibromo-4,1-phenylene)oxy]]bis[3-(2,4,6-tribromophenoxy)-			v		
	-	Bis(tetrabromophenoxy) ethane			v		
Brominated aryls	85-22-3	Pentabromoethylbenzene		v	v		v
	87-82-1	Hexabromobenzene		v			v
	87-83-2	Pentabromotoluene		v	v		
	93-52-7	Benzene, (1,2-dibromoethyl)-		v			v
	147-82-0	2,4,6-Tribromoaniline		v			
	23488-38-2	Tetrabromoxylene		v	v		
	31780-26-4	Dibromostyrene		v		v	
	38521-51-6	Pentabromobenzyl bromide		v	v		
	59447-55-1	Pentabromobenzyl acrylate			v		
	61368-34-1	Tribromostyrene		v	v		
	84852-53-9	1,2-Bis(pentabromophenyl) ethane	v				
	-	Pentabromophenyl benzoate			v		
	-	Trichloromethyltetrabromobenzene			v		
Brominated alkanes and cycloalkanes	75-95-6	Pentabromoethane		v			
	79-27-6	1,1,2,2-Tetrabromoethane					v
	87-84-3	Pentabromochlorocyclohexane		v	v		
	1837-91-8	Hexabromocyclohexane		v	v		v
	3194-57-8	Tetrabromocyclooctane		v	v		v
	3322-93-8	1,2-Dibromo-4-(1,1-dibromomethyl)cyclohexane		v	v		v
	30178-92-8	Tetrabromocyclododecane		v	v		
	51936-55-1	Hexachlorocyclopentadienyl-dibromocyclooctane			v		
	-	Tetrabromo-2,3-dimethylbutane		v			
Brominated alkyl esters	5445-17-0	2-Bromopropanoic acid, methyl ester		v			
	5445-19-2	2-Bromohexanoic acid, methyl ester		v			
	-	2,2'-Dimethyl-3-bromopropanoic acid, isopropyl ester		v			

Group	CAS No.	Substance name	High tonnage	Aquatic hazard	Potential PBT/ vPvB	Possible risk	Low critical tonnage
Brominated phosphates	126-72-7	Tris(2,3-dibromopropyl)phosphate		v			
	5412-25-9	Bis(2,3-dibromopropyl)phosphoric acid		v			
	49690-63-3	Tris(2,4-dibromophenyl)phosphate			v		
	-	Tris(2,4,6-tribromophenyl)phosphate			v		
	-	Tris(tribromoneopentyl)phosphate			v		
Miscellaneous brominated organics	3066-70-4	2,3-Dibromopropylmethacrylate		v			
	3072-84-2	Epoxy resin, brominated		v			v
	3234-02-4	2,3-Dibromo-2-butene-1,4-diol		v		v	
	40703-79-5	5,6-Dibromohexahydro-2-phenyl-4,7-methano-1H-isoindole-1,3(2H)-dione					v
	41291-34-3	Ethylene-bis(5,6-dibromonorbornane-2,3-dicarboximide)				v	
Chloroalkyl phosphates and related substances	78-43-3	Tris(2,3-dichloro-1-propyl)phosphate		v			
	115-98-0	Bis(2-chloroethyl)vinylphosphonate		v			
	140-08-9	Tris-(2-chloroethyl)phosphite					v
	4351-70-6	Oligomeric chloroalkyl phosphate					v
	6145-73-9	Tris(2-chloro-1-propyl)phosphate	v	v		v	
	6294-34-4	Bis(2-chloroethyl)-2-chloroethylphosphonate based		v			v
	6749-73-1	Tris(dichloropropyl)phosphite		v			
	53461-82-8	Tetrakis(2-chloroethyl)diethylene-oxy diphosphate					v
	61090-89-9	Bis(1,3-dichloro-2-propyl)-(3-chloro-2,2-dibromomethylpropyl) phosphate		v	v		v
Non-halogenated alkyl phosphates and related substances	78-38-6	Diethylethylphosphonate		v			
	78-42-2	Tris(2-ethylhexyl) phosphate				v	
	78-51-3	Tri-butoxyethyl phosphate		v			
	101-02-0	Triphenyl phosphite		v			v
	126-73-8	Tri-n-butyl phosphate	v				
	301-13-3	Trioctyl phosphite		v			v
	512-56-1	Trimethylphosphate		v			
	1806-54-8	Trioctyl phosphate		v			v
	60763-39-5	Diphenyl isopropyl phosphate					v
	-	Xylyl diphenyl phosphate					v

Group	CAS No.	Substance name	High tonnage	Aquatic hazard	Potential PBT/ vPvB	Possible risk	Low critical tonnage
	-	Tris (isopropyl) phosphate		v			
	-	Bisphosphates	v				
Chlorendic acid derivatives	115-27-5	Chlorendic anhydride		v			
	1770-80-5	Dibutyl chlorendate		v	v		
	1773-89-3	Dimethyl chlorendate		v			
	18300-04-4	Dibromochlordene		v	v		v
Others	96-69-5	4,4'-Thio-bis(2-t-butyl-5-methylphenol)			v		
	108-78-1	Melamine	v				
	124-64-1	Tetrakis(hydroxymethyl)phosphonium chloride	v	v			
	593-85-1	Guanidine carbonate		v			
	2385-85-5	Dodecachlorooctahydrometheno-1H-cyclobutapentalene		v	v		v
	13560-89-9	Dodecachlorodimethan-o-dibenzocyclooctane		v	v		v
	20120-33-6	Dimethylphosphono-N-hydroxymethyl-3-propionamide	v				
	20208-95-1	Melamine phosphate		v			
	31107-44-5	Dodecachlorooctahydrodimethanodibenzofuran		v	v		
	-	Dimethyl-3-(hydroxymethylamino)-3-oxopropyl phosphonate	v				
	-	HET acids/others	v				

2. In many cases, further data will need to be gathered before an adequate assessment can be attempted. Should any decisions about hazard or risk depend on an estimated value, the performance of the predictive software must be checked in detail for each particular substance. Those substances flagging as high tonnage with data gaps could be suitable candidates for an ICCA/OECD-style hazard assessment, so that at least a basic but high quality data set can be assembled. Substances for which important data gaps exist have been listed in Appendix 7, though this is by no means exhaustive. The Project Database indicates those substances currently being assessed in international hazard/risk assessment programmes where some of these data may be available. Any further investigation should be conducted in parallel with these programmes where possible for greatest efficiency.

3. The Project Database is a unique resource, and should be kept up-to-date if possible. This will be far easier if it remains confidential.

4. Emissions during the service-life and disposal of flame retarded articles are potentially the most significant sources of environmental exposure, yet they are not well understood. Further research in this area would be very useful to ensure that decisions on the need for risk management are based on the most realistic assessment possible.

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CIA, 2002	Comments made by CIA on the second draft of the BREF (reference taken from ref 48 above; not reviewed)
Danish Environmental Protection Agency, 1999	Brominated Flame Retardants: Substance Flow Analysis and Assessment of Alternatives
Danish Environmental Protection Agency, 2001	Danish Environmental Protection Agency. Action Plan for Brominated Flame Retardants. (http://www.mst.dk/)
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Environment Agency, 2002a	Plastics in the Environment
Environment Agency, 2002b	EA Environment Action Spring 2002 waste supplement
Environment Agency, 2002c	Strategic monitoring of chemicals in the environment: Identification and investigation of potential PBT substances. Environment Agency August 2002
European Commission, 2002	EC 2002: IPPC Reference Document on Best Available Techniques for the Textiles Industry. European Commission, November 2002
European Commission, 2003	Technical Guidance Document on Risk Assessment, in support of Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances, and Commission Directive 93/67/EEC on Risk Assessment for new notified substances
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IAL Consultants, 1999	The European Flame Retardant Chemicals Industry, IAL Market Report, IAL Consultants, Ealing, London
Interscience Communications, 1998	[Proceedings of conference] Flame Retardants ’98, British Plastics Federation
IPCS, 1997	EHC 192: Flame Retardants: A General Introduction, IPCS, World Health Organisation, Geneva
KemI, 1996	The Flame Retardants Project, Swedish National Chemicals Inspectorate (KemI) Report 5/96
KemI, 1999	Phase-out of PBDEs and PBBs: Report on a Governmental Commission, the Swedish National Chemicals Inspectorate
Santillo, D. et al, 2003	Greenpeace Technical Research laboratories, Technical Note 01/2003.
Sweden, 2001	Information submitted by Sweden about Emission and Consumption Levels in some textile finishing mills (reference taken from ref 48 above; not reviewed)
Wiley, ca. 1991	*Flame Retardants*, Kirk-Othmer Encyclopaedia of Chemical Technology.

Reference Number	**IPCS Environmental Health Criteria summaries**	
EHC 44	Mirex	IPCS, World Health Organisation, Geneva, 1984
EHC 110	Tricresyl phosphate	IPCS, World Health Organisation, Geneva, 1990
EHC 111	Triphenyl Phosphate	IPCS, World Health Organisation, Geneva, 1991
EHC 152	Polybrominated Biphenyls	IPCS, World Health Organisation, Geneva, 1994
EHC 172	Tetrabromobisphenol-A and derivatives	IPCS, World Health Organisation, Geneva, 1995
EHC 173	Tris(2,3-dibromopropyl) phosphate and Bis(2,3-dibromopropyl) phosphate	IPCS, World Health Organisation, Geneva, 1995
EHC 185	Chlorendic Acid and Anhydride	IPCS, World Health Organisation, Geneva, 1996
EHC 209	Tris(2-chloroisopropyl) phosphate, Tris(1,3-dichloro-2-propyl) phosphate and Tris (2-chloroethyl) phosphate	IPCS, World Health Organisation, Geneva, 1998
EHC 218	Tris(2-ethylhexyl) phosphate, Tetrakis (hydroxymethyl) phosphonium chloride, Tetrakis (hydroxymethyl) phosphonium sulfate and Tri-butoxyethyl phosphate	IPCS, World Health Organisation, Geneva, 2000

ESR Risk Assessment Reports and Drafts	
Environment Agency, 2002c	ESR Draft RAR for Medium chain chlorinated paraffins (C14-17) (MCCPs)
Environment Agency, 2002d	ESR Draft RAR for Tris(2-chloro-1-methylethyl) phosphate (TCPP)
European Communities, 2000	ESR RAR for Short-chain chlorinated paraffins (C10 – 13) (SCCPs)
European Communities, 2000	ESR RAR for Pentabromodiphenyl ether
European Communities, 2002	ESR Draft RAR for Octabromodiphenyl ether
European Communities, 2002	ESR Draft RAR for Decabromodiphenyl ether
KEMI, 2002	ESR Draft RAR for Hexabromocyclododecane
UBA, 1998	ESR Draft RAR for Tris (2-chloroethyl) phosphate (TCEP)

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Meerts et al (2001). In vitro estrogenicity of polybrominated diphenyl ethers (PBDEs), hydroxylated PBDEs (OH-PBDEs) and several polybrominated bisphenol-A compounds. Environ Health Perspect. 109: 399-407 from ref 42
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Wenne, N. (2002). The new features of EG based fire retardants, British Plastics Federation, Flame Retardants 2002 conference, Interscience communications, 57-62, 2002

Other data sources used in the project database	
ASL	Approved Supply List (classifications)
CCRIS	Chemical Carcinogenesis Research Information System
CFDB	SRC ChemFate data base
DESRRAR	draft Risk Assessment Report under ESR

DK	Danish EPA: Brominated Flame Retardants: Substance Flow Analysis and Assessment of Alternatives
EEDB	Elsevier Ecotox database
ESRRAR	Risk Assessment Report under ESR
HSDB	Hazardous substances databank
IPCS###	IPCS EHC document number ###
IRIS	Integrated Risk Information System
IUCLID	International Uniform Chemicals Information Database, available from the Office for Official Publications of the European Communities, L-2985 Luxembourg, through 80 sales agents worldwide. The references to catalogue number are LB-NA-19-559-EN-Z or ISBN 92-828-8647-7.
MSDS (xxxxx)	Materials safety data sheet (source company)
NONS	Notification dossier for new substances (data and identification information present only in confidential version of the database)
PPDB	SRC PhysProp database
SIAR	OECD SIDS (screening initial data set) initial assessment report (available only for Melamine, CAS no. 108-78-1)
Other	Information direct from industry (source named)
	Lists available on the internet for various HPV programmes (see web pages)
	Open literature

9. USEFUL WEB SITES

Organisation	Website (http://…)
Manufacturers	
Akzo Chemicals	www.functionalchemicals.com/phosphorus/flame.htm
Albemarle	www.albemarle.com
Borax	www.borax.com
Budenheim	www.budenheim.es/applicat.htm
Ciba Speciality Chemicals	www.cibasc.com
Clariant	www.additives.clariant.com
Climax molybdenum	www.climaxmolybdenum.com/
Dead Sea Bromine Group	www.dsbg.com/brome/files.nsf/lookup/products.htm
Great Lakes Chemical Corporation	www.greatlakeschem.com
Nabaltec	www.nabaltec.de/seiten_e/index_e.html
Rhodia	www.rhodia.com
Joseph Storey Limited	www.josephstorey.co.uk
Unitex	www.unitexchemical.com/flame.htm
Trade associations	
Chemical Industries Association, Fire Retardants Sector Group	www.cia.org
The European Chemical Industry Council (CEFIC)	www.cefic.be/cefic
British Rubber Manufacturers Association	www.brma.co.uk/index.htm
Bromine Science and Environmental Forum	www.bsef.com
European Flame Retardants Association	efra.cefic.org/pages/fsmain.html
CIRCA (construction industry), Fire interest group	www.europa.int/comm/enterprise/construction/groups/groups.htm
Rapra (formerly the Rubber and Plastics Research Association – RAPRA)	www.rapra.com
European Brominated Flame Retardants Industry Panel	www.ebfrip.org

Organisation	Website (http://…)
Regulatory authorities	
Environment Agency	www.environment-agency.gov.uk
Health and Safety Executive (HSE)	www.hse.gov.uk/hthdir/noframes/chip/chip7.htm
Danish Environmental Protection Agency	www.mst.dk/udgiv/publications/1999/87-7909-416-3/html
KEMI (Sweden)	www.kemi.se
US Environmental Protection Agency	www.epa.gov
European Chemicals Bureau	ecb.jrc.it/existing-chemicals/
Other data sources	
CAS Registry	chemistry.rsc.org
ChemFinder	www.chemfinder.com
HSDB, IRIS, CCRIS	www.toxnet.nlm.nih.gov
ChemIndustry	www.chemindustry.com
CIA Sourceror	www.sourceror.co.uk
Sigma-Aldrich catalogue	www.sigma-aldrich.com
Other information	
IARC	www.193.51.164.11/
ENDS report online	www.endsreport.com
Greenpeace	www.greenpeace.org.uk
Worldwide Fund for Nature	www.panda.org
US EPA HPV	www.epa.gov/chemrtk/hpvchmlt.htm
ICCA HPV	www.cefic.org/activities/hse/mgt/hpv/hpvinit.htm
OECD HPV	cs3-hq.oecd.org/scripts/hpv/
Underwriters Laboratories	www.ul.com

10. GLOSSARY OF TERMS

Acronym	*Full name and description*
Acute toxicity	A toxic effect resulting from a short-term exposure. The effect is often mortality but may also include immobilisation.
Adsorption	The uptake of a substance from the water phase onto the solid phase. Such adsorption can typically occur from water onto sediments, suspended sediments and soil. Usually expressed as Koc, the adsorption coefficient normalised for the organic carbon content of the soil or sediment.
BCF	The Bioconcentration Factor is the ratio between the concentration in an organism (usually fish) and the concentration in water.
Bioaccumulation	A term to describe transfer of a substance from the environment into an organism. Thus bioaccumulation can occur typically from sediment, soil, water or via the food chain, or any combination of them. The transfer of a substance from water alone into an organism is called bioconcentration.
Bioavailability	The extent to which a substance is available for uptake into an organism.
Bioconcentration	The uptake of a substance into an organism from water. One component of the total process called bioaccumulation. Bioconcentration factors are usually determined as the ratio between the concentration in the organism and the exposure concentration.
Biodegradation	The actions of biological processes to break down a substance; usually implied to mean bacterial action (in soil, water or WWTP) whereby the organisms utilise the substance as food. Biodegradation can be complete, resulting in complete breakdown to minerals, or partial, producing particular end products, or may not occur at all. There are many standard tests of biodegradability, the ready and inherent studies leading to substances being described as ‘readily biodegradable’, ‘not inherently biodegradable’, ‘non-biodegradable’, etc.
CAS No./number	Chemical Abstracts Service (Registry Number), international unique number allocated to a chemical substance listed in the CAS Registry. CAS is a division of the American Chemical Society.
CHIP	Chemicals (Hazard Information and Packaging for Supply) Regulations, 2002
Chronic toxicity	A toxic effect resulting from a longer-term exposure. The effect is often a reduction in growth or reproduction.
CMR	Carcinogenicity, mutagenicity, reproductive toxicity
CSF	Chemicals Stakeholder Forum of the UK Government, created as part of the 2000 Chemicals Strategy. Web site http://www.defra.gov.uk/environment/chemistrat/stakehol/index.htm
Daphnia	A type of invertebrate commonly used in aquatic toxicity tests. Also sometimes referred to as a “water flea”.
DSD	EU Dangerous Substances Directive (76/464/EEC) List 1 and 2.
EC50	The concentration that causes adverse effects (but not necessarily mortality) in 50% of the exposed population. This is the toxicity measure normally used to express the results of short-term Daphnia and algal tests.
ECB	European Chemical Bureau. A part of the European Commission with responsibility for co-ordinating chemical regulation in the EU. http://ecb.ei.jrc.it/
EINECS	European Inventory of Existing Chemical Substances. This lists all chemical substances that were supplied to the market prior to 18th September 1981.
Endocrine disruptors	Substances that cause effects on the endocrine (or hormonal) system – these can be inhibition or stimulation. A potentially significant effect, not usually associated with toxicity.

Acronym	***Full name and description***
EQS	Environmental Quality Standard; a statutory maximum tolerable level of a specific substance
ESR	Existing Substances Regulation, EC 793/93. Under this regulation, data have been collected and published in IUCLID, and some substances have been selected to be subject to risk assessment on a priority basis.
EU	European Union
EUSES	European Union System for the Evaluation of Substances. A computer program that carries out many of the calculations in the TGD automatically.
Half-life	The time taken for 50% of the substance to be degraded or removed.
HPV(C)	High Production Volume (Chemical) – in the EU and Japan this implies production at over 1000 tonnes per annum, however in the US the trigger tonnage for an HPV is different, at 450 tonnes per annum.
HPVC or HPV	High Production Volume Chemical; according to the European Chemicals Bureau web-site a chemical is defined as a High Production Volume Chemical, when it is produced or imported in excess of 1,000 tonnes/year by at least one industry.
HSDB	Hazardous Substances Databank (see reference above)
Hydrolysis	The action of water to break down a substance. It is almost always partial, giving rise to definite end products. It usually depends strongly on pH.
ICCA	International Council of Chemical Associations; a council of leading trade associations representing chemical manufacturers worldwide. Leading the voluntary industry HPV programme of chemical assessment. http://www.iccahpv.com/
IUCLID	International Uniform ChemicaL Information Database; a database compiled by the Joint Research Centre of the European Chemicals Bureau based on data submitted by industry (see reference above).
L(E)C50	A short hand term to describe both LC50 and EC50 together.
L(E)L50	A short hand term to describe both LL50 and EL50 together
LC50	The concentration that is lethal to 50% of the exposed population. This is the toxicity measure normally used to express the results of short-term fish toxicity tests.
LD50	The dose that is lethal to 50% of the exposed population. This is the endpoint measured in sum mammalian toxicity studies.
Life cycle	The uses and applications of a substance from manufacture through to disposal or destruction.
Log Kow	The log10 value of the octanol-water partition coefficient. Also sometimes known as log P.
Long-term toxicity study	Long term toxicity studies are usually considered those where more than one life cycle stage of an organism is tested. The duration of the exposure period in a long-term study is normally >2 weeks. The end point derived from a long-term study is often a NOEC. The commonest examples of long-term studies are the fish early life stage (FELS) test and the Daphnia reproduction test. An algal growth inhibition test conducted over only 3 to 4 days is also considered a long-term study since it assesses effects over multiple generations.
NOEC	No Observed Effect Concentration. This is defined as the highest concentration tested that caused no adverse effects on the test organisms compared to controls. This is usually the endpoint measured on long-term toxicity studies.
OECD and OECD Guideline	Organisation for Economic Co-operation and Development. The OECD co-ordinates international chemical assessment activity under its HPV programme. It also publishes Guidelines for the Testing of Chemicals, which are the approved methods for carrying out tests on substances. OECD has also published guidance on testing difficult

Acronym	***Full name and description***
	substances. http://www.oecd.org/
OSPAR	The OSPAR Commission for protection of the marine environment of the North East Atlantic. http://www.ospar.org/eng/html/welcome.html.
Partition coefficient	The ratio between the concentrations of a substance in more than one phase. Examples include suspended sediment-water, sediment-water, soil-water, air-water (also known as Henry's constant), fish-water (better known as BCF), and octanol-water (better known as Kow)
PBT	Persistence, bioaccumulation potential and toxicity: chemical properties that are key indicators of potential concern for the environment.
Photodegradation	The action of light on a substance to break it down. It may be direct, or via a mediator (photosensitiser) which traps light energy and then transfers it to the substance.
Photo-oxidation	Action of light to generate oxidising agents in the air, such as the hydroxyl radical, which then can oxidise substances.
PPDB	Syracuse Research Corporation PhysProp Database (see reference above).
QSAR	Quantitative Structure-Activity Relationship, a mathematical relationship between properties of a chemical compound.
SIDS	Screening Information Data Set. Dossier of chemical data, prepared for OECD assessment (see OECD)
Short-term toxicity study	Short-term studies normally only assess effects on one sensitive life-stage of an organism. The duration of the exposure period typically ranges between <1day to 4 days. The end point derived from a short-term study is often an LC50 or EC50. The common short-term toxicity studies are the 96-hour fish toxicity test, the 48-hour Daphnia toxicity test. An EC50 obtained from a 72-96 hour growth inhibition test with a unicellular alga is also considered to be a short-term result.
SIDS	Screening Information Datasets. These are compiled for OECD priority substances for the purposes of environmental and human health hazard assessment. http://www.oecd.org/ehs/sidstable/index.htm
TGD	Technical Guidance Document on Risk Assessment (in support of Commission Directive 93/67/EEC on risk assessment for new notified substances, Commission Regulation 1488/94 on risk assessment for existing substances, Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market), European Chemicals Bureau, European Commission, 2003 Web site http://ecb.jrc.it/existing-chemicals/
vPvB	Very persistent and very bioaccumulative. See also PBT

Appendix 1: The Access Database

This discussion assumes familiarity with the basic functioning and terminology of Microsoft Access, and no detailed explanation of how to use the basic tools is offered.

The Project Database is constructed mainly on the basis of three key tables of information, the contents of which are set out below. The Project Database unique number links these tables. Supporting information is provided in further tables which can be used to 'look up' information.

The main data table is *Substance Information*. It contains the information on identity, overall scale of availability, and environmental fate properties. Information contained includes CAS and EINECS number, trade names, suppliers, tonnage in the UK and EU, physicochemical and environmental fate and distribution properties.

The breakdown of applications/use pattern is in the table entitled *Industry data*. Information contained includes polymer types, final products if known, use of synergists, fraction (usually by weight) of the flame retardant substance in the final product.

The table entitled *Effects* contains the ecotoxicological data, i.e. details of tests. Information contained includes species, time scale, endpoints, and results. The priority ranking (discussed in section 7) is also included (based on toxicity to most sensitive species). The source of reference is also given.

The tables of supporting information set out the types of flame retardant, types of mode of action, and polymer type abbreviation glossary (e.g. PU = polyurethane).

The chief uses of the Project Database are in the queries and the 'front-end' form. The information may also be printed in the form of Access Reports. Many queries have been created, from the findings of which the sector summary tables were developed. These queries are named for the applications listed in section 5, Appendix 5 and associated tables. The main query, called *all linked* links the main substance information (identification, overall supply tonnage, and chemical properties) with a breakdown of the applications and also the ecotoxicological data. The current version of the front-end form links the substance information with the industrial applications; the ecotoxicological data are not shown.

The queries may be used to search for data as required in the usual way. Through knowledge of the location of the terms of interest, and through familiarity with the Project Database in terms of the types of data entered against a particular item (e.g. text or numbers, true/false) it is possible to search for the data required. It is recommended that the user first becomes familiar with the Project Database by opening the tables, and also investigating their design.

N.B. Two versions of the Project Database are available from the Project Manager on request. One holds confidential data for a number of substances (e.g. tonnage and use pattern details), and so can only be provided to regulatory authorities. The other version is non-confidential.

Appendix 2: The Contents of the Project Record

The contents of the Project Record are set out below.

1.	**CONTACT WITH INDUSTRY**	
1.1	Summary of contacts	Extends the summary version given in the main report.
1.2	Consultation meeting reports	Details of discussions with consultees, by telephone and face-to-face. Email communications are not included.
2.	**SUBSTANCES, DATA AND APPROACH**	
2.1	CAS search strategies and results	Details of the search terms used, and hit rates. For papers obtained see below.
2.2	Literature	References and some brief summaries for books, reports and papers consulted in the course of the project.
2.3	Filling data gaps	Strategy for estimating the properties where measured data were not available. Expands upon the information given in the main report.
2.4	Environment Agency data	Details of consultation with the Agency to obtain monitoring data
2.5	Generic risk assessment of flame retardants	Describes the principles and outcomes of this approach, formerly used as a tool for prioritisation.
3.	**WEB SITES**	
		Sites consulted in the course of the project, with web addresses and brief comments
APPENDICES		
A1.	Typical enquiry letters	
A2.	Questionnaire for distribution by trade associations	

Appendix 3: Environment Agency monitoring data

The National Centre for Environmental Data and Surveillance was asked in 2001 to search centrally held Environment Agency data bases for environmental monitoring concentration data for sixteen of the highest priority flame retardant substances. A search of the “WIMS“ database revealed that monitoring data was held for only two of the substances (TCEP and TCPP) and that these had been collected by only one Agency region (Midland) to monitor historical contamination from a former production site.

The list of substances searched:

CAS No.	**Name**
79-94-7	Tetrabromobisphenol-A
115-96-8	Tris(monochloroethyl) phosphate (TCEP)
124-64-1	Tetrakis(hydroxymethyl) phosphonium chloride types
756-79-6	Dimethyl methyl phosphonate
1163-19-5	Decabromodiphenyl ether
1309-64-4	Antimony oxide
1332-07-6	Zinc borate
3296-90-0	Dibromoneopentyl glycol
12036-37-2	Zinc stannate
13674-84-5	Tris(2-chloro-1-propyl) phosphate (TCPP)
13674-87-8	Tris(1,3-dichloro-2-propyl) phosphate (TDCP)
21645-51-2	Aluminium trihydrate
25637-99-4	Hexabromocyclododecane
32534-81-9	Pentabromodiphenyl ether
32536-52-0	Octabromodiphenyl ether
68333-79-9	Ammonium polyphosphate

Appendix 4: Details of data gap filling

A4.1 Introduction

Property prediction was performed using the established quantitative structure-activity relationships (QSARs) provided in the Syracuse Research Corporation (SRC) software package EPIWIN (version 3.05). The Chemicals Assessment Section of the National Centre for Ecotoxicology and Hazardous Substances uses the suite, so full discussion of the QSARs used in the programs is not presented here. For more details, the SRC web site on http://esc.syrres.com/ can be consulted. All the programs have been described in peer-reviewed journals.

Ideally, the performance of the programs for the structural types under consideration should be investigated, and certainly is required if any decision is strongly dependent on a measured value. Whilst test data are optimal for evaluating the properties of a substance it is apparent that predictive methods can play a valuable role in cases where such data are lacking. Predictive methods can however only be applied to substances that fall within groups defined by properties and modes of action for which prediction software algorithms have been established. It is also essential that the algorithms are validated before being applied generally. Validation is achieved by comparing predicted data with data obtained by testing where such data exist. In the absence of test data considerable caution must be exercised in interpreting predicted data. The performance checks used in this report have not utilised every available data point, but only those available to the authors in 2001.

Care must also be taken to ensure that the interpretation of predicted aquatic ecotoxicity is consistent with those of other measured or predicted properties – most notably water solubility. A predicted ecotoxic concentration that exceeds the water solubility of a test substance should be treated with caution since this implies that undissolved test substance would be contributing to the toxic effects on the test organism. This is not supported by the science. It is much more likely that one, or other, or both of the toxic concentration or water solubility are in error.

In the case of substances for which it is clear that the programs' estimates do not represent the environmental form of the substance (e.g. octanol-water partition coefficients of strong acids or bases), the values would need to be adjusted as appropriate, by estimating the value for environmentally relevant pH values.

A4.2 Ecotoxicity

Sample output

```
ECOSAR Program (v0.99f) Results:
===============================
SMILES : FC(F)(C(F)(F)C1(F)F)C1(F)F
CHEM   : Cyclobutane, octafluoro-
CAS Num:
ChemID1:
ChemID2:
ChemID3:
MOL FOR: C4 F8
MOL WT : 200.03
Log Kow: 2.29  (KowWin estimate)
Melt Pt:
Wat Sol: 450.1 mg/L  (calculated)

ECOSAR v0.99f Class(es) Found
------------------------------
Neutral Organics
                                                                  Predicted
ECOSAR Class                 Organism            Duration  End Pt   mg/L (ppm)
===========================  ==================  ========  ======   ==========
Neutral Organic SAR        : Fish                14-day    LC50      150.144
(Baseline Toxicity)

Neutral Organics           : Fish                96-hr     LC50       79.159
Neutral Organics           : Fish                14-day    LC50      150.144
Neutral Organics           : Daphnid             48-hr     LC50       86.536
Neutral Organics           : Green Algae         96-hr     EC50       55.011
Neutral Organics           : Fish                30-day    ChV        10.686
Neutral Organics           : Daphnid             16-day    EC50        5.038
Neutral Organics           : Green Algae         96-hr     ChV         6.505
Neutral Organics           : Fish  (SW)          96-hr     LC50       20.864
Neutral Organics           : Mysid Shrimp        96-hr     LC50       18.561
Neutral Organics           : Earthworm           14-day    LC50     1001.794 *

 Note:  * = asterick designates: Chemical may not be soluble
        enough to measure this predicted effect.
         Fish and daphnid acute toxicity log Kow cutoff: 5.0
         Green algal EC50 toxicity log Kow cutoff: 6.4
         Chronic toxicity log Kow cutoff: 8.0
         MW cutoff: 1000
```

A4.3 Biodegradability

The Biodegradation Probability Program (BIOWIN) estimates the probability for the rapid aerobic biodegradation of an organic chemical in the presence of mixed populations of environmental micro-organisms. Estimates are based upon fragment constants that were developed using multiple linear and non-linear regression analyses.

Version 3 of the Biodegradation Probability Program includes a model that predicts the time required for primary and ultimate biodegradation. Primary biodegradation is the transformation of a parent compound to an initial metabolite. Ultimate biodegradation is the transformation of a parent compound to carbon dioxide and water. The model is based upon a survey of 17 biodegradation experts conducted by EPA in which the experts were asked to evaluate 200 chemicals in terms of the time required to achieve ultimate and primary biodegradation. In the current survey, each expert rated the ultimate and primary biodegradation of each chemical on a scale of 1 to 5. For the purposes of the Biodegradation Probability Program, the ratings correspond to the following time units: 5 - hours; 4 - days; 3 - weeks; 2 - months; 1 - longer. The ratings were then averaged for each chemical.

A matrix was then formulated for both primary and ultimate biodegradation using the same 36 fragments and molecular weight parameter as used in the Linear/Non-Linear Model. Linear regressions were then performed on the matrices using the averaged expert ratings as the solution matrices.

Calculation of Ultimate/Primary Rating

The ultimate or primary rating of a chemical is calculated by summing the values (fragment coefficients) of each fragment and then adding the summation to a constant coefficient value that was determined for the entire data set. The constant coefficient is 3.8477 for primary biodegradation and 3.1992 for ultimate biodegradation. The summed values of each fragment coefficient and the model constant appear in the "VALUE" column of the results screens .

Ultimate/Primary Rating in Time Units

The following table summarises the conversion of a rating (as predicted by the ultimate-primary models) to the time required to achieve ultimate or primary biodegradation:

Predicted Rating	Time Required for Biodegradation
5.0	hours
4.5	hours- days
4.0	days
3.5	days- weeks
3.0	weeks
2.5	weeks- months
2.0	months
1.0	longer

```
Fragment Coefficients for Biodegradation Models
Ultimate-Primary Biodegradability
Coefficients in BIOWIN v 4.00:
                                              ULTIMATE     PRIMARY
 Nitroso   [-N-N=O]                          -0.38513      0.01848
 Linear C4 terminal chain  [CCC-CH3]          0.29834      0.26907
 Aliphatic alcohol  [-OH]                     0.15997      0.12945
 Aromatic alcohol  [-OH]                      0.05638      0.03969
 Aliphatic acid   [-C(=O)-OH]                 0.364605     0.38557
 Aromatic acid   [-C(=O)-OH]                  0.08787      0.00775
 Aldehyde   [-CHO]                            0.02232      0.19664
 Ester   [-C(=O)-O-C]                         0.14021      0.22896
 Amide   [-C(=O)-N  or -C(=S)-N]             -0.05421      0.20543
 Triazine ring (symmetric)                   -0.24586     -0.05752
 Aliphatic chloride   [-CL]                  -0.17318     -0.10061
 Aromatic chloride   [-CL]                   -0.20660     -0.16534
 Aliphatic bromide   [-Br]                    0.02895      0.03538
 Aromatic bromide   [-Br]                    -0.13600     -0.15351
 Aromatic iodide   [-I]                      -0.04494     -0.12707
 Aromatic fluoride   [-F]                    -0.40694      0.01346
 Carbon with 4 single bonds & no hydrogens   -0.21212     -0.15344
 Aromatic nitro  [-NO2]                      -0.16959     -0.10838
 Aliphatic amine   [-NH2  or  -NH-]           0.02444      0.04328
 Aromatic amine   [-NH2  or  -NH-]           -0.13495     -0.10838
 Cyanide / Nitriles   [-C#N]                 -0.08238     -0.06520
 Sulfonic acid / salt -> aromatic attach      0.14221      0.02162
 Sulfonic acid / salt -> aliphatic attach     0.19259      0.17714
 Polyaromatic hydrocarbon (4 or more rings)  -0.79934     -0.70224
 Pyridine ring                               -0.21417     -0.01874
 Aromatic ether  [-O-aromatic carbon]        -0.05812      0.07712
 Aliphatic ether  [C-O-C]                    -0.00867     -0.00974
 Ketone   [-C-C(=O)-C-]                      -0.02248     -0.02222
 Tertiary amine                              -0.25480     -0.28800
 Phosphate ester                              0.15373      0.46535
 Alkyl substituent on aromatic ring          -0.07485     -0.06853
 Azo group   [-N=N-]                         -0.30036     -0.05279
 Carbamate or Thiocarbamate                  -0.04671      0.19363
 Trifluoromethyl group   [-CF3]              -0.51296     -0.27440
 Unsubstituted aromatic (3 or less rings)    -0.58591     -0.34280
 Unsubstituted phenyl group (C6H5-)           0.02201      0.00489
 Molecular Weight Parameter                  -0.00220987  -0.001442756
 Equation Constant                            3.19917051   3.847737
```

Sample output

```
SMILES : c(cccc1)(c1)C
CHEM   : Benzene, methyl-
MOL FOR: C7 H8
MOL WT : 92.14
--------------------------- BIOWIN v4.00 Results ----------------------------

    Linear Model Prediction    :  Biodegrades Fast
    Non-Linear Model Prediction:  Biodegrades Fast
    Ultimate Biodegradation Timeframe:  Weeks
    Primary  Biodegradation Timeframe:  Days-Weeks
    MITI Linear Model Prediction    :  Readily Degradable
    MITI Non-Linear Model Prediction:  Readily Degradable
```

Biowin Sample output continued

```
------+-----+--------------------------------------------+---------+---------
 TYPE | NUM |        BIOWIN FRAGMENT DESCRIPTION         |  COEFF  |  VALUE
------+-----+--------------------------------------------+---------+---------
 Frag |  1  |  Alkyl substituent on aromatic ring         | 0.0547 |  0.0547
 Frag |  1  |  Unsubstituted phenyl group (C6H5-)         | 0.1281 |  0.1281
 MolWt|  *  |  Molecular Weight Parameter                 |        | -0.0439
 Const|  *  |  Equation Constant                          |        |  0.7475
============+============================================+=========+=========
   RESULT   |     LINEAR BIODEGRADATION PROBABILITY      |         |  0.8864
============+============================================+=========+=========

------+-----+--------------------------------------------+---------+---------
 TYPE | NUM |        BIOWIN FRAGMENT DESCRIPTION         |  COEFF  |  VALUE
------+-----+--------------------------------------------+---------+---------
 Frag |  1  |  Alkyl substituent on aromatic ring         | 0.5771 |  0.5771
 Frag |  1  |  Unsubstituted phenyl group (C6H5-)         | 1.7991 |  1.7991
 MolWt|  *  |  Molecular Weight Parameter                 |        | -1.3084
============+============================================+=========+=========
   RESULT   |   NON-LINEAR BIODEGRADATION PROBABILITY    |         |  0.9833
============+============================================+=========+=========

 A Probability Greater Than or Equal to 0.5 indicates --> Biodegrades Fast
 A Probability Less Than 0.5 indicates --> Does NOT Biodegrade Fast

------+-----+--------------------------------------------+---------+---------
 TYPE | NUM |        BIOWIN FRAGMENT DESCRIPTION         |  COEFF  |  VALUE
------+-----+--------------------------------------------+---------+---------
 Frag |  1  |  Alkyl substituent on aromatic ring         | -0.0749 | -0.0749
 Frag |  1  |  Unsubstituted phenyl group (C6H5-)         |  0.0220 |  0.0220
 MolWt|  *  |  Molecular Weight Parameter                 |         | -0.2036
 Const|  *  |  Equation Constant                          |         |  3.1992
============+============================================+=========+=========
   RESULT   |   SURVEY MODEL - ULTIMATE BIODEGRADATION   |         |  2.9427
============+============================================+=========+=========

------+-----+--------------------------------------------+---------+---------
 TYPE | NUM |        BIOWIN FRAGMENT DESCRIPTION         |  COEFF  |  VALUE
------+-----+--------------------------------------------+---------+---------
 Frag |  1  |  Alkyl substituent on aromatic ring         | -0.0685 | -0.0685
 Frag |  1  |  Unsubstituted phenyl group (C6H5-)         |  0.0049 |  0.0049
 MolWt|  *  |  Molecular Weight Parameter                 |         | -0.1329
 Const|  *  |  Equation Constant                          |         |  3.8477
============+============================================+=========+=========
   RESULT   |   SURVEY MODEL - PRIMARY BIODEGRADATION    |         |  3.6512
============+============================================+=========+=========

 Result Classification:   5.00 -> hours     4.00 -> days    3.00 -> weeks
  (Primary & Ultimate)    2.00 -> months    1.00 -> longer

------+-----+--------------------------------------------+---------+---------
 TYPE | NUM |        BIOWIN FRAGMENT DESCRIPTION         |  COEFF  |  VALUE
------+-----+--------------------------------------------+---------+---------
 Frag |  1  |  Aromatic-CH3                               | 0.0415 |  0.0415
 Frag |  5  |  Aromatic-H                                 | 0.0082 |  0.0411
 MolWt|  *  |  Molecular Weight Parameter                 |        | -0.2741
 Const|  *  |  Equation Constant                          |        |  0.7121
============+============================================+=========+=========
   RESULT   |  MITI LINEAR BIODEGRADATION PROBABILITY    |         |  0.5206
============+============================================+=========+=========
```

Biowin Sample output continued

```
------+-----+--------------------------------------------+---------+---------
 TYPE | NUM |        BIOWIN FRAGMENT DESCRIPTION         |  COEFF  |  VALUE
------+-----+--------------------------------------------+---------+---------
 Frag |  1  |  Aromatic-CH3                              |  0.3072 |  0.3072
 Frag |  5  |  Aromatic-H                                |  0.1201 |  0.6007
 MolWt|  *  |  Molecular Weight Parameter                |         | -2.6600
============+============================================+=========+=========
   RESULT   | MITI NON-LINEAR BIODEGRADATION PROBABILITY |         |  0.6843
============+============================================+=========+=========

 A Probability Greater Than or Equal to 0.5 indicates --> Readily Degradable
 A Probability Less Than 0.5 indicates --> NOT Readily Degradable
-----------------------------------------------------------------------------
```

A4.4 Physicochemical properties

The Log Octanol-Water Partition Coefficient Program (KOWWIN) estimates the logarithmic octanol-water partition coefficient (log K_{ow}) of organic compounds. KOWWIN uses a "fragment constant" methodology to predict log K_{ow}. In a "fragment constant" method, a structure is divided into fragments (atom or larger functional groups) and coefficient values of each fragment or group are summed together to yield the log K_{ow} estimate.

To estimate log K_{ow}, KOWWIN initially separates a molecule into distinct atoms/fragments. In general, each non-hydrogen atom (e.g. carbon, nitrogen, oxygen, sulfur, etc.) in a structure is a "core" for a fragment; the exact fragment is determined by what is connected to the atom. Several functional groups are treated as core "atoms"; these include carbonyl (C=O), thiocarbonyl (C=S), nitro (-NO2), nitrate (ONO2), cyano (-C/N), and isothiocyanate (-N=C=S). Connections to each core "atom" are either general or specific; specific connections take precedence over general connections. For example, aromatic carbon, aromatic oxygen and aromatic sulfur atoms have nothing but general connections; i.e., the fragment is the same no matter what is connected to the atom. In contrast, there are 5 aromatic nitrogen fragments: (a) in a five-member ring, (b) in a six-member ring, (c) if the nitrogen is an oxide-type {i.e. pyridine oxide}, (d) if the nitrogen has a fused ring location {i.e. indolizine}, and (e) if the nitrogen has a +5 valence {i.e. N-methyl pyridinium iodide}; since the oxide-type is most specific, it takes precedence over the other four. The aliphatic carbon atom is another example; it does not matter what is connected to -CH3, -CH2-, or -CH< , the fragment is the same; however, an aliphatic carbon with no hydrogens has two possible fragments: (a) if there are four single bonds with 3 or more carbon connections and (b) any other not meeting the first criteria.

Results of two successive multiple regressions (first for atom/fragments and second for correction factors) yield the following general equation for estimating log K_{ow} of any organic compound:

log K_{ow} =Sum(fini) + Sum(cjnj) + 0.229
(n = 2413 r2 = 0.981 sd = 0.219 mean error = 0.161)
where Sum(fini) is the summation of f i (the coefficient for each atom/fragment) times n i (the number of times the atom/fragment occurs in the structure), and
Sum(cjnj) is the summation of c j (the coefficient for each correction factor) times nj (the number of times the correction factor occurs (or is applied) in the molecule).

Sample output

```
                  Log Kow(version 1.66 estimate): 0.17

Experimental Database Structure Match:
  Name     :  2-Hydroxypropyl acrylate
  CAS Num  : 999-61-1
  Exp Log P:  0.35
  Exp Ref  :  Hansch,C et al. (1995)

SMILES : O=C(OCC(O)C)C=C
CHEM   : 2-Hydroxypropyl acrylate
MOL FOR: C6 H10 O3
MOL WT : 130.14
-------+-----+--------------------------------------------+---------+--------
 TYPE  | NUM |        LOGKOW FRAGMENT DESCRIPTION         |  COEFF  |  VALUE
-------+-----+--------------------------------------------+---------+--------
 Frag  |  1  |  -CH3    [aliphatic carbon]                | 0.5473  |  0.5473
 Frag  |  1  |  -CH2-   [aliphatic carbon]                | 0.4911  |  0.4911
 Frag  |  1  |  -CH     [aliphatic carbon]                | 0.3614  |  0.3614
 Frag  |  1  |  =CH2    [olefinic carbon]                 | 0.5184  |  0.5184
 Frag  |  1  |  =CH- or =C<  [olefinc carbon]            | 0.3836  |  0.3836
 Frag  |  1  |  -OH     [hydroxy, aliphatic attach]       |-1.4086  | -1.4086
 Frag  |  1  |  -C(=O)O  [ester, aliphatic attach]       |-0.9505  | -0.9505
 Const |     |  Equation Constant                         |         |  0.2290
-------+-----+--------------------------------------------+---------+--------
                                                         Log Kow   =   0.1717
-----------------------------------------------------------------------------
```

The program WSKOWWIN estimates the water solubility (WSol) of an organic compound using the compounds log octanol-water partition coefficient (K_{ow}).

The estimation methodology is:
log S (mol/L) = 0.796 - 0.854 log K_{ow} - 0.00728 MW + Corrections
log S (mol/L) = 0.693 - 0.96 log K_{ow} - 0.0092(Tm-25) - 0.00314 MW + Corrections
(used when a measured MP is available)
(where MW is molecular weight, Tm is melting point (MP) in deg C [used only for solids]).

Corrections are applied to 15 structure types (e.g. alcohols, acids, selected phenols, nitros, amines, alkyl pyridines, amino acids, PAHS, multi-nitrogen types, etc); application and magnitude depends on available MP.

Results of two successive multiple regressions (first for atom/fragments and second for correction factors) yield the following general equation for estimating log K_{ow} of any organic compound:

log K_{ow} =Sum(fini) + Sum(cjnj) + 0.229
(n = 2413   r2 = 0.981   sd = 0.219   mean error = 0.161)
where Sum(fini) is the summation of f i (the coefficient for each atom/fragment) times n i (the number of times the atom/fragment occurs in the structure), and
Sum(cjnj) is the summation of c j (the coefficient for each correction factor) times nj (the number of times the correction factor occurs (or is applied) in the molecule).

Sample output

```
                  Log Kow(version 1.66 estimate): 0.17

Experimental Database Structure Match:
  Name     :  2-Hydroxypropyl acrylate
  CAS Num  : 999-61-1
  Exp Log P:  0.35
  Exp Ref  :  Hansch,C et al. (1995)

SMILES : O=C(OCC(O)C)C=C
CHEM   : 2-Hydroxypropyl acrylate
MOL FOR: C6 H10 O3
MOL WT : 130.14
-------+-----+--------------------------------------------+---------+--------
 TYPE  | NUM |        LOGKOW FRAGMENT DESCRIPTION         |  COEFF  |  VALUE
-------+-----+--------------------------------------------+---------+--------
 Frag  |  1  |  -CH3    [aliphatic carbon]                | 0.5473  |  0.5473
 Frag  |  1  |  -CH2-   [aliphatic carbon]                | 0.4911  |  0.4911
 Frag  |  1  |  -CH     [aliphatic carbon]                | 0.3614  |  0.3614
 Frag  |  1  |  =CH2    [olefinic carbon]                 | 0.5184  |  0.5184
 Frag  |  1  |  =CH- or =C<  [olefinc carbon]            | 0.3836  |  0.3836
 Frag  |  1  |  -OH     [hydroxy, aliphatic attach]       |-1.4086  | -1.4086
 Frag  |  1  |  -C(=O)O  [ester, aliphatic attach]        |-0.9505  | -0.9505
 Const |     |  Equation Constant                         |         |  0.2290
-------+-----+--------------------------------------------+---------+--------
                                                        Log Kow   =   0.1717
----------------------------------------------------------------------------
```

The program WSKOWWIN estimates the water solubility (WSol) of an organic compound using the compounds log octanol-water partition coefficient (K_{ow}).

The estimation methodology is:
$\log S$ (mol/L) = 0.796 - 0.854 log K_{ow} - 0.00728 MW + Corrections
$\log S$ (mol/L) = 0.693 - 0.96 log K_{ow} - 0.0092(Tm-25) - 0.00314 MW + Corrections
(used when a measured MP is available)
(where MW is molecular weight, Tm is melting point (MP) in deg C [used only for solids]).

Corrections are applied to 15 structure types (e.g. alcohols, acids, selected phenols, nitros, amines, alkyl pyridines, amino acids, PAHS, multi-nitrogen types, etc); application and magnitude depends on available MP.

A4.5 Octanol-water partition coefficient

This property is particularly important, because it is needed for other predictions, and is also used itself as an input to environmental fate models. Table A4.1 shows a comparison of measured values with predicted values.

Table A4.1 Measured and predicted log K_{ow} values

Name	CAS No.	Type	log Kow	KOWWIN	MEASURED value type	KOWWIN set to 8?
Tetrabromobisphenol-A	79947	B	4.54	7.2	IUCLID	
Hexabromobenzene	87821	B	6.07	7.33	HSDB	
Pentabromochlorocyclohexane	87843	B	4.72	4.71	PPDB	
2,4,6-Tribromophenol	118796	B	4.13	4.18	PPDB	
Tris(2,3-dibromopropyl)phosphate	126727	B	3.71	4.19	HSDB	
Vinyl bromide	593602	B	1.57	1.52	PPDB	
2,4-Dibromophenol	615587	B	3.22	3.29	PPDB	
Decabromodiphenyl ether	1163195	B	6.27	8	ESRRAR	Yes
Dibromoneopentyl glycol	3296900	B	1.06	0.85	PPDB	
Hexabromocyclododecane	25637994	B	5.63	7.74	DESRRAR	
Pentabromodiphenyl ether	32534819	B	6.57	7.66	ESRRAR	
Octabromodiphenyl ether	32536520	B	6.29	8	ESRRAR	Yes
Hexachlorocyclopentadiene	77474	C	5.04	4.63	PPDB	
Chlorendic acid	115286	C	2.3	3.14	IPCS185	
Dodecachlorooctahydrometheno-1H-cyclobutapentalene	2385855	C	5.28	7.01	HSDB	
Tris (2-chloroethyl) phosphate	115968	CP	1.78	1.63	DESRRAR	
Tris (2-chloroisopropyl) phosphate	13674845	CP	2.59	2.89	IPCS209, MSDS (Rhodia)	
Tris(1,3-dichloro-2-propyl)phosphate	13674878	CP	3.76	3.65	HSDB	
Melamine	108781	N	-1.37	-0.38	HSDB	
Diethylethylphosphonate	78386	P	0.66	0.89	PPDB	
Triethyl phosphate	78400	P	0.8	0.87	HSDB	
Tris(2-ethylhexyl) phosphate	78422	P	4.22	8	IPCS218	Yes
Tri-butoxyethyl phosphate	78513	P	3.65	3	HSDB	
Triphenyl phosphate	115866	P	4.59	4.7	PPDB	
Tri-n-butyl phosphate	126738	P	4.0	3.82	HSDB	
Trimethylphosphate	512561	P	-0.65	-0.6	PPDB	
Tris(1-aziridinyl)phosphine	545551	P	-0.62	-0.56	PPDB	
Dimethylmethyl phosphonate	756796	P	-0.61	-0.59	PPDB (MSDS Rhodia has 0.46)	
Dimethyl phosphonate	868859	P	-1.2	-1.13	IUCLID	
2-Ethylhexyl diphenyl phosphate	1241947	P	5.73	6.3	HSDB	
Tricresyl phosphate	1330785	P	5.11	4.9	HSDB	
Dimethylphosphono-N-hydroxymethyl-3-propionamide	20120336	P	-1.68	-3.09	IUCLID	
Trixylyl phosphate	25155231	P	5.63	7.98	HSDB	
Cresyl diphenyl phosphate	26444495	P	4.51	4.77	PPDB	
Isopropylphenyl diphenyl phosphate	28108998	P	5.31	6.16	HSDB	
Isodecyl diphenyl phosphate	29761215	P	5.44	7.28	HSDB	
Tris(isopropylphenyl) phosphate	68937417	P	5.1	8	IUCLID	Yes

These are presented graphically in figure A5.1. It can be seen that the correlation and accuracy are high particularly between log K_{ow} or KOWWIN >-1.5 and <5.1 (see regression statistics below which apply to this range), outside which there is more variability in performance. This may be due in part to the fact that measuring high and low log K_{ow} can be difficult, which diminishes the quality of the data on which the predictions are based. No particular class of substances was found to be problematic.

Regression Statistics	
R Square	0.9212
Adjusted R Square	0.9176
Standard Error	0.6221
Observations	24

	Coefficients	*Standard Error*
Intercept	0.0213	0.195
KOWWIN	0.9222	0.058

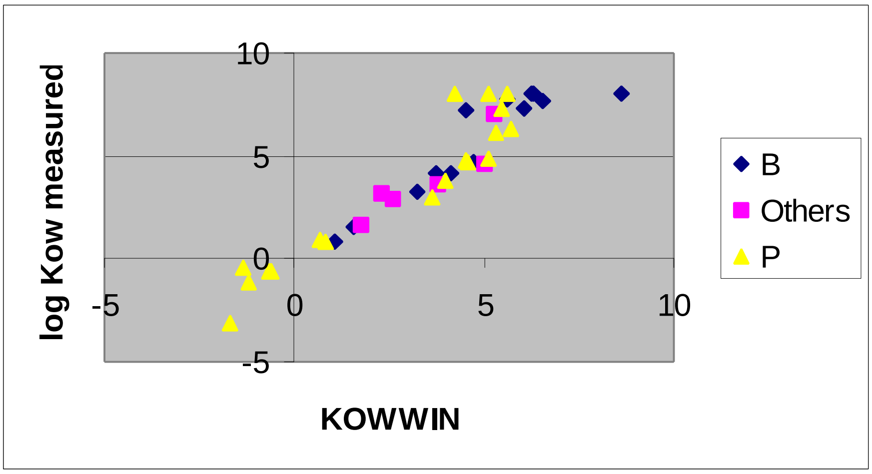

Figure A4.1: Correlation between measured log K_{ow} and that predicted by KOWWIN.

A4.6 Water solubility

Comparison of predicted water solubility with measured values

Water solubility values are important for several purposes. Some substances have ecotoxicity data with no measured water solubility, and it is possible that the toxicity studies might have been conducted at 'loadings' above the true solubility.

To validate prediction, it is necessary to compare measured values with predicted first.

The method is the SRC WSKOWWIN program. For the best predictions molecular weight, measured melting point and log K_{ow} are necessary.

The equation used is: $\log S \text{ (mol/L)} = 0.693 - 0.96 \log K_{ow} - 0.0092(Tm-25) - 0.00314 \text{ MW}$

The results are expressed in the following table (A4.2) and figure (A4.2). There are outliers, but they are not particularly related to flame retardant type. The graph shows the line of perfect fit (not the regression line) and therefore suggests predictions as made by the program can be used, but the results can only be considered acceptable as an order of magnitude, as shown by regression statistics:

Regression Statistics	
R Square	0.85081
Adjusted R Square	0.84432
Standard Error	1.01895
Observations	25

	Coefficients	*Standard Error*
Intercept	0.1973	0.216
logWSpred	0.85219	0.074

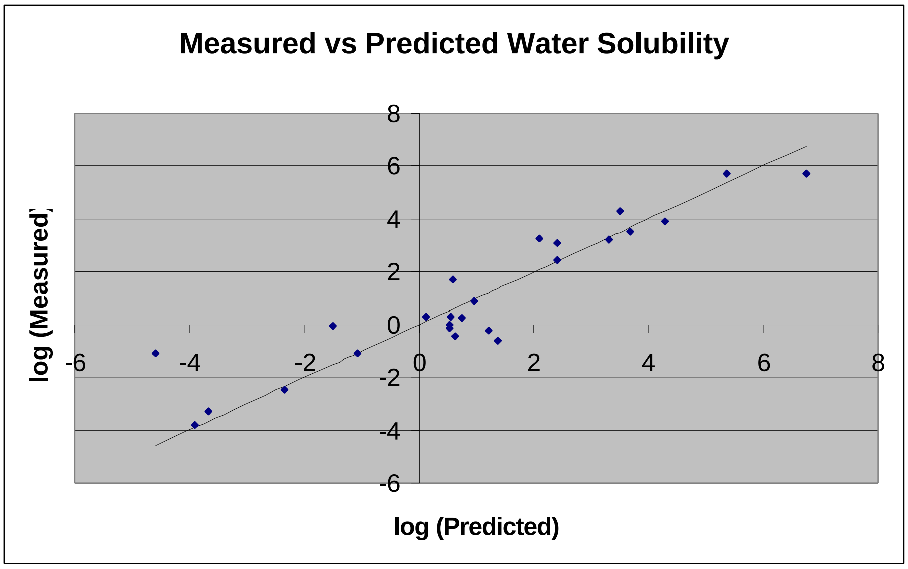

Figure A4.2: Correlation between measured Water Solubility and that predicted by WSKOWWIN

Table A4.2 Comparison of measured and predicted water solubility values

CAS No.	Name	Type	Water Solubility (mg/l)	Melting Point (deg C)	log Kow	Mol wt	logS	Prediction mg/l	logWSpred	logWSmeas
79947	Tetrabromobisphenol-A	B	0.08	181	4.54	543.88	-6.8084	0.08455	-1.0729	-1.0969
87821	Hexabromobenzene	B	1.60E-04	327	6.07	551.49	-9.6443	0.00013	-3.9027	-3.7959
118796	2,4,6-Tribromophenol	B	50	93	4.13*	330.80	-4.9361	3.83225	0.58345	1.69897
126727	Tris(2,3-dibromopropyl)phosphate	B	8	5.5	3.71	697.62	-4.8797	9.20221	0.96389	0.90309
615587	2,4-Dibromophenol	B	1.90E+03	38	3.22	251.91	-3.3088	123.722	2.09245	3.27875
3296900	Dibromoneopentyl glycol	B	2.00E+04	109.5	1.06	261.94	-1.9245	3116.81	3.49371	4.30103
25637994	Hexabromocyclododecane	B	3.40E-03	180	5.63	641.70	-8.1527	0.00451	-2.3454	-2.4685
32536520	Octabromodiphenyl ether	B	5.00E-04	212	6.29	801.38	-9.5821	0.00021	-3.6783	-3.301
77474	Hexachlorocyclopentadiene	C	1.80	-9	5.04	272.77	-4.6891	5.58083	0.7467	0.25527
2385855	Dodecachlorooctahydrometheno-1H-cyclobutapentalene	C	0.085	485	5.28	545.55	-10.321	2.6E-05	-4.584	-1.0706
115968	Tris (2-chloroethyl) phosphate	CP	7.82E+03	-55	1.78	285.49	-1.1762	19026.2	4.27935	3.89321
13674845	Tris (2-chloroisopropyl) phosphate	CP	1.60E+03	-42	2.59	327.57	-2.2056	2040.49	3.30973	3.20412
19186971	Tris (3-Bromo-2,2(Bromomethyl)Propyl)Phosphate	CP	0.9	183	3.7	1018.5	-7.5107	0.03142	-1.5027	-0.0458
108781	Melamine	N	3.24E+03	354	-1.37	126.12	-1.4146	4854.75	3.68617	3.51055
78400	Triethyl phosphate	P	5.00E+05	-56	0.8	182.16	0.09822	228387	5.35867	5.69897
78422	Tris(2-ethylhexyl) phosphate	P	0.6	-7.4	4.22	434.65	-4.4249	16.3387	1.21322	-0.2218
78513	Tri-butoxyethyl phosphate	P	1.20E+03	-70	3.65	398.48	-3.1882	258.333	2.41218	3.07918
115866	Triphenyl phosphate	P	1.9	49	4.59	326.29	-4.9588	3.58801	0.55485	0.27875
126738	Tri-n-butyl phosphate	P	280	-79	4	266.32	-3.0264	250.587	2.39896	2.44716
512561	Trimethylphosphate	P	5.00E+05	-54	-0.65	140.08	1.60395	5627622	6.75032	5.69897
1241947	2-Ethylhexyl diphenyl phosphate	P	1.90	-30	5.73	362.41	-5.4398	1.31654	0.11943	0.27875
1330785	Tricresyl phosphate	P	0.36	-33	5.11	416.37	-4.9864	4.29613	0.63308	-0.4437
26444495	Cresyl diphenyl phosphate	P	0.24	-38	4.51	356.42	-4.1762	23.7576	1.3758	-0.6198
29761215	Isodecyl diphenyl phosphate	P	0.75	-50	5.44	390.46	-5.0654	3.3584	0.52613	-0.1249
68937417	Tris(isopropylphenyl) phosphate	P	1.0	-19	5	452.54	-5.1232	3.40786	0.53248	0

* an alternative log Kow = 3.7 is also available

WSKOWWIN also can predict solubility for substances when there is no melting point available. Its predictive ability is usually slightly less good than when there is a melting point input. This method is used in that case, and all the predictions have been added to the database.

Table A4.3 gives those substances where an ecotoxicity result is available and a water solubility prediction is required.

Table A4.3 Substances for which a predicted water solubility value is needed to interpret ecotoxicity results

Name	CAS No.	Type	Value predicted / comment
Pentabromophenol	608-71-9	B	0.21 mg/l
Tetrabromophthalic anhydride	632-79-1	B	0.15 mg/l
Ethylene-bistetrabromophthalimide	32588-76-4	B	8 x 10^{-7} mg/l
Chlorinated diphosphate ester	-	CP	No prediction possible
Chlorinated phosphate ester	-	CP	No prediction possible
Halogen-phosphate ester mixture	-	CP	No prediction possible
Tris(2,3-dichloro-1-propyl)phosphate	78-43-3	CP	8.7 mg/l
Mixture of chlorinated diphosphate and chlorinated phosphonate esters	-	CP	No prediction possible
Ammonium salts of phosphorous and sulphuric acids	-	I	No prediction possible
Antimony (III) oxide	1309-64-4	I	No prediction possible– likely to be very low
Magnesium carbonate, basic	12125-28-9	I	No prediction possible – likely to be moderate
Potassium fluorotitanate	16919-27-0	I	No prediction possible
Mixture of ammonium and urea salts of polyphosphoric acid	-	I	No prediction possible – likely to be high
Mixture of salts of bromine, polyphosphoric acid and sulphamic acid	-	I	No prediction possible
Mixture of salts of polyphosphoric acid	-	I	No prediction possible– likely to be high
Guanyl urea	141-83-3	N	1.5 x 10^5 mg/l
Ammonium salt of complex phosphonate	-	P	No prediction possible
Mixture of complex phosphonates	-	P	No prediction possible
Organo phosphate/phosphonate	-	P	No prediction possible
Dimethyl phosphonate	868-85-9	P	2.2 x 10^6 mg/l

A4.7 Ecotoxicity

Predictions of ecotoxicity were needed where the substance has:

- relatively high tonnage, above 300 tonnes/year in the EU, *or*
- a measured water solubility.

Predictions were not performed for the inorganic substances. Predicted values, obtained using the ECOSAR program, are not tabulated here, but the processes of examining the accuracy of the method used is described below.

The overall conclusions drawn regarding the effectiveness of ECOSAR in predicting the fish 96-hour LC_{50} values for chlorinated phosphate, phosphate and brominated flame retardant substances were as follows:

- A true comparison of reported and ECOSAR predicted values was only possible for four chlorinated phosphate, five phosphate and two brominated substances. The reported toxicity values of the remaining substances were not quantified precisely, being expressed either as <x or >y where x and y are respectively the lowest or highest test concentration.
- ECOSAR predictions of LC_{50} values for the eleven substances are, with two exceptions, within an order of magnitude of the reported values. For the two outliers the predicted values are within a factor of 35.
- In the majority of cases ECOSAR underestimated the LC_{50} values, i.e. the predicted values are higher than the reported values.
- ECOSAR predictions were valuable in confirming that the toxicity of a substance was close to its water solubility in circumstances where the reported LC_{50} appeared to be anomalously high.
- A cautious approach should be adopted to interpreting predicted values in circumstances where they are close to the water solubility of the test substance and the water solubility is low (<1 mg/l). Experience suggests that under such circumstances the predicted toxicity is often not manifest in the test and that this is often a consequence of the difficulty of achieving exposure concentrations close to the limit of solubility of the test substance.

ECOSAR therefore appears to have a useful role in determining the toxicity of these three classes of flame retardant substances.

Halogenated phosphates

The available data are shown in Table A4.4. It is difficult to make any meaningful comparison between the reported and predicted LC_{50} values for the substances with CAS numbers 38051-10-4 and 19186-97-1 because the reported values are only expressed as being greater than the highest test concentration. Furthermore, there appears to be an anomaly between some or all of the reported LC_{50} values and the reported or predicted water solubility value. The anomaly is represented by the LC_{50} values for the substances being significantly higher than the water solubility values. The most probable explanation for the anomaly is that the true LC_{50} values for the substances lie close to their water solubility. However because of the difficulty of achieving a true solution at the solubility concentration it is often deemed necessary to add an excess of test substance. Expressing the exposure concentration relative to the nominal concentration results in an LC_{50} value that can be considerably in excess of the true value.

Table A4.4 Measured and predicted ecotoxicological results for halogenated phosphates

Substance name	CAS Number	Water solubility (mg/l)	Reported 96-h LC$_{50}$ to fish (mg/l)	Lowest reported 96-h LC$_{50}$ to fish (mg/l)	Mean reported 96-h LC$_{50}$ to fish (mg/l)	ECOSAR 96-h LC$_{50}$ to fish (mg/l)
2,2-Bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate)	38051-10-4	2.1[1]	>10*	>10	>10	9.6
Tris (3-Bromo-2,2(bromomethyl)-propyl)Phosphate	19186-97-1	0.90	>100*	>100*	>100*	0.06
Tris (2-chloroisopropyl) phosphate	13674-84-5	1600	51	51	62	8.9
			84			
			51			
Tris(1,3-dichloro-2-propyl)phosphate	13674-87-8	7.0	1.1	1.1	1.1	4.7
			1.1			
Tris(2,3-dichloro-1-propyl)phosphate	78-43-3	8.7[1]	1.1	1.1	1.1	4.7
Tris (2-chloroethyl) phosphate	115-96-8	7800	250	6.3	153	35
			6.3			
			170			
			250			
			90			

[1] Predicted water solubility

*Indicates test concentration exceeding water solubility

Predicted LC$_{50}$ values for the four remaining substances are within an order of magnitude of all the reported values and within a factor of about 5 of the lowest values and the means of all the values. For three of the four substances the predicted LC$_{50}$ values are higher than the reported values.

Non-halogenated phosphates

The available data are shown in Table A4.5. It is difficult to make any definitive comparisons between the reported and predicted LC_{50} values for the substances with CAS Numbers 78-38-6, 756-79-6, 20120-33-6, 1482-17-6 and 29761-21-5 because the reported values are only expressed as being greater than the highest test concentration. However, for three of these substances that are readily soluble (CAS Numbers 78-38-6, 756-79-6 and 20120-33-6) it is possible to state that the ECOSAR predictions do confirm the low reported toxicity of the substances.

For the substances with CAS Numbers 26444-49-5, 29761-21-5, 78-42-2 and 25155-23-1 there appears to be an anomaly between some or all of the reported LC_{50} values and the reported or predicted water solubility values. As for the chlorinated phosphates, and as a result of the same probable cause, the anomaly is represented by the LC_{50} value for a substance being significantly higher than the water solubility value.

Predicted LC_{50} values for the five remaining substances are within factors of between 3 and 35 of all the reported values, 1.5 and 35 of the lowest values and 1.1 and 35 of the means of all the values. The predicted values are higher than the reported values for four of the five substances and approximately equal for the other substance.

Brominated organics

The available data are shown in Table A4.6. It is not possible to make any meaningful comparison between the reported and predicted LC_{50} values for the substances with the CAS Numbers 25637-99-4 and 632-79-1 and the substance with CAS Number 126-72-7. This is because the reported values are only expressed as being either greater than the highest or below the lowest test concentration. For one substances with a reported LC50 greater than the highest test concentration (CAS Number 3296-90-0) it is however possible to state that the ECOSAR prediction does confirm the low reported toxicity of the substance.

For the substances with CAS Numbers 25637-99-4, 608-71-9, 79-94-7 and 632-79-1 there appears to be an anomaly between some or all of the reported LC_{50} values and the reported or predicted water solubility value. The probable reason for this anomaly is discussed earlier in respect of the halogenated phosphates.

Predicted LC_{50} values for the two remaining substances are within an order of magnitude of all the reported values, the lowest reported values, and the means of all the values. For one substances the predicted LC_{50} value is higher than the reported values whilst for the other substance it is either higher or equal to the reported values.

Conclusions

The ECOSAR program is useful for the present project as a means of establishing the highest value of acute fish LC_{50} that might be anticipated. The extent of validation has necessarily been limited, but the values are of use for purposes of prioritisation.

Table A4.5 Measured and predicted ecotoxicological results for non-halogenated phosphates

Substance name	CAS Number	Water solubility (mg/l)	Reported 96-h LC$_{50}$ to fish (mg/l)	Lowest reported 96-h LC$_{50}$ to fish (mg/l)	Mean reported 96-h LC$_{50}$ to fish (mg/l)	ECOSAR 96-h LC$_{50}$ to fish (mg/l)
Cresyl diphenyl phosphate	2644-49-5	0.24	10*	10	10	1.0
Diethylethylphosphonate	78-38-6	Miscible	>100	>100	>100	1400
Dimethyl phosphonate	868-85-9	2200000[1]	230	230	230	71000
Dimethylmethyl phosphonate	756-79-6	Miscible	>1000	>1000	>1000	25000
Dimethylphosphono-N-hydroxymethyl-3-propionamide	20120-33-6	>800000	>1000	>1000	>1000	>9.0 x 10^6
Ethylene diamine phosphate	14852-17-6	3000	>100	>100	>100	0.06
			>100			
Isodecyl diphenyl phosphate	29761-21-5	0.75	>0.030	>0.030	>0.030	0.060
			>0.030			
			>1000*			
			>1000*			
Tri-butoxyethyl phosphate	78-51-3	1100	6.8	6.8	14	9.5
			11			
			16			
			24			
Tricresyl phosphate	1330-78-5	0.36	0.26	0.061	0.9	1.0
			3.3*			
			0.061			
			0.15			
			0.75*			
Trimethylphosphate	512-56-1	500000	6.7	6.7	6.7	240
Triphenyl phosphate	115-86-6	1.9	0.66	0.30	0.42	1.0
			0.31			
			0.30			
Tris(2-ethylhexyl) phosphate	78-42-2	0.60	>100*	>100*	>100*	0.005
Tris(isopropylphenyl) phosphate	68937-41-7	1.4	1-10*	1-10	1-10	0.008
Trixylyl phosphate	25155-23-1	0.89	100*	100*	100*	0.026

[1] Predicted water solubility

*Indicates test concentration exceeding water solubility

Table A4.6 Measured and predicted ecotoxicological results for brominated flame retardants

Substance name	CAS Number	Water solubility (mg/l)	Reported 96 h LC_{50} to fish (mg/l)	Lowest reported 96 h LC_{50} to fish (mg/l)	Mean reported 96 h LC_{50} to fish (mg/l)	ECOSAR 96 h LC_{50} to fish (mg/l)
2,4,6-Tribromophenol	118-79-6	50	1.0	0.24	2.6	2.2
			6.6			
			0.24			
Dibromoneopentyl glycol	3296-90-0	20000	>500	>500	>500	2300
Hexabromocyclododecane	25637-99-4	0.0034	>0.0068*	>0.0025	>0.0025	0.0020
			>0.0025			
			>100*			
			>100*			
Pentabromophenol	608-71-9	0.21[1]	0.090	0.090	0.090	0.26
			93*			
Tetrabromobisphenol A	79-94-7	0.080	0.40*	0.40*	0.47*	0.050
			0.54*			
Tetrabromophthalic anhydride	632-79-1	0.15[1]	>10	>10	>10	0.13
Tris(2,3-dibromopropyl)phosphate	126-72-7	8.0	<1	<1	≤1	4.0
		8.0	1			

[1] Predicted water solubility

*Indicates test concentration exceeding water solubility

Appendix 5: Breakdown of flame retardant types and uses in different sectors

All of the materials that are named in the Project Database are listed in Table 4.1 in the main text. Not all of these are broken down, although several of the most common plastic types are tabulated below.

Note:

There are substances in the Project Database that do not have CAS numbers and cannot be readily identified. In addition, notified new substances were included in the confidential Project Database only when the notifiers have given permission. It is therefore difficult to be certain about the numbers of substances (for instance, it is impossible to categorically rule out duplication) and so the numbers contained in the tables should be considered as indicators only.

It is important to note that the significant substances named in the tables are significant in the industry overall, but not necessarily significant in that particular application.

Table A5.1 Textiles

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	20	16	1	13	7	5
Number with known tonnage	11	11	1	7	5	3
Significant substances	Antimony (III) oxide	DecaBDE, HBCD, 1,2-Bis(2,4,6-tribromophenoxy) ethane		Tris(isopropylphenyl) phosphate		Melamine
Additive/Reactive	A/R	A/R	A	R	A/R	A
Examples* of loading rates, and use of synergists	8 – 10%, 15 – 20%, 20 – 30%. Can be used with halogenated flame retardants	5 – 10%, 10 – 15%, can be used with antimony trioxide	Unknown	7%.	5 – 12%	Unknown
Common uses	Wool, cotton, polyester, and polyamide fibres and their blends, for e.g. upholstery fabrics, roof insulating fabric	Polyester and cellulosic fibres, modacrylic fibres, nonwovens. Used for drapery, upholstery and clothing, and textile coatings	Textile finishes and back-coatings	Cellulosic, nylon and polyester fibres, for e.g. upholstery fabric, garments and flexible ducting	Car, rail and aircraft furnishing trim	Unknown

*(these should not necessarily be considered representative of the whole category)

Table A5.2 Carpeting

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	1	2	0	0	0	0
Number with known tonnage	1	1	-	-	-	-
Additive/Reactive	A	A	-	-	-	-
Examples* of loading rates, and use of synergists	Unknown	10-15%. Can be used with antimony oxide	-	-	-	-
Common uses	Carpet backing	Carpet backing, synthetic carpets	-	-	-	-

*(these should not necessarily be considered representative of the whole category)

5.3 Plastics

5.3a Polyethylene
5.3b Polypropylene
5.3c Unsaturated polyesters
5.3d Epoxies
5.3e PVC
5.3f Polystyrenes
5.3g Polyurethane

Table A5.3a Polyethylene

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	3	9	1	4	2	3
Number with known tonnage	3	4	1	0	0	2
Significant substances	Aluminium trihydroxide	TBBPA derivatives				Melamine derivatives
Additive/Reactive	A	A/R	Unknown	A	Unknown	A
Examples* of loading rates, and use of synergists	2-10%.	Can be used with antimony oxide	Can be used with antimony oxide	Unknown	Unknown	-
Common uses	Plastics, foams, polymer adhesives	Thermoset resins, crosslinked PE. Final use unknown	-	Thermoplastic and thermoset resins. Final application unknown	Thermoplastic resins. Final application unknown	-

*(these should not necessarily be considered representative of the whole category)

Table A5.3b Polypropylene

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	2	12	2	3	0	3
Number with known tonnage	2	5	2	2	-	2
Significant substances	Aluminium trihydroxide	DecaBDE, TBBPA derivatives	Chlorendic acid			Melamine derivatives
Additive/Reactive	A	A/R	A/R	A	-	A
Examples* of loading rates, and use of synergists	2-10%; can be used with nitrogen- or halogen-containing	10-15%, can be used with antimony oxide	Can be used with antimony oxide	Unknown	-	-
Common uses	Plastics, foams, polymer adhesives	Tapes and fibres; textiles, drapery and upholstery; electrical and electronic products	Unknown	Unknown	-	-

*(these should not necessarily be considered representative of the whole category)

Table A 5.3c Polyesters

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	5	13	3	5	4	3
Number with known tonnage	3	11	3	1	3	3
Significant substances	Aluminium trihydroxide	TBBPA, DecaBDE	Chlorendic acid			Melamine derivatives
Additive/Reactive	A	A/R	A/R	A	A	A
Examples* of loading rates, and use of synergists	Unknown	5-30%, can be used with antimony trioxide	Unknown	Unknown	3-12%	-
Common uses	Resins, textiles; final use unknown	Floor tiles, bowling balls, furniture parts, sewer-pipe coupling compound, encapsulating electrical parts; resins for electrical and electronic products	Electrical systems, panelling, engineering, plastic and paints	Textiles	Resins, final use unknown; furniture, textiles, roof insulation, car, rail, aircraft furnishings	-

*(these should not necessarily be considered representative of the whole category)

Table A5.3d Epoxies

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	4	8	2	2	1	4
Number with known tonnage	4	5	2	2	1	3
Significant substances	Antimony V oxide	TBBPA derivatives				Melamine derivatives
Additive/Reactive	A	A/R	R	A	Unknown	A
Examples* of loading rates, and use of synergists	2-10%.	5-35%. Can be used with antimony oxide	Can be used with antimony oxide	Unknown	Unknown	-
Common uses	Resins and adhesives, plastics, foams, polymer adhesives	Resins for electronics applications	Resins, final products unknown	Thermoplastic and thermoset resins; final application unknown	Unknown	Unknown

*(these should not necessarily be considered representative of the whole category)

Table A5.3e PVC

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	7	3	0	12	2	0
Number with known tonnage	4	0	-	7	2	-
Significant substances	Antimony (III) oxide			Tri(isopropylphenyl) phosphate		
Additive/Reactive	A	A	-	Unknown	A	-
Examples* of loading rates, and use of synergists	0.75%	Unknown	-	Unknown	5-12%	-
Common uses	Wire/cable coating, transit vehicle interior, carpet backing and building materials. Open celled foam for trim padding	Wire/cable insulation, film and sheeting, etc	Note: Medium-chain chlorinated paraffins are used in PVC as plasticisers.	Film and sheeting, upholstery fabric and moulded PVC, wire/cable insulation and electrical applications	Furniture, textiles, roof insulation, car, rail, aircraft furnishings	-

*(these should not necessarily be considered representative of the whole category)

Table A5.3f Polystyrenes

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	1	25	0	3	3	2
Number with known tonnage	1	14	-	2	0	2
Significant substances	Red phosphorus	1,2-bis(pentabromophenyl) ethane, TBBPA, HBCD, DecaBDE		Trixylyl phosphate		Melamine derivatives
Additive/Reactive	A	A/R	-	A	Unknown	A
Examples* of loading rates, and use of synergists	2-10%. Can be used with nitrogen or halogen containing flame retardants	10-15%. Can be used with antimony oxide	-	Unknown	Unknown	Unknown
Common uses	Plastics, foams, polymer adhesives	Electrical and electronics parts, insulation panels, packaging	-	Unknown	Unknown	Unknown

*(these should not necessarily be considered representative of the whole category)

Table A5.3g Polyurethane

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	3	13	4	12	11	4
Number with known tonnage	3	10	4	5	5	3
Significant substances	Aluminium trihydroxide	Pentabromophenol	SCCP, MCCP		TCPP, TCEP, TDCP, V6	
Additive/Reactive	A	A/R	A/R	A	A	A
Examples* of loading rates, and use of synergists	2 –10%, ≤ 75%	1 – 2 %, ~10%, 5 – 30%. Can be used with antimony trioxide, phosphorus-based flame retardants or melamine derivatives	10 – 14%. Can be used with antimony trioxide	Unknown	≤ 2%, 3 – 14%. Can be used with melamine	3 – 17%. Can be used with TCPP
Common uses	Rigid and flexible foams for mattress padding etc.	Rigid foams; flexible foams, e.g. for upholstered furniture and mattresses; elastomers for instrument casings and wire insulation	Adhesives and sealants	Rigid foams, flexible foams, e.g. for upholstered furniture, transportation and bedding	Rigid foams, flexible foams, e.g. for upholstered furniture. Rigid foams for building insulation and refrigerator casings	Soft foams for upholstered furniture and bedding

*(these should not necessarily be considered representative of the whole category)

Table A5.4 Rubber

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	4	2	3	1	0	0
Number with known tonnage	4	2	3	0	-	-
Significant substances	Aluminium trihydroxide, antimony (III) oxide		Chlorinated paraffins			
Additive/Reactive	A	A	A	Unknown	-	-
Examples* of loading rates, and use of synergists	Mostly 1-15%, 43%. Can be used with antimony oxide, halogenated flame retardants	Unknown	1-10%, 15%. Can be used with antimony oxide or aluminium hydroxide.	Unknown	-	-
Common uses	Automotive, aerospace and railway applications, military face masks, gaskets/sealing rings, belts	Unknown	Conveyor belts, hoses, gaskets; building and automotive applications	Unknown	-	-

*(these should not necessarily be considered representative of the whole category)

Table A5.5 Coatings

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	4	20	3	7	5	6
Number with known tonnage	3	14	3	4	3	3
Significant substances	Ammonium polyphosphate	HBCD, 1,2-Bis(2,4,6-tribromophenoxy)ethane				Melamine derivatives
Additive/Reactive	A	A/R	A/R	unknown	A	unknown
Examples* of loading rates, and use of synergists	Can be used with melamine	Can be used with antimony trioxide	10%	7%	5 – 12%	unknown
Common uses	Intumescent coatings, paints, wire and cable coatings	Textile coatings, paints, lacquers and varnishes, paper coatings	Paints and inks, textile coatings	Intumescent coatings, latex paints, lacquers and varnishes, textile coatings	Intumescent coatings, paints, lacquers and varnishes, textile coatings	Intumescent coatings

*(these should not necessarily be considered representative of the whole category)

Table A5.6 Construction

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	5	3	1	Used, number not known	2	0
Number with known tonnage	5	3	1		2	-
Significant substances	Aluminium trihydroxide, boric acid and borate	HBCD	MCCP		TCPP, TCEP	
Additive/Reactive	A	A/R	A	-	A	-
Examples* of loading rates, and use of synergists	20 – 30%	Used with antimony trioxide or other brominated flame retardants.	15%	-	5 – 12%	-
Common uses	Insulation, flooring and other building materials. Particularly in PVC and cellulosics	Engineering plastics and insulation	Unspecified building applications	-	Foams for building and roof insulation	-

*(these should not necessarily be considered representative of the whole category)

Table A5.7 Electrical and electronic equipment

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	4	10	2	2	0	0
Number with known tonnage	3	5	2	2	-	-
Significant substances	Aluminium trihydroxide	TBBPA, HBCD, DecaBDE	Chlorendic acid			
Additive/Reactive	A	A/R	A/R	Unknown	-	-
Examples* of loading rates, and use of synergists	Unknown	10 – 15%, 34%. Can be used with antimony trioxide	-	Unknown	-	-
Common uses	PVC wire and cable coatings, electrical insulation and unspecified applications	Printed circuit boards, electronics parts, lighting fixtures, wire/cable insulation	Electrical systems	PVC wire/cable insulation and other unspecified applications; electrical parts	-	-

*(these should not necessarily be considered representative of the whole category)

Table A5.8 Fluids

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	0	0	0	2	0	0
Number with known tonnage	-	-	-	1	-	-
Significant substances				Tricresyl phosphate		
Additive/Reactive	-	-	-	Unknown	-	-
Examples* of loading rates, and use of synergists	-	-	-	Unknown	-	-
Common uses	-	-	-	Hydraulic fluid, other unspecified flame retardant fluid	-	-

*(these should not necessarily be considered representative of the whole category)

Table A5.9 Paper

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	7	3	0	0	1	1
Number with known tonnage	5	3	-	-	1	0
Significant substances						Melamine derivative
Additive/Reactive	A	A/R	-	-	R	Unknown
Examples* of loading rates, and use of synergists	15-20%, 20-30%.		-	-	Unknown	Unknown
Common uses	Roof insulation material, other unspecified paper use	Paper coatings, packaging	-	-	Not specified	Not specified

*(these should not necessarily be considered representative of the whole category)

Table A5.10 Transport

	Inorganic	Brominated	Chlorinated	Organo-phosphorus	Halogenated phosphorus	Nitrogen-based
Number of substances	4	2	1	2	3	0
Number with known tonnage	4	2	1	2	2	-
Significant substances			MCCP			
Additive/Reactive	A	A/R	A	Unknown	A	-
Examples* of loading rates, and use of synergists	<15%. Can be used with halogenated flame retardants	Unknown	15%	Unknown	3.4-3.5%, 5-12%. Can be used with Tris(isopropylphenyl) phosphate	-
Common uses	In rubbers for unspecified automotive, aerospace and railway applications. In PVC for vehicle interiors	Automotive parts	Unspecified automotive applications	Automotive parts including air filters	PU and other foams for road/rail/air interior furnishings	-

*(these should not necessarily be considered representative of the whole category)

Appendix 6: Details of substances with low priority hazard rankings

A6.1 No chronic or acute aquatic toxicity at the limit of water solubility

C-0

CAS No.	Name
1163-19-5	Decabromodiphenyl ether
32536-52-0	Octabromodiphenyl ether
155613-93-7	Brominated trimethylphenylindane

A-0 Measured

CAS No.	Name
-	Ammonium salts of phosphorous and sulphuric acids
-	Mixture of ammonium and urea salts of polyphosphoric acid
-	Mixture of salts of bromine, polyphosphoric acid and sulphamic acid
-	Mixture of salts of polyphosphoric acid
78-42-2	Tris(2-ethylhexyl) phosphate
632-79-1	Tetrabromophthalic anhydride
762-04-9	Phosphinic acid, diethyl ester
3296-90-0	Dibromoneopentyl glycol
13654-09-6	Decabromobiphenyl
18755-43-6	Phosphonic acid, propyl-, dimethyl ester
19186-97-1	Tris (3-bromo-2,2(bromomethyl)propyl)phosphate
20566-35-2	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, mixed esters with diethylene glycol and propylene glycol
25713-60-4	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine {Tris(tribromophenyl) cyanurate}
29761-21-5	Isodecyl diphenyl phosphate
32588-76-4	Ethylene-bistetrabromophthalimide
37640-57-6	Melamine cyanurate
58965-66-5	Tetradecabromodiphenoxybenzene
59447-55-1	Pentabromobenzyl acrylate
59447-57-3	Poly(pentabromobenzylacrylate)
68333-79-9	Ammonium polyphosphate
84852-53-9	1,2-Bis(pentabromophenyl) ethane
181028-79-5	Phosphoric trichloride, reaction product with Bisphenol A and Phenol

A-0 Predicted

CAS No.	Name
-	1,4-Bis(bromomethyl)-tetrabromobenzene
-	Bis(tetrabromophenoxy) ethane
-	Pentabromophenylbenzoate
-	Trichloromethyltetrabromobenzene
-	Tris(2,4,6-tribromophenyl)phosphate
-	Tris(hydroxymethyl)phosphine oxide
-	Tris(tribromoneopentyl)phosphate
-	Tris(tribromophenyl)cyanurate
96-13-9	2,3-Dibromopropanol
141-83-3	Guanyl urea

CAS No.	Name
756-79-6	Dimethylmethyl phosphonate
1502-47-2	2,5,8-Triamino-1,3,4,6,7,9,9b-heptaaza-phenalene (Cyamelurotriamide)
2781-11-5	O,O-diethyl-N,N-bis(2-hydroxyethyl)aminomethylphosphonate
10310-38-0	Ethylene bis(tris(2-cyanoethyl)-phophonium)bromide
21850-44-2	Tetrabromobisphenol A bis(2,3-dibromopropyl) ether
25357-79-3	Tetrabromophthalic acid, sodium salt
40703-79-5	5,6-Dibromohexahydro-2-phenyl-4,7-methano-1H-isoindole-1,3(2H)-dione
41291-34-3	Ethylene-bis(5,6-dibromonorbornane-2,3-dicarboximide)
49690-63-3	Tris(2,4-dibromophenyl)phosphate
53506-00-6	1,4-di(cyanoethylphospine oxide)-2,3,5,6-tetramethylbenzene
55566-30-8	Tetrakis(hydroxymethyl) phosphonium sulfate (2:1)
61262-53-1	Benzene, 1,1'- 1,2-ethanediylbis(oxy) bis 2,3,4,5,6-pentabromo-

A6.2 Substances that do not meet the PBT criteria

N.B. Some substances in this list are not considered by industry to be flame retardants. Inorganics have been excluded because the PBT criteria were developed for organic chemicals.

Investigation stopped as soon as it was clear that any one particular criterion was not fulfilled. These substances are not necessarily harmless. Readers are advised to consult the Project Database to review information that is relevant to this classification.

CAS no.	Name
-	Xylyl diphenyl phosphate
-	Dimethyl-3-(hydroxymethylamino)-3-oxopropyl phosphonate
-	Tris(hydroxymethyl)phosphine oxide
-	Tris (isopropyl) phosphate
-	2,2'-Dimethyl-3-bromo-propanoic acid, isopropyl ester
-	Tetrabromo-2,3-dimethylbutane
75-95-6	Pentabromoethane
78-30-8	Tris(o-cresyl)phosphate
78-32-0	Tri (p-cresyl phosphate)
78-38-6	Diethylethylphosphonate
78-40-0	Triethyl phosphate
78-42-2	Tris(2-ethylhexyl) phosphate
78-43-3	Tris(2,3-dichloro-1-propyl)phosphate
79-08-3	Bromoacetic acid
79-27-6	1,1,2,2-Tetrabromoethane
87-82-1	Hexabromobenzene
87-84-3	Pentabromochlorocyclohexane
93-52-7	Benzene, (1,2-dibromoethyl)-
96-13-9	2,3-Dibromopropanol
96-32-2	2-Bromoacetic acid, methyl ester
101-02-0	Triphenyl phosphite
102-54-5	Ferrocene
105-36-2	2-Bromoacetic acid, ethyl ester
115-28-6	Chlorendic acid
115-88-8	Diphenyl octyl phosphate
115-89-9	Methyl diphenyl phosphate

CAS no.	Name
115-98-0	Bis(2-chloroethyl)vinylphosphonate
117-08-8	Tetrachlorophthalic anhydride
118-79-6	2,4,6-Tribromophenol
124-64-1	Tetrakis(hydroxymethyl) phosphonium chloride
124-73-2	Dibromotetrafluoroethane
126-72-7	Tris(2,3-dibromopropyl)phosphate
126-73-8	Tri-n-butyl phosphate
140-08-9	Tris-(2-chloroethyl)phosphite
141-83-3	Guanyl urea
298-07-7	Phosphoric acid, bis(2-ethylhexyl) ester
301-13-3	Trioctyl phosphite
512-56-1	Trimethylphosphate
545-55-1	Tris(1-aziridinyl)phosphine
563-04-2	Tri (m-cresyl phosphate)
593-60-2	Vinyl bromide
598-72-1	2-Bromopropanoic acid
615-58-7	2,4-Dibromophenol
632-79-1	Tetrabromophthalic anhydride
756-79-6	Dimethylmethyl phosphonate
762-04-9	Phosphinic acid, diethyl ester
1241-94-7	2-Ethylhexyl diphenyl phosphate
1330-78-5	Tricresyl phosphate
1470-82-0	2,4,6-Tribromoaniline
1502-47-2	2,5,8-Triamino-1,3,4,6,7,9,9b-heptaaza-phenalene (Cyamelurotriamide)
1773-89-3	Dimethylchlorendate
1806-54-8	Trioctyl phosphate
2623-87-2	4-Bromobutanoic acid
2781-11-5	O,O-Diethyl-N,N-bis(2-hydroxyethyl)aminomethylphosphonate
3066-70-4	2,3-Dibromopropylmethacrylate
3234-02-4	2,3-Dibromo-2-butene-1,4-diol
3290-92-4	Trimethylolpropane trimethacrylate
3296-90-0	Dibromoneopentyl glycol
5412-25-9	Bis(2,3-dibromopropyl)phosphoric acid
5445-17-0	2-Bromopropanoic acid, methyl ester
5445-19-2	2-Bromohexanoic acid, methyl ester
6145-73-9	Tris(2-chloro-1-propyl)phosphate
6749-73-1	Tris(dichloropropyl)phosphite
7415-86-3	Bis-(2,3-dibromo-1-propyl)phthalate
10310-38-0	Ethylene bis(tris(2-cyanoethyl)-phophonium)bromide
13674-87-8	Tris(1,3-dichloro-2-propyl)phosphate
14852-17-6	Ethylene diamine phosphate
18755-43-6	Phosphonic acid, propyl-, dimethyl ester
19186-97-1	Tris (3-Bromo-2,2(Bromomethyl)Propyl)Phosphate
20217-01-0	2,4-Dibromophenylglycidyl ether
20566-35-2	Tetrabromophthalic acid diol
25155-23-1	Trixylyl phosphate
25357-79-3	Tetrabromophthalic acid, sodium salt
27104-30-9	Tetrakis-hydroxymethyl phosphonium chloride based prepolymer
28108-99-8	Isopropylphenyl diphenyl phosphate
31780-26-4	Dibromostyrene
33125-86-9	Tetrakis(2-chloroethyl)ethylene diphosphate

CAS no.	Name
34432-82-1	Ammonium bis(2,3-dibromopropyl)phosphate
36483-57-5	Tribromoneopentyl alcohol (different isomers)
37640-57-6	Melamine cyanurate
37853-59-1	1,2-Bis(2,4,6-tribromophenoxy)ethane
38051-10-4	2,2-Bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate)
40703-79-5	5,6-Dibromohexahydro-2-phenyl-4,7-methano-1H-isoindole-1,3(2H)-dione
41291-34-3	Ethylene-bis(5,6-dibromonorbornane-2,3-dicarboximide)
53461-82-8	Tetrakis(2-chloroethyl)diethylene-oxy diphosphate
53506-00-6	1,4-Di(cyanoethylphospine oxide)-2,3,5,6-tetramethylbenzene
53587-44-3	Melamine borate
56803-37-3	tert-Butylphenyl diphenyl phosphate
57583-54-7	Resorcinol bis-diphenylphosphate
60763-39-5	Diphenyl isopropyl phosphate
84852-53-9	1,2-Bis(pentabromophenyl) ethane
109678-33-3	Tetrabromodipentaerythritol

A6.3 Substances for which the PBT status is uncertain

The uncertainties in this group have arisen for one of several reasons:

- The SRC EPI database does not recognise the CAS number, and attempts have not yet been made to enter structures manually.
- Structures are too unclear to make any attempt to predict properties.
- Nomenclature is generic or the substance identity is proprietary.

It would be appropriate to go back to Industry and check these cases before work on predictions is performed. It is possible that some of them are already in the Project Database.

CAS no.	Name
-	Cyclic phosphonate (speciality blend)
-	Phosphate ester
-	Organophosphorus compounds containing halogens
-	Organophosphorus
-	Organo phosphate/phosphonate
-	Organic phosphorus compound
-	Oligomeric methyl phosphonate
-	Bromine compound containing LDPE masterbatch
-	Octabromotriethylphenyl indane
-	Chlorinated diphosphate ester
-	Phosphate/phosphate
-	Cyclic phosphonate
-	Mixture of complex phosphonates
-	Diethyl-N,N-bis (2-hydroxyethyl)aminomethyl phosphonate
-	Mixture of chlorinated diphosphate and chlorinated phosphonate esters
-	Isopropylated triphenyl phosphate
-	Isopropylated phenyl phosphate
-	HET acids/others
-	Halogen-phosphate ester mixture
-	Halogen-containing polyphosphonate
-	Epoxy resin (brominated)
-	Chlorinated phosphate ester

CAS no.	Name
-	Tertiary butylated triphenyl phosphate
-	Tris(tribromoneopentyl)phosphate
-	Ammonium salt of complex phosphonate
-	Tris 1,3-dichloropropyl phosphate (it is likely that this is a synonym for CAS 13674-87-8)
-	Tris (chloroethyl) phosphate
-	Tris (2,2-dichloroisopropyl) phosphate (it is likely that this is a poor synonym for CAS 13674-87-8)
-	Tribromophenol allyl ether (likely to be a misnomer for tribromophenyl allyl ether
-	Tribromoneopentyl phenyl allyl ether
-	Tribromoneopentyl phenol
-	Tetrakis(hydroxymethyl)phosphonium urea condensates
-	Tetrabromophthalate ester
-	Bis(diphenyl) phosphate
-	Organophosphorus compounds
-	Tetrabromobenzoate
-	Resorcinol bisphosphate
-	Phosphates of organic bases
-	Poly(dibromostyrene) grafted poly(propylene)
-	Brominated epoxy - partially endcapped
-	Brominated epoxy - endcapped
-	Resorcinol bis(diphenyl phosphate)
-	Brominated aromatic ether/phosphate ester
-	Bisphenol-A bisphosphate
-	Proprietary blend pentabromodiphenyl oxide
-	Polymer nanocomposites
-	Low melting glasses and glass ceramics
-	Polymer organic char former
1031-38-0	Bis(Tris(cyanoethyl)phosphonium bromide)
3072-84-2	Epoxy resin, brominated
4351-70-6	Oligomeric chloroalkyl phosphate
6294-34-4	Bis(2-chloroethyl)-2-chloethylphosphonate based
6519-18-4	Potassium bis(2,3-dibromopropyl)phosphate
9003-08-1	1,3,5-Triazine-2,4,6-triamine, polymer resin with formaldehyde
13518-93-9	Dimelamine pyrophosphate
20208-95-1	Melamine phosphate
28205-79-0	Tris(2-chloroethyl)phosphate polymer
32844-27-2	Tetrabromobisphenol-A diglycidyl ether - carbonate oligomer
36711-31-6	Magnesium bis(2,3-dibromopropyl)phosphate
40088-47-9	Benzene, 1,1-oxybis-, tetrabromo deriv.
42595-45-9	Complex mixture of organic phosphonate esters
49690-63-3	2,4-Dibromophenylphosphate
56974-60-8	Dimelamine phosphate
57137-10-7	Polytribromostyrene
61840-22-0	Cyclic phosphonate ester
62354-98-7	Poly(dibromostyrene)
64864-08-0	Sodium bis(2,3-dibromopropyl)phosphate
67326-33-4	Phosphate-EO oligomers
68441-46-3	1,3-Butadiene homopolymer, brominated
68441-62-3	Brominated polyetherpolyol
68928-70-1	Brominated epoxy [Tetrabromobisphenol-A - Tetrabromobisphenol-A diglycidyl ether]
68952-35-2	Tar acids, cresylic, Ph phosphates

CAS no.	Name
69882-11-7	Poly(2,6-dibromophenylene oxide)
70776-17-9	Melamine pyrophosphate
71342-77-3	Tetrabromobisphenol-A carbonate oligomer (fully brominated; phenoxy-terminated)
71720-64-4	Oligomeric chloroalkyl phosphate
77098-07-8	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, mixed esters with diethylene glycol and propylene glycol
88497-56-7	Brominated polystyrene
94334-64-2	Tetrabromobisphenol-A - carbonate oligomer
109640-81-5	Chlorinated oligomeric phosphate ester
125997-20-8	Chlorinated brominated phosphate ester
135229-48-0	Brominated epoxy resin / tribromophenol
137370-67-3	Polypropylene/dibromostyrene copolymer
155613-93-7	Brominated trimethylphenylindane
171091-06-8	Dibromostyrene grafted
181028-79-5	Phosphoric Trichloride, reaction product with Bisphenol-A and Phenol

Appendix 7: Substances with important data gaps

Some of the information on the substances is held within the confidential database and not listed in the report.

Table A7.1 High tonnage, but few details of the use pattern[21]

CAS No.	Name	Total EU tonnage	Source (EU)
-	Dimethyl-3-(hydroxymethylamino)-3-oxopropyl phosphonate	>1,500	IPCS
-	HET acids/others	3,600	IAL
615-58-7	2,4-Dibromophenol	>1,500	IPCS
1302-42-7	Sodium aluminate	5,000	IUCLID (1992)
1332-07-6	Zinc borate	1,000	IPCS
1345-04-6	Antimony sulphide	>1,500	IPCS
3234-02-4	2,3-Dibromo-2-butene-1,4-diol	1,000	IPCS
6145-73-9	Tris(2-chloro-1-propyl)phosphate	>1,500	IPCS
7631-90-5	Sodium bisulfate	10,000	IUCLID (range 5000-10000, 1993)
13701-59-2	Barium metaborate	1,000<500	IPCSIndustry
13826-83-0	Ammonium fluoroborate	>1,500	IPCS
16923-95-8	Potassium fluorozirconate	>1,500	IPCS
28205-79-0	Tris(2-chloroethyl)phosphate polymer	1,000	IPCS
68441-46-3	1,3-Butadiene homopolymer, brominated	1,000	IPCS
69882-11-7	Poly(2,6-dibromophenylene oxide)	1,000	IPCS
86675-46-9	CONFIDENTIAL		CONFIDENTIAL

Table A7.2 No details of the tonnage

CAS No.	Name
-	Organophosphorus compounds
-	Synergistic blend of phosphate and nitrogen-containing compounds
-	Isopropylated phenyl phosphate
-	Isopropylated triphenyl phosphate
-	Magnesium/zinc complex
-	Mixture of ammonium and urea salts of polyphosphoric acid
-	Mixture of chlorinated diphosphate and chlorinated phosphonate esters
-	Mixture of complex phosphonates
-	Mixture of salts of bromine, polyphosphoric acid and sulphamic acid
-	Mixture of salts of polyphosphoric acid
-	Polymer nanocomposites, intercalated structure
-	Inorganic sulphur-nitrogen compound
-	Organo phosphate/phosphonate
-	Inorganic phosphate and urea derivative
-	Organophosphorus compounds containing halogens

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[21] Note: The Industry (*Great Lakes, 2003*) has indicated that "many of these substances appear not to be flame retardants, but substances that are fire fighting agents, chemical intermediates or used for other purposes".

CAS No.	Name
-	Phosphate ester
-	Polymer organic char former of PVA, starch, glucose derivatives, polyfunctional alcohols
-	Phosphate/phosphate
-	Phosphates of organic bases
-	Poly(dibromostyrene) grafted poly(propylene)
-	Polyammonium phosphate
-	Proprietary blend pentabromodiphenyl oxide
-	Red phosphorus containing halogens
-	Organic phosphorus compound
-	Brominated epoxy - endcapped
-	Aluminium Trihydroxide and Silane (S1, S3A, S5, S21) Stearic Acid(ST)
-	Ammonium carbamate phosphate
-	Ammonium salt of complex phosphonate
-	Ammonium salts of phosphorous and sulphuric acids
-	Antimony complex
-	Antimony/magnesium/phosphate/zinc complex
-	Antimony/magnesium/zinc complex
-	Antimony/zinc complex
-	Bis(diphenyl) phosphate
-	Bis(tetrabromophenoxy) ethane
-	Intumescent blends
-	Brominated aromatic ether/phosphate ester
-	Octabromotriethylphenyl indane
-	Brominated epoxy - partially endcapped
-	Bromine compound containing LDPE masterbatch
-	Chlorinated phosphate ester
-	Cyclic phosphonate
-	Cyclic phosphonate (speciality blend)
-	Epoxy resin (brominated)
-	Halogen-containing polyphosphonate
-	Halogen-phosphate ester mixture
-	Inorganic bromine compound containing nitrogen
-	Inorganic phosphate
-	Bisphenol A bisphosphate
-	Tribromochlorobisphenol A
-	Tris(tribromophenyl)cyanurate
-	Chlorinated naphthalene
-	Expandable graphite
-	Tris(hydroxymethyl)phosphine oxide
-	Tetrabromobisphenol A epoxy oligomer
-	Tris (isopropyl) phosphate
-	Tribromoneopentyl phenyl allyl ether
-	Tribromoneopentyl phenol
-	Low-melting glasses and galss ceramics K2CO3-SiO2, K2WO4- Na2SO4- ZnSO4
-	Tetrabromobenzoate
-	2,2'-dimethyl-3-bromo-propanoic acid, isopropyl ester
-	ZHS/Zinc borate blend
-	Tribromoneopentyl phenyl maleimide

CAS No.	Name
75-25-2	Bromoform
75-95-6	Pentabromoethane
79-27-6	1,1,2,2-Tetrabromoethane
79-28-7	Tetrabromoethylene
93-52-7	Benzene, (1,2-dibromoethyl)-
96-13-9	2,3-Dibromopropanol
96-32-2	2-Bromoacetic acid, methyl ester
96-69-5	4,4'-Thio-bis(2-t-butyl-5-methylphenol)
101-02-0	Triphenyl phosphite
115-77-5	2,2-bis(hydroxymethyl)-1,3-Propanediol (pentaerythritol)
115-89-9	Methyl diphenyl phosphate
124-73-2	Dibromotetrafluoroethane
141-83-3	Guanyl Urea
298-07-7	Phosphoric acid, bis(2-ethylhexyl) ester
301-13-3	Trioctyl phosphite
512-56-1	Trimethylphosphate
563-04-2	Tri (m-cresyl phosphate)
593-85-1	Guanidine carbonate
598-72-1	2-Bromopropanoic acid
762-04-9	Phosphinic acid, diethyl ester
791-28-6	n-Triphenylphosphine oxide
1031-38-0	Bis(Tris(cyanoethyl)phosphonium bromide)
1303-86-2	Diboron trioxide
1314-98-3	Sphalerite (Zinc sulfide)
1332-81-6	Antimony IV oxide
1502-47-2	2,5,8-Triamino-1,3,4,6,7,9,9b-heptaaza-phenalene (Cyamelurotriamide)
1806-54-8	Trioctyl phosphate
2623-87-2	4-Bromobutanoic acid
3066-70-4	2,3-Dibromopropylmethacrylate
3072-84-2	Epoxy resin, brominated
3194-57-8	Tetrabromocyclooctane
3290-92-4	Trimethylolpropane trimethacrylate
3486-35-9	Carbonic acid
4351-70-6	Oligomeric chloroalkyl phosphate
5205-93-6	Dimethylamino propyl methacrylamide
5445-17-0	2-Bromopropanoic acid, methyl ester
5445-19-2	2-Bromohexanoic acid, methyl ester
5974-60-8	Dimelamine phosphate
6294-34-4	Bis(2-chloroethyl)-2-chloethylphosphonate based
7760-50-1	Magnesium, tetrakis[carbonato(2-)]dihydroxypenta-
7783-28-0	Diammonium phosphate
9003-08-1	1,3,5-Triazine-2,4,6-triamine, polymer resin with formaldehyde
10025-91-9	Antimony Trichloride
10101-41-4	Calcium Sulfate Dihydrate
10124-31-9	Ammonium orthophosphate
11112-10-0	Sodium antimonate
12125-02-9	Ammonium chloride
12280-03-4	Disodium octaborate

CAS No.	Name
12770-65-9	Ammonium metaphosphorimide
13518-93-9	Dimelamine pyrophosphate
14852-17-6	Ethylene diamine phosphate
15432-85-6	Sodium antimonate
18755-43-6	Phosphonic acid, propyl-, dimethyl ester
19186-97-1	Tris (3-Bromo-2,2(Bromomethyl)Propyl)Phosphate
24623-77-6	Aluminum hydroxide oxide
25713-60-4	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine {Tris (tribromophenyl) cyanurate}
26040-45-9	none
26040-51-7	Phthalic acid, tetrabromo-, bis(2-ethylhexyl) ester
26780-96-1	Poly(1,2-dihydro-2,2,4-trimethylquinoline)
28108-99-8	Isopropylphenyl diphenyl phosphate
30178-92-8	Tetrabromocyclododecane
38521-51-6	Pentabromobenzyl bromide
40088-47-9	Diphenylether-, tetrabromo derivative
42595-45-9	Complex mixture of organic phosphonate esters
53461-82-8	Tetrakis(2-chloroethyl)diethylene-oxy diphosphate
53506-00-6	1,4-di(cyanoethylphospine oxide)-2,3,5,6-tetramethylbenzene
53587-44-3	Melamine borate
56803-37-3	tert-Butylphenyl diphenyl phosphate
59789-51-4	Tribromophenyl maleimide
61368-34-1	Tribromostyrene
62354-98-7	Poly(dibromostyrene)
67326-33-4	Phosphate-EO oligomers
68441-62-3	Brominated polyetherpolyol
68952-35-2	Tar acids, cresylic, Ph phosphates
70715-06-9	Oligomeric methyl phosphonate
71342-77-3	Tetrabromo bisphenol A carbonate oligomer (fully brominated; phenoxy-terminated)
71720-64-4	Oligomeric chloroalkyl phosphate
88497-56-7	Brominated polystyrene
94334-64-2	Tetrabromobisphenol A - carbonate oligomer
98923-48-9	2-Chloroethyl, 2-bromoethyl, 3-bromoneopentyl phosphate
137370-67-3	Polypropylene/dibromostyrene copolymer
139638-58-7	2-Propanol,1,1'-[(1-methylethylidene)bis[2,6-dibromo-4,1-phenylene)oxy]]bis[3-(2,4,6-
155613-93-7	Brominated trimethylphenylindane
171091-06-8	Dibromostyrene grafted
181028-79-5	Phosphoric Trichloride, reaction product with Bisphenol A and Phenol

Table A7.3 Predicted supply of or exceeding 1,000 tonnes per year in the EU, but physicochemical data important for assessment missing

CAS No.	Name
-	Dimethyl-3-(hydroxymethylamino)-3-oxopropyl phosphonate
-	HET acids/others
87-83-2	Pentabromotoluene
115-27-5	Chlorendic anhydride
117-08-8	Tetrachlorophthalic anhydride
1345-04-6	Antimony Sulphide
3234-02-4	2,3-Dibromo-2-butene-1,4-diol
4162-45-2	Tetrabromobisphenol A-bis-(2-hydroxyethylether)
11113-50-1	Boric acid
13472-45-2	Sodium tungstate
13560-89-9	Dodecachlorodimethan-o-dibenzocyclooctane
16919-27-0	Potassium fluorotitanate
16923-95-8	Potassium fluorozirconate
20566-35-2	Tetrabromophthalic acid diol
25327-89-3	Tetrabromobisphenol A-bis-(allylether)
28205-79-0	Tris(2-chloroethyl)phosphate polymer
31780-26-4	Dibromostyrene
32844-27-2	Tetrabromobisphenol A diglycidyl ether - carbonate oligomer
57137-10-7	Polytribromostyrene
57583-54-7	Resorcinol bis-diphenylphosphate
58965-66-5	Tetradecabromodiphenoxybenzene
60763-39-5	Diphenyl isopropyl phosphate
61262-53-1	Benzene, 1,1'- 1,2-ethanediylbis(oxy) bis 2,3,4,5,6-pentabromo-
68441-46-3	1,3-Butadiene homopolymer, brominated
86675-46-9	CONFIDENTIAL
125997-20-8	Chlorinated brominated phosphate ester

Appendix 8: List of industry consultees and possible contacts

Full details are presented in the Project Record. The list includes more than sixteen trade associations for downstream users. Note that if a name is shown in italics, this indicates that the organisation was not contacted, or was not contacted directly (e.g. only via a trade association).

If a name is shown in bold type, this indicates that the organisation has responded with comments on a draft of this report in a consultation exercise conducted through the Chemical Industries Association (CIA) in the UK.

1. PRODUCERS INDUSTRY ASSOCIATIONS

Flame Retardants – Industry Associations and Groups

Bromine Science and Environmental Forum

Chemical Industries Association, Fire Retardants Sector Group

Chlorinated Paraffins Sector Group, Euro Chlor

European Brominated Flame Retardants Industry Panel

European Flame Retardants Association

European Melamine Poducers Association

International Workshop on Brominated Flame Retardants

Royal Society of Chemistry, Fire Chemistry Discussion Group

University of Surrey, Polymer Research Centre

Phosphate Ester Flame Retardant Council (PEFRC) (did not exist at the time of the main phase of consultation)

Basic chemicals – Industry Associations

The European Chemical Industry Council (CEFIC)

2. PRODUCER COMPANIES

Flame Retardants - Companies

Albermarle Europe Sprl

Alcan Chemicals Limited

Akzo Nobel Chemicals

Aluiuisse Martinswerk GmbH

Anzon

Bayer AG

Borax

Budenheim Iberica

Ciba Speciality Chemicals Limited

Clariant

Climax molybendum

Dead Sea Bromine Group

DSM Melamine

DSM Melapur

Duslo

Elf Atochem

Ferro

FMC

Great Lakes Chemical Corporation

Joseph Storey

Nablatec

Recticel

Rhodia

Rohm and Haas

Solvay Fluor und Derivate

William Blythe

Basic chemicals – Companies

3M United Kingdom PLC

3. DOWNSTREAM USERS

Polymers - Trade Associations

Association of Plastics Manufacturers In Europe
British Plastics Federation, Additives Sector Group
BPF, Business Research Officer
BPF, Environmental person
European Polymer Dispersion and Latext Association
European Phenolic Resins Association
European Resin Manufacturers Association
European Vinyl Chloride Manufacturers Association

Rubber and Foams - Trade Associations

British Rubber Manufacturers Association, HSE Director
BRMA, Consultant
BRMA, Chair of Technical Committee
British Rigid Urethane Foam Manufacturers Association
Rubber and Plastics Research Association

European Association of Flexible Polyurethane Blocks Manufacturers (EUROPUR)
European Isocyanate Producers Association (ISOPA)
Urethanes Technology

Polymers – Companies

Recticel UK

Paints, lacquers and varnishes

Nullifire

Textile Processing - Companies

Allied Carpets
Carpetright
Headlam
Mobel Test Quality Services

Carpet - Trade Asssociations

British Carpet Manufacturers Association
British Carpet Technical Centre
Carpet Foundation
Wholesale Flooring Distributors Association

Mineral oil and fuel - Trade Associations

Additives Technical Committee, Chair of H and S Committee
British Lubricants Federation

Adhesives and Sealants

Association of European Adhesives Manufacturers (FECIA)
British Adhesives and Sealants Association
Hot Extruded Sealants Association

Textiles - Trade Asssociations

British Apparel and Textile Confederation
British Interior Textiles Association
British Textile Technology Group
British Wool Secretariat
Clothing Industry Association Limited
Confederation of British Wool Textiles
Co-ordination Committee for Textile Industries in the EC
European Clothing Association
European Sporting Goods Association
European Textile Finishers Association
Knitting Industries Federation Limited
Textile Distribution Association
Textile Finishers Association
Textile Finishing Group

Textile Institute
Textile Services Association

Construction

Association of Specialist Fire Protection
CIRCA, Fire
Confederation of Construction Specialists
Construction Industry Research Association, Environmental Department
Construction Industry Research Information Association (CIRIA), Waste Minimisation
Construction Products Association
Fire Research Station, BRE
National Council of Building Material Producers
Steel Construction Institute
Timber Research and Development Association
Timber Trade Federation
Wood Panel Industries Federation
UK Steel Association

Automotive - Trade Associations

Motor Industry Research Association
Society of Motor Manufacturers and Traders

Electrical/Electronic Engineering - Trade Associations

Association of Manufacturers of Domestic Electrical Appliances
Environmental Energy Helpline
British Radio and Electronic Equipment Manufacturers Association
Federation of British Electrotechnical and Allied Manufacturers' Associations
Federation of the Electronics Industry
GEMI UK Limited
Printed Circuit Interconnection Federation,
PCIF, Chair of PCIF Environment Committee
PCIF, statistics
RETRA

Pulp, paper and board - Trade Asssociations

Paper Chemcials Association
Paper Federation of Great Britain
Paper Industry Research Association (PIRA)
Pulp, paper and board - Companies
Devon Valley Mill
Henry Cooke Makin
Hollingsworth and Vose
Max Hunt
St Regis - Higher Kings Mills

Electrical/Electronic Engineering - Companies

Electrolux
IBM

Isola, Technical Director
Paragon Chartered Chemists
NEC
Shipley Electronics
Siemens

Furniture - Trade Asssociations

Association of Master Upholsterers
British Contract Furniture Manufacturers Association
British Furniture Association
British Furniture Manufacturers
BFM, Environmental Consultant
Furniture Industry Research Association

Leather processing industry

British Leather Confederation
British Luggage and Leather Goods Association
British Footwear Association
European Footwear Manufacturers Association (CEC)
Leather Technology Centre

Paints, lacquers and varnishes - Trade Associations

British Coatings Federation
British Printing Industries Federation
European Council of the Paint, Printing Ink and Artists' Colours Industry (CEPE)
Paint Research Association
Flame retardants panel of the British Wood and Damp-proofing Association

Appendix 9: Extracts from the IPPC BREF for textiles

The following text (indented, from several parts of the original text) is copied from the IPPC BREF for textiles (EC, 2002), an extensive description of the industry sector.

When speaking about flame-retardant finishing it is useful to differentiate between durable and non-durable treatments. Durable flame-retardants react with the fibre, thereby providing permanent fire retardancy properties to the treated product. This is not the case with non-durable retardants, which although effective, are removed by laundering and are thus suitable only for fabrics which are seldom or never laundered or which can be re-treated whenever laundering is carried out.

Flame retardant agents function by different mechanisms depending on their chemical characteristics. The most commonly used flame retardant agents in the textile sector belong to the following chemical classes:

- inorganic compounds
- halogenated organic compounds
- organo-phosphorus compounds.

Inorganic flame retardant agents

Inorganic flame retardant agents, used for cellulosic fibres, are water-soluble salts such as diammonium phosphate, aluminum sulphate, ammonium sulphate, etc. They are applied from aqueous solution by padding or spraying followed by drying. They are non-durable retardants, which means that they render the product flame retardant until it is laudered or otherwise exposed to water.

Other types of inorganic flame retardant agents are used in the wool carpet sector. Although wool may be generally regarded as resistant to burning, the introduction of stringent flammability standards for floor coverings fitted in aircraft and public service buildings necessitates the use of flame retardant agents in some specific cases. Zirconium and titanium salts have been developed to meet the needs of this specialised market. Zirconium salts, commonly referred to as "Zirpro treatments", are the most widely used (potassium hexafluorozirconate).

Aluminum hydroxide ($Al2O3·3H2O$) is another flame-retardant widely used in the carpet sector. It is commonly added to the foam coating of the carpet, partially replacing [Calcium carbonate] $CaCO3$ (inactive filler).

Halogenated flame retardant agents

Discharges of halogenated flame retardant into waste water from textile finishing operations may come from excess liquor dumps, end-of-run bath drops and draining of washing water. However, since the amount/load of active substance applied on the fabric is typically in the order of 20 – 30 % w/w, the amount of flame retardant not retained by the sludge and therefore potentially released into the environment may be significant. Process design and operation should avoid the discharge of concentrated liquors to waste water, minimise losses to the effluent, and ensure that adsorption to the sludge is effective in the waste water treatment plant.

Phosphor-organic flame retardant agents

Organo-phosphorus compounds used in textile applications, particularly for cotton, are available as reactive (durable) and non-reactive (non-durable) systems.

There are two principle chemical types of reactive phosphor-organic flame retardant agents. Both of them are halogen-free formulations.

The flame retardant is applied to cotton via the pad-dry-bake technique in combination with a melamine resin, a fabric softener and phosphoric acid. After padding, the fabric is dried and cured thermally to achieve fixation. No ammonia is used in curing. Because of the presence of melamine resins as cross-linking agents, formaldehyde and methanol are evolved as off-gases (emissions are normally abated via scrubbers). Following the curing process, the fabric is washed off, resulting in some unreacted P-containing reagents being discharged to the waste water.

Residual finishing liquors and rinse water containing phosphor-organic flame retardant of this type should be collected and not mixed with the other effluent in the waste water treatment system.

With the other type of reactive phosphor-organic flame retardant (self-reactive systems), the fabric is impregnated with phosphonium salt and urea precondensates. The subsequent drying process step does not require complete drying. Processing temperatures are therefore low (between 60 and 100°C). After drying, the fabric is treated with ammonia to produce an insoluble polymer within the fibres. The fabric is subsequently oxidised with hydrogen peroxide and washed. In this process there is no curing treatment other than the treatment with ammonia.

No methanol is present in the emissions and no melamine resins or cross-linking agents are used in the process. Phosphonium salt and urea precondensates have been shown to have levels of fixation of 95 % or higher [(CIA, 2002), from (EC, 2002)]. However, since washing is necessary with these flame-retardants to remove unreacted agents and by-products, some residual phosphorous organic compounds end up in the waste water treatment plant.

Concentrated padding liquors and rinse water containing phosphor-organic flame retardants of this type should be collected and not discharged with the other effluents in the waste water treatment [(Sweden, 2001), from (EC, 2002)].

Non-durable phosphor-organic flame-retardants do not react with the fibre. As articles treated with non-durable phosphor-organic flame-retardants are not washed after the finishing treatment (and also as the final product is rarely washed), this results in a minimisation of any release of P-containing reagents to waste water [(CIA, 2002), from (EC, 2002)].

Flame-retardant treatments

Potassium salts of fluoro complexes of zirconium (potassium hexafluorozirconate) are typically used for wool and wool-blend fibres. Typical application conditions for carpet wool yarn are as follows:

- rinsing is required to remove interfering sulphate and phosphate ions, if present;

- bath set up at 20 – 30 ºC, pH 3 with hydrochloric acid (10 % o.w.f.[22]) or formic acid (15 % o.w.f.) and citric acid (4 % o.w.f.);
- addition of potassium hexafluorozirconate (3 to 8 % o.w.f. depending on the final specification to be achieved and the substrate) dissolved in 10 times its weight of hot water;
- temperature raised at 1 – 2 ºC per minute to 60 ºC and held at this temperature for 30 minutes;
- rinsing in cold water for 10 - 20 minutes.

Environmental issues associated with continuous finishing processes

With some exceptions (e.g. application of phosphor-organic flame-retardant), continuous finishing processes do not require washing operations after curing.

The range of pollutants that can be found in the waste water varies widely depending on the type of finish applied. In particular, the release of the following substances in the environment gives rise to significant concerns:

- ethylene urea and melamine derivatives in their “not cross-linked form” (cross-linking agents in easy-care finishes);
- organo-phosphorous and polybrominated organic compounds (flame retardant agents);
- polysiloxanes and derivatives (softening agents);
- alkyphosphates and alkyletherphosphates (antistatic agents); and
- fluorochemical repellents.

In the drying and curing operation air emissions are produced due to the volatility of the active substances themselves as well as that of their constituents (e.g. monomers, oligomers, impurities and decomposition by-products). Furthermore air emissions (sometimes accompanied by odours) are associated with the residues of preparations and fabric carry-over from upstream processes (for example, polychlorinated dioxins/furans may arise from the thermal treatment of textiles that have been previously treated with chlorinated carriers or perchloroethylene).

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[22] O.w.f.: On the weight of the fibre.

Appendix 10: Substances showing concern under the criteria of this study but which are already under investigation

CAS No.	Name	Who is reviewing the substance?
77-47-4	Hexachlorocyclopentadiene	The Netherlands (ESR priority substance)
79-94-7	Tetrabromobisphenol-A	UK (ESR priority substance)
115-86-6	Triphenyl phosphate	Environment Agency (national assessment)
115-96-8	Tris (2-chloroethyl) phosphate	Germany (ESR priority substance)
1163-19-5	Decabromodiphenyl ether	UK/France (ESR priority substance)
1241-94-7	2-Ethylhexyl diphenyl phosphate (includes diphenyl octyl phosphate)	Environment Agency (national assessment)
1330-78-5	Tricresyl phosphate	Environment Agency (national assessment)
13674-84-5	Tris (2-chloroisopropyl) phosphate	UK/Eire (ESR priority substance)
13674-87-8	Tris(1,3-dichloro-2-propyl)phosphate	UK/Eire (ESR priority substance)
25155-23-1	Trixylyl phosphate	Environment Agency (national assessment)
25637-99-4	Hexabromocyclododecane	Sweden (ESR priority substance)
26444-49-5	Cresyl diphenyl phosphate	Environment Agency (national assessment)
28108-99-8	Isopropylphenyl diphenyl phosphate	Environment Agency (national assessment)
29761-21-5	Isodecyl diphenyl phosphate	Environment Agency (national assessment)
32534-81-9	Pentabromodiphenyl ether	UK (ESR priority substance)
32536-52-0	Octabromodiphenyl ether	UK/France (ESR priority substance)
38051-10-4	2,2-Bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate)	UK/Eire (ESR priority substance)
56803-37-3	tert-Butylphenyl diphenyl phosphate	Environment Agency (national assessment)
57583-54-7	Resorcinol bis-diphenylphosphate	Environment Agency (national assessment)
63449-39-8	Paraffin waxes and hydrocarbon waxes, chloro (Long-chain chlorinated paraffins; includes Paraffin oils, chloro (CAS no. 85422-92-0))	Environment Agency (national assessment)
85535-84-8	Short-chain chlorinated paraffins (C10 - 13, commercial product 49 - 70% wt Cl depending on application)	UK (ESR priority substance)
85535-85-9	Medium chain chlorinated paraffins (C14-17, commercial product ~40 - 60% wt Cl depending on application)	UK (ESR priority substance)