Toxic Transformers;
- a review of the hazards of brominated & chlorinated substances in electrical and electronic equipment

Authors: Alan Watson, Kevin Brigden, Melissa Shinn and Madeleine Cobbing.

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EXECUTIVE SUMMARY

A growing market exists for electrical and electronic goods, many of which have ever shortening life spans. Consequently, waste electrical and electronic equipment (WEEE), is the fastest growing waste stream, up to three times as fast as the growth of general municipal waste. Current global electronic waste (e-waste) production has been estimated to be 20-25 million tonnes per year, with Europe, the U.S. and Australasia being the biggest producers. For the EU, estimates of annual WEEE production for 2005 range from 5 to 9 million tonnes per year, with an annual growth of between 2.5% and 2.7%.

E-waste contains many substances and materials with a relatively high market value when isolated from the mixed waste. However, e-waste also contains numerous substances which are hazardous to human health and the environment, many of which are still used in the production of new equipment. The presence of these substances poses potential impacts, particularly during the disposal and recycling of e-waste after the consumer has finished with the equipment. Furthermore, large quantities of e-waste generated within the EU and other developed countries are exported, often illegally, to developing countries, including China, India and some African countries, where much is recycled using substandard processes. Such processes can further increase the release of hazardous substances from e-waste. Processes which involve the open-burning of waste are a particular concern, because some substances in e-waste can give rise to incomplete combustion products. These include chlorinated and brominated dioxins and furans formed as a result of chlorinated substances such as PVC plastic and brominated substances, primarily brominated flame retardants (BFRs), within the e-waste.

Much electrical and electronic equipment (EEE) contains a very large number of different substances, including many metals and organic chemical substances. The uses of key substances in EEE are summarised within this report, with a particular focus on BFRs and chlorinated polymers.

The electrical and electronics industries account for more than half of all consumption of halogenated (brominated and chlorinated) flame retardants. Approximately 30 – 40 different BFRs are widely found in WEEE plastics. BFR treated plastics typically contain 5-10% by weight of BFRs, though some materials can contain even higher levels, particularly circuit boards. For many types of products, however, examples exist where the use of BFRs and PVC has been avoided in various components.

Brominated flame retardants (BFRs)

Three groups of BFRs have been widely used in EEE for some time, and for these considerable data do exist; tetrabromobisphenol-A (TBBPA), polybrominated diphenyl ethers (PBDEs), and hexabromo cyclododecane (HBCD). Unfortunately, very little information is available on the quantities of individual BFRs used in the electronics sector, including for these three BFRs. The hazardous properties of TBBPA, PBDEs and HBCD have been addressed in detail elsewhere, and are not discussed in this document. One significant change has occurred in the use of BFRs in recent years, as a result of various restrictions within the EU on the use of PBDEs, particularly for EEE.

‘Emerging’ BFRs

In response to growing concerns about certain BFRs, and increasing regulation of their use, alternative flame retardants are being developed and used, including for EEE. It has been estimated that the total worldwide production volume of so called 'emerging' BFRs (those BFRs other than TBBPA, PBDEs and HBCD) is around 100000 metric tonnes per year (for all uses, not only EEE).

Although far less studied compared to PBDEs, TBBPA and HBCD, some ‘emerging’ BFRs have already been found in a wide range of environmental samples, including in sediments,

air, indoor dusts, and the eggs of birds. Some of these substances have been identified in the environment at high levels, including BTBPE (1,2-bis-2,4,6-tribromophenoxy-ethane), which has been used as a replacement for PBDEs, in some instances at higher concentrations than PBDEs. Similarly, numerous studies demonstrate that another ‘emerging’ BFR, decabromodiphenyl ethane (DBDPE), is widespread in the environment, with distributions similar to those of PBDEs in some locations. Despite their ongoing use, there is very little publically available data on the environmental distribution and toxicity for many ‘emerging’ additive BFRs. However, even with the little data available, concerns have already been raised for many of these substances.

PVC

In addition to BFRs, the use of the chlorinated polymer PVC in EEE contributes to the presence of halogenated substances in e-waste, thereby increasing the potential for the formation and release of hazardous substances under certain recycling and disposal processes, including the release of chlorinated dioxins and furans. Furthermore, the use of PVC in EEE often requires the use of additive substances to improve the properties of the materials. Some PVC additives, including phthalate esters (phthalates), are toxic substances. In addition to the intrinsic hazardous properties of BFRs and other halogenated substances used in EEE, these substances pose additional hazards when products reach their end of life and become e-waste. During some recycling and disposal operations (e.g incineration, smelting and particularly by the use of open burning), halogenated substances can act as precursors to the formation of hazardous substances, most notably halogenated dioxins and furans.

Transformation of brominated and chlorinated substances into dioxins and furans

It is widely recognized, including by industry, that some BFRs have the potential to form brominated dioxins/furans during processing and disposal. Considerable data exists demonstrating this potential for PBDEs (including deca-BDE) and TBBPA, including brominated polymers manufactured using TBBPA which are widely used in circuit boards. This hazard, however, is not restricted to PBDEs and TBBPA. Studies have demonstrated the potential for the formation of halogenated dioxins/furans for a diverse range of BFRs, including non-aromatic BFRs (HBCD) as well as ‘emerging’ BFRs (BTBPE), and that their formation is not dependant on specific characteristics of a BFR. The available data indicates that all BFRs have the potential to act as precursors for the formation of brominated dioxins/furans. The chlorinated polymer PVC can also act as a precursor to the formation of chlorinated dioxins/furans.

Where both chlorinated substances and brominated substances are present in e-waste, the potential exists for the formation of **mixed chlorinated-brominated dioxins/furans**, a group of substances which have been subject to few studies on their potential impacts on human health and the environment. E-wastes predominantly contain substances that are either chlorinated or brominated. The formation of mixed dioxins/furans from the treatment of e-waste demonstrates that these compounds are formed from multiple precursor halogenated substances; therefore an approach that assesses single substances is unable to adequately assess the potential for formation of halogenated dioxins/furans. Available evidence indicates that all BFRs, including ‘emerging’ BFRs, are potential precursors to the formation of mixed dioxins/furans.

In addition to the formation of halogenated dioxins/furans during recycling and disposal, many BFR formulations and BFR treated materials have been shown to be contaminated with brominated dioxins/furans, highlighting the potential for dioxin/furan formation during the manufacturing and processing of BFRs, or BFR containing materials. While much of the evidence is associated with the use of PBDEs, there is also evidence for such contamination for other BFRs, including TBBPA, HBCD, as well as certain ‘emerging’ BFRs, for example BTBPE.

Toxicity and impacts of dioxins and furans

Chlorinated dioxins/furans are widely recognised global toxic pollutants. Although less studied, available data indicates that brominated dioxins/furans have equivalent toxicity to the chlorinated analogues. Many authors have commented that brominated dioxins/furans belong in the TEF (Toxic Equivalency Factor) concept that was developed for chlorinated dioxins and furans.

Mixed chlorinated-brominated dioxins/furans, a far larger group of substances, have been far less studied than other halogenated dioxins and furans. However, available data indicates that mixed dioxins/furans have similar, and for some congeners possibly greater, toxicity compared to chlorinated or brominated dioxins/furans. The few studies on the toxicity and environmental distribution of mixed dioxins/furans have investigated only a small number of individual substances within this large group of compounds, and the properties of the vast majority of this group remain unknown. Furthermore, most investigations of halogenated dioxins/furans in the environment have largely excluded mixed dioxins/furans, and in many cases have also excluded brominated dioxins/furans, and may therefore have significantly underestimated total halogenated dioxins/furans levels.

Unlike the chlorinated compounds, very few studies have investigated human body burdens of brominated or mixed dioxins/furans. Despite this, there is evidence of general population exposure to brominated dioxins/furans, which have been detected in human breast milk and in human adipose tissues, all be it at lower levels than chlorinated dioxins/furans. No data is publicly available for individuals likely to have higher levels of exposure to brominated or mixed dioxins and furans due to their occupation, such as the informal recycling of e-waste, or those living in the vicinity of such activities.

E-waste recycling and disposal

There is considerable data that demonstrates the release of hazardous substances from e-waste at locations where recycling and disposal take place, both the release of additive substances such as BFRs, as well as substances generated during recycling/disposal processes, including halogenated dioxins/furans.

A substantial part of the e-waste generated within the EU does not enter the formal WEEE recycling sector, and there is evidence that significant quantities of e-waste arising within the EU is transported to countries outside the EU and dealt with by the informal sector, often using sub-standard processes.

Impacts have been demonstrated in locations where e-waste is recycled and disposed of within the informal recycling sector, where processes include the open burning of mixed e-waste for the recovery of metals contained within the waste. Extremely high levels of certain additive BFRs have been reported in the environment around recycling areas, as well as extensive contamination by chlorinated, brominated and mixed dioxins/furans. One study found that levels of chlorinated dioxins/furans in the air were the highest documented values of these compounds found in ambient air in the world. At some sites, mixed dioxins/furans were found to be the predominate forms of halogenated dioxins/furans, at levels exceeding those of both chlorinated and brominated analogues, highlighting the significance of mixed dioxins/furans as environmental pollutants arising under these conditions from e-wastes containing halogenated substances. Human exposure to additive BFRs and halogenated dioxins/furans has also been demonstrated at these locations.

Impacts are not limited to the informal sector, having also been demonstrated for the formal recycling sector within the EU, including elevated levels of human exposure to BFRs for e-waste recycling workers, as well the detection of BFRs in indoor air at recycling facilities, including some ‘emerging’ BFRs. Furthermore, chlorinated, brominated and mixed dioxins/furans have been detected in incinerator emissions and in fly ashes, including studies involving the incineration of e-waste. It is possible that chlorinated, brominated and mixed dioxins/furans are released by smelters and metal refineries that use e-waste as feed stock, though almost no published data is available for such emissions from most facilities, particularly for brominated and mixed dioxins/furans. Furthermore, the presence of halogens in e-waste can also increase releases of heavy metals from the feedstock during incineration.

Conclusion

In conclusion, there is considerable evidence that demonstrates human health and environmental impacts during the end-of-life phase of electrical and electronic equipment that contains brominated or chlorinated substances, both through the release of hazardous halogenated substances contained in the e-wastes, as well as from the generation of new hazardous substances through recycling and disposal processes, particularly halogenated dioxins/furans. While concerns over chlorinated dioxins/furans are widely recognised, there is evidence that brominated and mixed brominated-chlorinated dioxins/furans are of equivalent concern.

The body of evidence compiled in this report, and in particular the evidence that all BFRs, including so called ‘emerging’ BFRs, have the potential to form dioxins/furans demonstrates the need to protect human health and the environment from the consequence of the use of these hazardous substances used in EEE. Restrictions on hazardous substances are needed which recognise the extent of the use of substandard recycling and disposal practices, and include all halogenated substances, with restriction on a group basis rather than using a substance-by substance approach.

Introduction

The market for electrical and electronic goods continues to expand; many products have ever shorter life spans – often driven by fashion, particularly in the case of mobile phones, which are often replaced years before they would otherwise wear out, and now have typical lifetimes of only 12 – 18 months. Similarly, the average lifespan of a computer is decreasing rapidly, having fallen from between 4 to 6 years in 1997, to only 2 years in 2005 (Widmer, Oswald-Krapf *et al.* 2005). As a result, the waste electrical and electronic equipment (WEEE) waste stream, often referred to as e-waste, which is already extremely large, is growing at an alarming rate – up to three times as fast as the growth of general municipal waste, and is the fastest growing waste stream (Bertram, Graedel *et al.* 2002).

A recent review (Robinson 2009) has estimated current global e-waste production at 20-25 million tonnes per year. This review found that Europe, the U.S. and Australasia are the biggest producers of e-waste, but predicts that China, Eastern Europe and Latin America will become major e-waste producers in the coming ten years. It does, however, note the potential of miniaturisation and more efficient cloud computing networks for offsetting increased e-waste production due to global economic growth and the development of pervasive new technologies.

Precise data for the quantities of WEEE arising within the EU is not available. The total amount of European WEEE produced in 1998 has been estimated as being 6 million tonnes, which increased to between an estimated 8.3 and 9.1 million tonnes by 2005 (Hester and Harrison 2009). It has been predicted that total amounts of WEEE arising in Europe will grow annually at between 2.5% and 2.7%, to more than 12 million tonnes by 2020[1] (Hester and Harrison 2009).

For 2005, the European Commission estimates that, of the current 8.8 million tonnes of WEEE arising across the 27 EU member states, only 58%[2] of household WEEE is estimated to be collected and treated, leaving 42% or 3.7[3] million tonnes unaccounted for every year (European Commission, 2008). Other estimates put the quantities treated at only 2.1 million tons or 25% *(*Huisman et al, 2007) which infers that the remaining 6.6 million tonnes, or 75%, is unaccounted for.

Similarly, large quantities of e-waste are generated in many countries outside of the EU. For example, in China, approximately 2.5 million tonnes of domestic e-waste[4] was generated in 2005. This is projected to rise to 3 million tonnes in 2010 (Cobbing 2006). A study by MAIT and GTZ (Manufacturers' Association for Information Technology (MAIT) and Deutsche Gesellschaft fuer Technische Zusammenarbeit (GTZ) 2007) reported that a total of 330,000 tonnes of e-waste (computers, televisions and mobile handsets only) was generated in India in 2007.

E-waste may be one of the largest sources of heavy metals and organic pollutants in municipal waste (Boghe 2001). EMPA [5] say that pollutants comprise 2.70% of WEEE (Widmer, Oswald-Krapf *et al.* 2005), and that the hazardous materials are largely integrated into the equipment and are difficult to isolate. Many of the substances in WEEE are hazardous to human health and the environment, with potential for impacts during

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[1] The author notes that although "this increase does partly represent a real growth in the quantities of WEEE that Europe generates, it should also be remembered that Europe has also grown in size to embrace a number of new member states".

[2] 58% represents the sum of 33% household WEEE arisings reported by EU governments as separately collected, 2% reused, 10% probably treated in line with the Directive even if treated by 'unauthorised traders and recyclers' and an unsorted fraction of 13%. Based on 2005 EERA estimates extrapolated by the European Commission to calculate arising from EU 27 MS in 2008.

[3] Assuming 8.8 million tonnes arisings according to 2005 data in : Final Report 2008 Review of Directive 2002/96 on Waste Electrical and Electronic Equipment (WEEE), UNU, Huisman J *et al.*, August 2007.

[4] Personal Computers, televisions, washing machines, refrigerators & air conditioners

[5] Swiss Federal Laboratories

manufacture, use, and especially after the consumer has disposed of the equipment.

The aggregate figures are enormous. Realff (Realff, Raymond *et al.* 2004) estimates that globally the 315 million computers which became obsolete between 1997 and 2004 resulted in the discarding of 550 000 tonnes of lead (Pb), 900 tonnes of cadmium (Cd), 180 tonnes of mercury (Hg) and 500 tonnes of hexavalent chromium (Cr VI). There was also additional waste in the form of an estimated 1,800 000 tonnes of plastic and at least 159 000 tonnes of brominated flame-retardants from monitors alone.

The metal fraction of e-waste, including iron, copper, aluminium, gold and other metals, can be over 60% of the total by weight; some of these metals have a relatively high market value when isolated from the mixed waste. There are obvious benefits from recovering the metals wherever it is possible and environmentally acceptable to do so. Unfortunately, most obsolete computers, and other forms of e-waste, are not recycled in environmentally sound ways.

It has been reported that most e-waste is still disposed in landfills (Robinson 2009), and that effectively recovering valuable materials from e-waste with minimal environmental impacts is currently very costly. These circumstances contribute to the illegal export of an unknown quantity of e-waste between countries, largely from rich countries to developing countries, including China, India and some African countries, where recycling may "include burning and dissolution in strong acids with few measures to protect human health and the environment." These and other substandard recycling techniques can further increase the impacts of the hazardous materials in the wastes, and in some instances are contributing to extremely high levels of contamination of local environments by a range of chemical pollutants, followed by migration of contaminants into the wider environment including water resources, as well as uptake in food chains. As a result, both e-waste workers and those in the surrounding communities may be suffering negative health effects. Moreover, Robinson warns "There is evidence that e-waste associated contaminants may be present in some agricultural or manufactured products for export."

Processes which involve the open-burning of waste are a particular concern because some substances in e-waste have the potential to give rise to a range of ‘products of incomplete combustion’ under these conditions, particularly where halogenated substances are present. The predominant sources of halogenated substances in WEEE are the use of brominated and chlorinated flame retardants, and chlorinated polymers, particularly polyvinyl chloride (PVC).

It is the presence of halogenated (chlorinated and brominated) substances in WEEE that are of greatest concern with regard to the formation of products of incomplete combustion, particularly the toxic brominated dioxins and furans from brominated flame retardants (BFRs). In addition to this, some BFRs are also hazardous substances in their own right. Likewise, the presence of PVC plastic or other chlorinated substances can give rise to similar products (chlorinated dioxins and furans), and where burned together with BFRs, to the largely overlooked group of mixed brominated-chlorinated dioxins and furans. These end of life and disposal impacts, which are the principal focus of this report, are discussed in detail below.

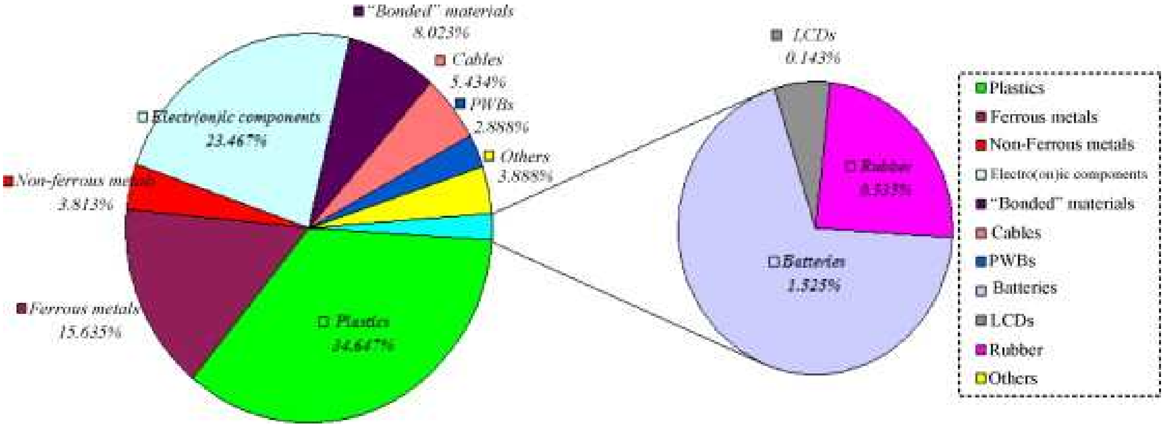
Chemical composition of electronic products

Analysis of the chemicals present in electronic products is not a simple matter. Some products such as computers and mobile phones can contain over one thousand different substances (Sepulveda, Schluep *et al.* 2010). The main hazardous materials and components are summarised in Table 1.

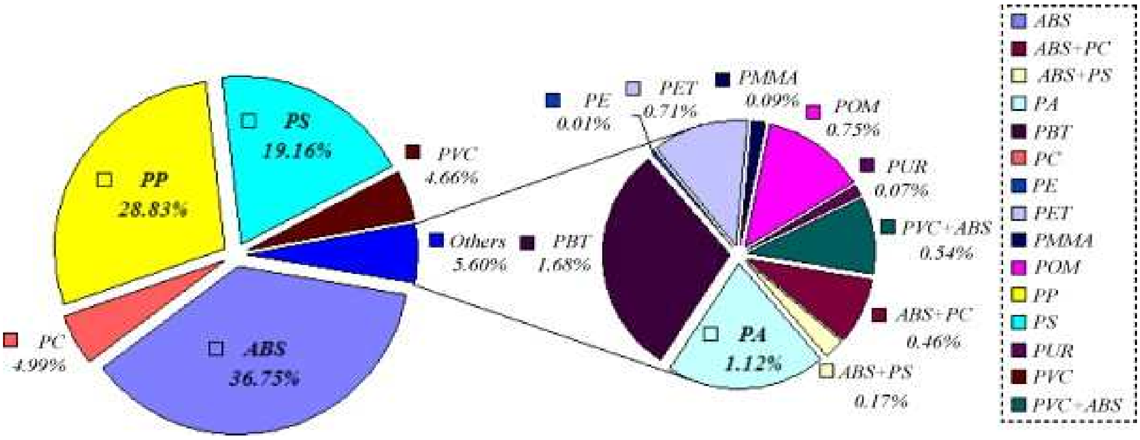
Materials and components	**Description**
Batteries	Heavy metals such as lead, mercury and cadmium are present in certain batteries.
Cathode ray tubes (CRTs)	Lead in the cone glass and cadmium/zinc/yttrium sulphide in the fluorescent coating
Mercury containing components, such as switches	Mercury is used in fluorescent lamps, and has historically been used in thermostats, sensors, relays and switches, for example, on printed circuit boards.
Liquid crystal displays (LCDs)	LCDs are used in mobile phones and flat screen computer monitors and may contain mercury.
Printed circuit boards	In printed circuit boards, cadmium occurs in certain components. Other hazardous metals such as chromium, lead, mercury, beryllium, zinc and nickel may are also be present. Brominated flame retardants and antimony trioxide are often used.
Plastics containing halogenated flame retardants	Certain halogenated flame retardants are hazardous, Also, combustion of the plastics and halogenated flame retardants can produce toxic substances.
Solder	Can contain lead, tin and other metals
Internal and External Wiring	Wiring is often coated in polyvinyl chloride (PVC) which commonly contains numerous additives, including heavy metal compounds and softeners such as phthalates. combustion of PVC can produce toxic substances

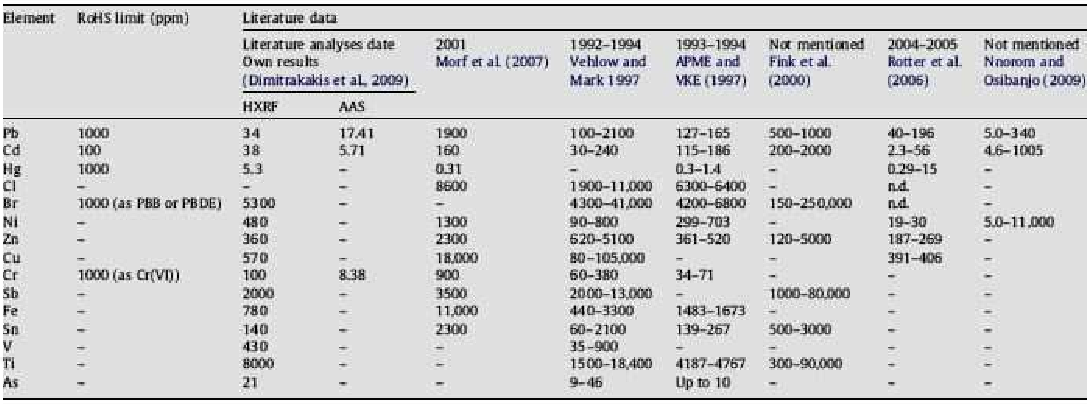
Table 1. Hazardous substances in specific materials and components of electrical equipment. Adapted from (Cui and Forssberg 2003).

Dimitrakakis (Dimitrakakis, Janz *et al.* 2009) has recently published an assessment of the material composition of small WEEE samples (%'s by weight):



The plastics component, in turn, contains a wide range of polymers with ABS being the most common:





Element	RoHS limit (ppm)	Literature data							
		Literature analyses date Own results (Dimitrakakis et al., 2009)		2001 Morf et al. (2007)	1992–1994 Vehlow and Mark 1997	1993–1994 APME and VKE (1997)	Not mentioned Fink et al. (2000)	2004–2005 Rotter et al. (2006)	Not mentioned Nnorom and Osibanjo (2009)
		HXRF	AAS						
Pb	1000	34	17.41	1900	100–2100	127–165	500–1000	40–196	5.0–340
Cd	100	38	5.71	160	30–240	115–186	200–2000	2.3–56	4.6–1005
Hg	1000	5.3	–	0.31	–	0.3–1.4	–	0.29–15	–
Cl	–	–	–	8600	1900–11,000	6300–6400	–	n.d.	–
Br	1000 (as PBB or PBDE)	5300	–	–	4300–41,000	4200–6800	150–250,000	n.d.	–
Ni	–	480	–	1300	90–800	299–703	–	19–30	5.0–11,000
Zn	–	360	–	2300	620–5100	361–520	120–5000	187–269	–
Cu	–	570	–	18,000	80–105,000	–	–	391–406	–
Cr	1000 (as Cr(VI))	100	8.38	900	60–380	34–71	–	–	–
Sb	–	2000	–	3500	2000–13,000	–	1000–80,000	–	–
Fe	–	780	–	11,000	440–3300	1483–1673	–	–	–
Sn	–	140	–	2300	60–2100	139–267	500–3000	–	–
V	–	430	–	–	35–900	–	–	–	–
Ti	–	8000	–	–	1500–18,400	4187–4767	300–90,000	–	–
As	–	21	–	–	9–46	Up to 10	–	–	–

Whilst the hazards associated with heavy metals are important, they have been well documented elsewhere, and the main focus of this chapter is halogenated substances, particularly brominated flame retardants – not least because, although many of these compounds are hazardous in their own right, they are also potential precursors for other hazardous substances which can be formed under some recycling processes, particularly brominated and mixed bromo-chloro dioxins and furans.

Brominated flame retardants (BFRs)

There are more than 175 different types of flame retardants available (Birnbaum and Staskal 2004). These are generally divided into classes, that include halogenated organic compounds, usually brominated or chlorinated substances (Alaee, Arias *et al.* 2003)[6], as well as phosphorus-containing compounds, nitrogen-containing compounds, and inorganic flame retardants.

The industry reported that about 75 different brominated flame retardants have been in "*significant commercial use*" this decade (Fisk, Girling *et al.* 2003). Brominated compounds are currently the largest market group of halogenated flame retardants because of their low cost and high performance efficiency (Yogui and Sericano 2009). They represent approximately 20% to 25% by volume of global flame retardant production (Harju, Heimstad

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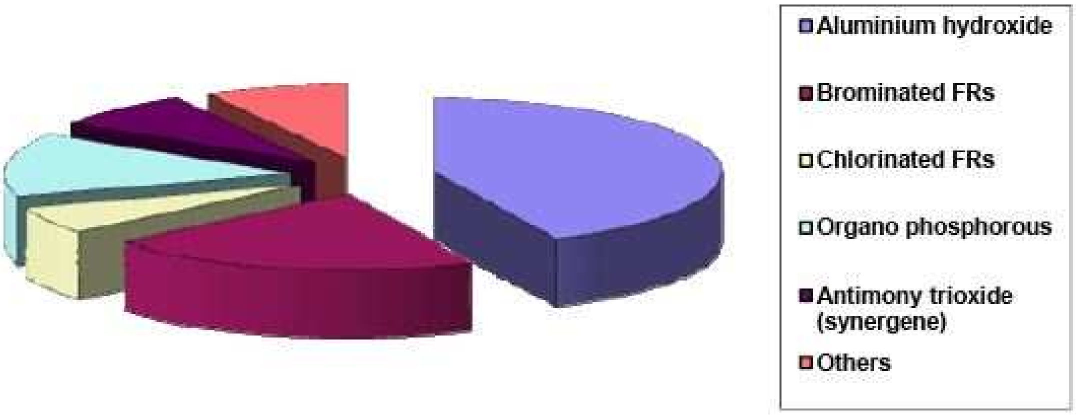
[6] Not all of the halogens are suitable for use in flame retardants. Alaee notes that fluorinated compounds are very stable and decompose at much higher temperatures than most organic matter burns, delivering their halogens too late to be effective as a flame retardant. On the other hand, iodinated compounds are not stable and decompose at only slightly elevated temperatures. Consequently, only organochlorine and organobromine compounds are used as flame retardants.

et al. 2008) and around 38% of total global production of bromine is currently used in the manufacturing of BFRs (Yogui and Sericano 2009) .



The global market share of groups of flame retardants for 2005, by quantities (tonnes) used in all sectors. These data are for global usage, for all uses not just EEE. The total amount of BFRs is 311,000 metric tonnes (Harju, Heimstad et al. 2008)

The electrical and electronics industries account for more than half of all consumption of halogenated (brominated and chlorinated) flame retardants (Pritchard 2005). Based on the global market share data presented above, this equates to annual use of over 150,000 metric tonnes. Asia is the fastest growing market in the world, largely because the great majority of electrical and electronic goods are manufactured in this area. Subsectors of special importance include (a) housings for televisions and business machines made of PC, ABS and other styrenic polymers, and (b) printed circuit boards and connectors (Pritchard 2005).

The industry confirms that BFRs can be found in plastic housings and casings, switches and connectors, printed circuit boards and occasionally also in electrical insulation (Tange, Brusselaers *et al.* 2006). Large fractions of electrical/electronic equipment, including mobile phones and computers, contain printed circuit boards.

Specifically for laptop computers, studies have identified a wide range of components that contain bromine, indicative of the use of BFRs (Brigden and Santillo 2006; Brigden, Webster *et al.* 2007), including; chips, ribbon cables, other internal coated wiring, insulation sheets, internal plastic connectors, fans, keyboard surrounds and touch mouse pads, and particularly in circuit boards. However, not all circuit boards tested in these studies contained bromine, indicating that the use of bromine free circuit boards is feasible across a wide range of applications. For many materials, the BFRs were predominantly substances other than PBDEs and additive TBBPA, though the substances were not identified in the study. In addition, the chlorinated plastic PVC was also identified in the coating of internal wires within laptop computers.

Similarly, a recent study of the chemical composition of a mobile phone identified bromine compounds in half of the components tested, as well as PVC in the plastic coating of cables (Santillo, Walters *et al.* 2007). Bromine compounds have also been identified at percent levels in numerous components within game consoles. Again, these products all contained PVC coated wires and cables (Brigden, Santillo *et al.* 2008)

Another study conducted for DEFRA (the UK Department for Environment, Food and Rural Affairs) on the composition of older WEEE from computers, printers, TVs and other waste electrical equipment from the UK found that circuit boards showed high levels of bromine (bromine in polymerised TBBPA), and that occasionally antimony (Sb) was also detected alongside bromine, possibly due to the use of mixtures of BFRs and antimony oxide as flame retardants (AEA Technology 2006)**.**

All of the above data indicate that brominated compounds, including known BFRs and other unidentified brominated compounds, are commonly used in electrical and electronic equipment (EEE), and furthermore, that the use of PVC as a coating for cables and wires is also common, though some exceptions for both BFRs and PVC do exist in certain components and brands.

Where they are used, BFR treated plastics contain typically 5-10% by weight of brominated flame retardants (Australian Government 2004; Lassen, Lokke *et al.* 1999), though some materials can contain even higher levels. Veit (Veit, Diehl *et al.* 2005) reports that the bromine content of plastic within circuit boards, especially as flame retardants, is 19%. It has been estimated that for some older products, a single personal computer could contain about 1.7kg of flame retardants, of which 70% is in the cabinet and the remainder in the printed circuit board (Menad, Bjorkman *et al.* 1998). In the mid 1990's, the World Health Organisation reported that up to 32% (by weight) of plastic products may have been PBDEs (World Health Organisation 1994). Plastics which contain BFRs may also contain antimony trioxide (a flame retardancy synergist commonly used alongside BFRs) at 3-5% (Tange, Brusselaers *et al.* 2006).

The bromine industry confirms that "*some 30 – 40 different BFRs are widely found in WEEE plastics*" (Tange, Brusselaers *et al.* 2006). Despite this, very little toxicity information is available for nearly half of the BFRs in use (Birnbaum and Staskal 2004). Hazards associated with various BFRs are further addressed in detail below.

Brominated flame retardants can be divided into three broad categories according to the type of organic skeleton on which they are based; aromatic, cyclo-aliphatic and aliphatic. Furthermore, flame retardants are used either as additives (i.e., they are mixed with, but not chemically bonded to the polymer) or co-reactants (in which case the reactive flame retardant is covalently chemically bound to the polymer, becoming an integral part of the polymer). (Lassen, Lokke *et al.* 1999; Rahman, Langford *et al.* 2001; Lassen, Havelund *et al.* 2006).

Additive BFRs are not chemically bound to the polymer matrix and may be released out into the environment at any time during the production, lifetime, or destruction of the product (de Wit 2002). However, BFRs that are chemically bonded to the polymer still have the potential to release hazardous substances into the environment at the end of a products life, when the polymeric BFR can be transformed into other hazardous substances, as discussed in some detail below

TBBPA, PBDEs and HBCD

Three types of BFR have been widely used in electrical and electronic equipment for some time and are discussed in the following section, these are;
Tetrabromobisphenol-A (TBBPA)
Polybrominated diphenyl ethers (PBDEs)
Hexabromo cyclododecane (HBCD)

Tetrabromobisphenol-A (TBBPA) is probably the most widely used BFR, with worldwide market demand estimated at 170,000 tonnes in 2004, of which 84.62% is used in Asia and only 9.38% and 6% in America and Europe respectively (Xie, Ebinghaus *et al.* 2007). Although it is used primarily as a reactive flame retardant in printed circuits boards (90%[7]) it also has uses as an additive flame retardant in certain plastics (World Health Organization (WHO) 1995), and as an intermediate in the production of other brominated flame retardants, namely TBBPA derivatives and brominated epoxy oligomers (Xie, Ebinghaus *et al.* 2007). As with all reactive flame retardants, even where TBBPA is used as a reactive flame retardant, small quantities of excess non-polymerized TBBPA are always present and can be emitted

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[7] The Bromine Science and Environmental Forum (BSEF) says TBBP-A "*is used in more than 95% of FR-4 printed circuit boards, the most commonly used board in electronic devices*" http://www.bsef.com/our-substances/tbbpa/applications-2/

from the polymer, thus potentially contaminating the environment during production, use and disposal (Tollback, Crescenzi *et al.* 2006). TBBPA is reported to be less expensive than PBDEs, but requires higher concentrations of the flame retardant to be effective (DEFRA. 2002).

Until recently, **polybrominated diphenyl ethers (PBDEs)** were the other most relevant BFRs. Used as additive flame retardants, this group of substances has been produced for the last twenty years or so primarily as three major commercial PBDE formulations: pentabromodiphenyl ether - $C_{12}H_5Br_5O$ (Penta-BDE), octabromodiphenyl ether - $C_{12}H_2Br_8O$ (Octa-BDE), and decabromodiphenyl ether $C_{12}Br_{10}O$ (DecaBDE)[8].

Each of the commercial PBDE mixtures have different degrees of bromination, the percentages of which vary depending upon the supplier; the following values are approximate (Darnerud, Eriksen *et al.* 2001):

- **Deca-BDE**, consisting of 97–98% decabromodiphenyl ether (DecaBDE); with 2-3% of nonabromodiphenyl and octabromodiphenyl (OcBDEs).
- **Octa-BDE**, consisting of 10–12% hexabromodiphenyl ether (HxBDEs), 43–44% heptabromodiphenyl ether (HeptaBDE) and 31–35% octabromodiphenyl (OcBDEs); and
- **Penta-BDE**, consisting of 50–62% pentabromodiphenyl ether (PeBDEs) and 24–38% tetrabromodiphenyl ethers (TeBDEs).

Hexabromocyclododecanes (HBCDs) are brominated cyclo-aliphatic flame retardants. The main downstream uses of HBCD are in the polymer and textile industries. The predominant use is for rigid insulation panels/boards for building construction (EPS and XPS). Only about 2 % of the total use of HBCD is in high impact polystyrene (HIPS), and use in electrical and electronic equipment is likely to be limited. It may also be used in PVC (wires, cables and textile coatings) (European Commission 2009). The recently published EU risk assessment for HBCD says in relation to these uses that "*industry has not confirmed that these uses are relevant in the EU. Thus, it cannot be excluded that HBCDD has been, is, or* will be used in these materials" (European Commission 2009).

HBCD can be used on its own or in combination with other flame retardants, for example antimony trioxide or decabromodiphenyl ether (deca-BDE). HBCD may also be used as an alternative for polybrominated diphenyl ethers (PBDEs) in some applications (Eljarrat, Guerra *et al.* 2009)

Unfortunately the bromine industry has been reluctant to publish information which would allow trends in the use of individual brominated flame-retardants to be derived. For example, the BSEF web site[9] simply says "*Deca-BDE, TBBPA and HBCD are the three main commercial brominated flame retardants*" and provides no production data for these compounds. Even the final EU summary of the risk assessment for DecaBDE (European Commission 2008) reported "*It was not possible to obtain information on the use of the total volume of substance produced in or imported into the European Community, therefore, some uses may exist which are not covered by this risk assessment."*

The most recent readily available data for worldwide usage of brominated flame-retardants is from the beginning of the decade:

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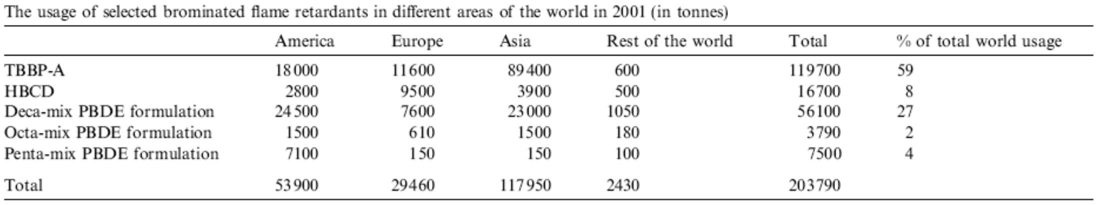
[8] Sometimes called Bis(pentabromophenyl)ether in EU reports

[9] http://www.bsef.com/our-substances/



The usage of selected brominated flame retardants in different areas of the world in 2001 (in tonnes)

	America	Europe	Asia	Rest of the world	Total	% of total world usage
TBBP-A	18000	11600	89400	600	119700	59
HBCD	2800	9500	3900	500	16700	8
Deca-mix PBDE formulation	24500	7600	23000	1050	56100	27
Octa-mix PBDE formulation	1500	610	1500	180	3790	2
Penta-mix PBDE formulation	7100	150	150	100	7500	4
Total	53900	29460	117950	2430	203790	

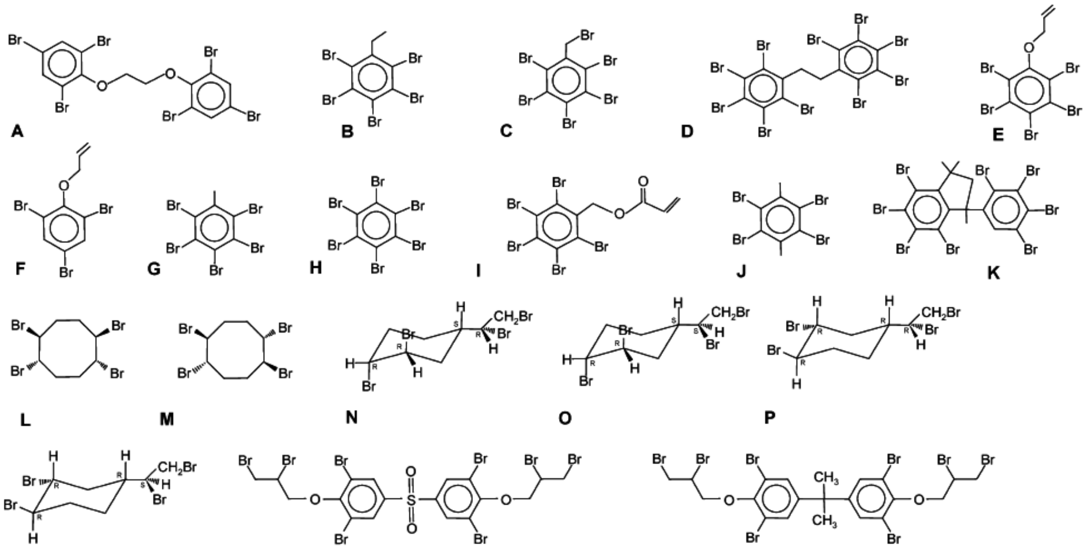
(Law, Allchin et al. 2006).

One significant change in the use of BFRs in recent years has resulted from various restrictions within the EU on the use of PBDEs. Following an assessment of penta- and octa-BDE under the EU Existing Substances Regulation, the marketing and use of both formulations has been banned in the EU since 15 August 2004 (European Parliament and Council 2003). Furthermore, the use of PBDEs in electrical and electronic products has been restricted since 2006 under the EU RoHS Directive (European Commission 2003). In 2008, the European Court of Justice held that European Commission acted illegally when it exempted Deca-BDE from an EU ban on several brominated flame retardants, including PBDEs, in electronic and electrical equipment (European Court of Justice 2008).

The hazardous properties of TBBPA, PBDEs and HBCD have been addressed in detail elsewhere, and are not discussed in this document (see Birnbaum & Staskal 2004).

Recent market developments for brominated flame retardants:

In response to increasing regulation in many countries and regions on certain BFR formulations, as well as the consideration of similar restrictions on other BFRs, alternative additive flame retardants for achieving commercial product fire safety standards are being developed and used (Verreault *et al.*, 2007). There is growing use and demand in the marketplace for non-regulated, additive non-PBDE BFRs (and other non-brominated compounds) as alternative flame retardants (Gauthier, Potter *et al.* 2009). It has been estimated that the total worldwide production volume of so called 'emerging' BFR (those BFRs other than TBBPA, PBDEs and HBCD) is around 100,000 metric tonnes per year (for all uses, not only EEE) (Harju, Heimstad *et al.* 2008). With increasing regulation and phasing-out of production of the commercial usage of PBDEs, it is expected that the production and usage of other BFRs will increase in the future (Ricklund, Kierkegaard *et al.* 2008).



Chemical structures of non-PBDE brominated flame retardants investigated by Gauthier (Gauthier, Potteret al. 2009): A, 1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE); B, pentabromoethylbenzene (PBEB); C, pentabromobenzyl bromide (PBBB); D, decabromodiphenylethane (DBDPE); E, pentabromophenyl allyl ether (PBPAE); F, 2,4,6-tribromophenyl allyl ether (TBPAE); G, pentabromotoluene (PBT); H, hexabromobenzene (HBB); I, pentabromobenzyl acrylate (PBBA); J, tetrabromo-p-xylene (pTBX); K, octabromo-1,3,3-trimethyl-1-phenylindane (OBIND), L/M, rand_-1,2,5,6-tetrabromocyclooctane (r- and _-TBCO); N/O/P/Q, r-, _-, γ-, and δ-1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (r-, _-, γ-, and δ-TBECH), respectively; R, tetrabromobisphenol-S-bis(2,3-dibromopropyl) ether (TBBP-DBPE); S, tetrabromobisphenol-A-bis (2,3-dibromopropyl) ether (TBBPA-DBPE). Most hydrogen atoms have been omitted for clarity.

Some examples of these so called ‘emerging’ BFRs include (Guerra, Eljarrat *et al.*);

- hexabromobenzene (hexaBBz),
- decabromodiphenylethane (DBDPE) (also known as Saytex 8010 or ethane 1,2 bis(pentabromophenyl), developed as an alternative to DecaBDE and used in applications similar to those in which the deca-BDE technical mixture was used
- 1,2-bis-2,4,6-tribromophenoxy-ethane (TBE or BTBPE)

Recent investigations have found some of these ‘emerging’ flame retardants in the environment at high levels, including BTBPE, which has been used as a replacement for OctaBDE and PentaBDE (Potrzebowksi and Chance 2004) and pentabromoethylbenzene (PEB or PBEB). In one study, the environmental concentration levels of BTBPE were higher than those of most PBDEs, and comparable to those of BDE 209 (the major constituent of deca-BDE) and TBBPA (Hoh, Zhu *et al.* 2005).

PBEB, hexaBBz, and DBDPE have been detected in environmental samples from Europe and North America, including sediments (Kierkegaard, Bjorklund *et al.* 2004; Hoh, Zhu *et al.* 2005; Leonards, Lopez *et al.* 2008; Lopez, Brandsma *et al.* 2008) , sewage sludge (Ricklund, Kierkegaard *et al.* 2008; Ricklund, Kierkegaard *et al.* 2009), air (Hoh, Zhu *et al.* 2005),house dust (Stapleton, Allen *et al.* 2008), blood and eggs of gulls (Gauthier, Hebert *et al.* 2007; Verreault, Gebbink *et al.* 2007).

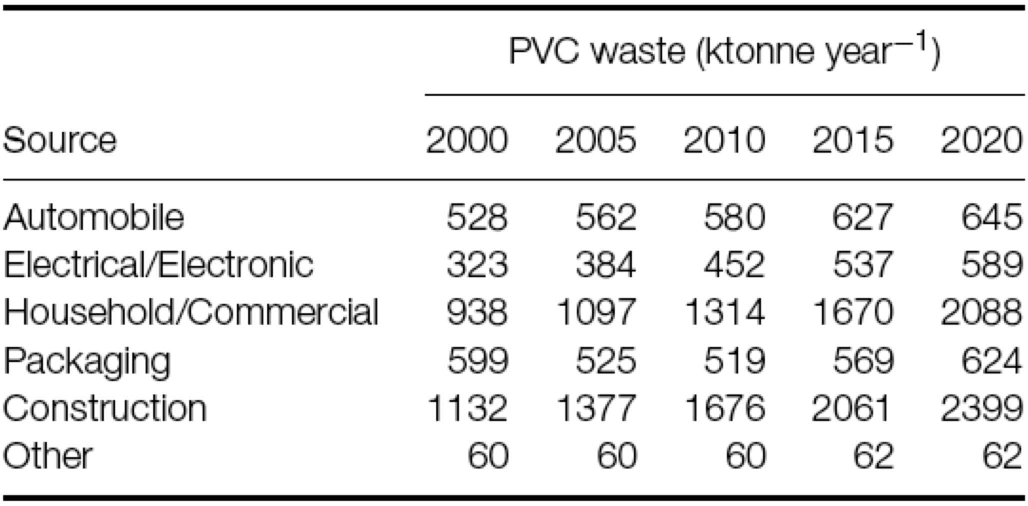
At least 10 articles in peer-reviewed journals now suggest that detectable amounts of DBDPE are escaping into the environment, and are being detected at up to the low parts-per million level. The American Chemical Society Journal Environmental Science and Technology (Betts 2009) described this as a “Glut of data” on the “new” flame retardant which “documents its presence all over the world”. Furthermore, spatial distribution patterns of DBDPE reported in China (Zhang, Luo *et al.* 2009) indicate that the emission sources of DBDPE are similar to those of PBDEs, consistent with the use of DBDPE as a replacement for deca-BDE (for all uses, not only for EEE).

Despite their ongoing use and widespread environmental distribution, there is little or no toxicological data available for wildlife or humans for these additive BFRs (Guerra, Eljarrat et al). A recent report commissioned by the Norwegian Pollution Control Authority summarised and assessed available data on so called emerging brominated flame retardants, including toxicological data and data on environmental distributions (Harju *et al.* 2009). The authors also noted the very limited data available on many of these compounds currently in use. Even with the relatively little data available, the authors recommended that 12 of the 21 BFRs investigated should be considered for further investigation and monitoring due to concerns over their properties, including DBDPE & BTBPE.

It is highly likely that the lists published to date of brominated compounds for which there is widespread environmental contamination are not comprehensive. One study of contaminants in bird eggs reported identifying “more than 15 chromatographically distinct peaks” over the elution times of the PBDEs and other non-PBDE BFRs, suggesting that there remain “numerous, unidentified brominated compounds and degradation products in glaucous gull samples, which warrants further research” (Gauthier, Hebert *et al.* 2007; Verreault, Gebbink *et al.* 2007). Similarly, numerous unidentified, bromine-containing compounds were also reported in egg homogenates of herring gulls from colonial sites in the Laurentian Great Lakes of North America, along with data showing that decabromodiphenyl ethane (DBDPE) concentrations surpassed those of DecaBDE (Gauthier, Potter *et al.* 2009). Both BTBPE and DBDPE are know to have been used in EEE (Schlummer, Gruber *et al.* 2007, Betts 2009).

Polyvinyl chloride (PVC)

The use of the chlorinated plastic polyvinyl chloride (PVC) is the predominant source of chlorinated organic substances in electrical and electronic equipment. The quantity of PVC in e-waste generated within the EU has been reported to be approximately one third of a million tonnes per year, a value which is predicted to increase in coming years, as outlined in the table below.



	PVC waste (ktonne year^{-1})				
Source	2000	2005	2010	2015	2020
Automobile	528	562	580	627	645
Electrical/Electronic	323	384	452	537	589
Household/Commercial	938	1097	1314	1670	2088
Packaging	599	525	519	569	624
Construction	1132	1377	1676	2061	2399
Other	60	60	60	62	62

Predicted (2000–2020) post-consumer PVC waste composition for the EU (Keane 2007):

Although PVC does not have direct toxicity, this plastic does present its own waste management problems by acting as a source of organic-bound chlorine to the waste stream. As with the presence of brominated flame retardants, this source of organo-halogens to WEEE can result in the formation and release of hazardous substances under certain recycling and disposal processes, including the formation of products of incomplete combustion, particularly during certain substandard processes such as open burning. Of particular concern is the potential for the formation of chlorinated dioxins and furans under these conditions. These end of life impacts are discussed in more detail in the section below.

The use of PVC in EEE is also associated with other potential impacts. Many PVC based materials incorporate additives to improve the properties of the materials, some of which are hazardous substances which can be released from the material both during use and following disposal. One example of this is the use of phthalate esters (phthalates) in some flexible PVC formulations. Phthalate formulations can be a single chemical substances such as di(ethylhexyl) phthalate (DEHP), or mixtures of compounds, such as di-iso-nonyl phthalate (DINP), or di-iso-decyl phthalate (DIDP), Phthalates are recognised as one of the most abundant man-made environmental contaminants, and some are toxic to humans and wildlife. DEHP, one of the most widely used phthalates, is toxic to reproductive development in mammals (AEA Technology plc 2006), and has been classified as “toxic to reproduction” within Europe.

Transformation of halogenated substances in e-waste into other hazardous substances during recycling and disposal.

In addition to the intrinsic hazardous properties of many halogenated substances used in EEE (Birnbaum & Staskal 2004), this group of substances poses additional hazards when products reach their end of life and become e-waste. During some recycling and disposal operations (e.g incineration, smelting and particularly by the use of open burning), the presence of halogenated substances can result in the formation of other hazardous substances. Of particular concern is the potential for the formation of halogenated dioxins and furans. Chlorinated substances, such as PVC, potentially give rise to polychlorinated dibenzo dioxins/furans (PCDD/Fs), often called chlorinated dioxins/furans; brominated substances can give rise to polybrominated dibenzo dioxins/furans (PBDD/Fs), or brominated dioxins/furans. Where both chlorinated and brominated substances are present in e-waste, there is the potential for the formation of mixed chlorinated-brominated dioxins/furans (polybrominated-polychlorinated dibenzo dioxins/furans, PXDD/Fs), a group of substances which have been subject to very few studies on their potential impact on human health and the environment, compared to chlorinated or brominated analogues. These transformation processes and the hazardous substances formed are discussed in the following sections.

The Industry accepts that some BFRs have the potential to form brominated dioxins/furans during processing and disposal, and says (European Chemical Industry Council (CEFIC) and European Flame Retardants Association 2005):

"*Because it [DecaBDE] is a bromine containing compound whose structure is such that there may be potential for forming brominated dibenzodioxins or furans (PBDD/F) in uncontrolled thermal processes. Therefore, all handling operations of DBDE containing plastics, such as compounding, converting, cleaning, recovery and recycling, have to be carried out under strictly controlled temperature conditions*".

And:

"*DecaBDE is a brominated compound so conditions conducive to the formation of dioxins/furans in thermal processes should be avoided in processing and disposal"*

Under thermal stress, brominated flame retardants release hydrogen bromide (HBr). HBr inhibits the spreading of fire by substituting the more reactive H and HO radicals in the radical chain reaction for less reactive Br radicals (Ebert and Bahadir 2003). The production of HBr means that BFR treated materials tend to produce corrosive and obscuring smoke when burned (Balabanovich, Luda *et al.* 2003). Antimony(III) oxide is commonly used as a synergist with BFRs, with the resulting effect that fire inhibition is increased (Ebert and Bahadir 2003).

However, according to Balabanovich (Balabanovich, Luda *et al.* 2003) "they [brominated aromatic substances] increase health and environment impact because they can give supertoxic polyhalogenated dibenzodioxins and dibenzofurans on heating".

There is a growing recognition that BHCs (brominated hydrocarbons), which includes PBDD/Fs (polybrominated dibenzo dioxins/furans), are formed and emitted during the thermal treatment of brominated flame retardants in fabrics, plastics and electronic materials (Cormier, Lomnicki *et al.* 2006).

For example, TBBPA is synthesized from bisphenol A in a not very selective process. This contributes to its use being responsible for producing bromobisphenols and bromophenols in the gases generated by heating. Molto (Molto, Font *et al.* 2009) sampled emissions during controlled heating of circuit boards containing TBBPA, from room temperature to higher than 1000 K, thereby covering "an extensive range of decomposition". Emissions of brominated dioxins/furans, as well as bromobenzene, dibromophenols and other bromo-chlorinated compounds were also identified. This study identified around 140 semi-volatile compounds as reaction products, 20 of which were brominated compounds. Molto concluded that "*thermal treatment of this kind of waste in no (sic) optimal conditions is that the emissions can be a health and environmental hazard that must be subjected to strong studies and controls*".

The potential for the presence of BFRs to contribute to the formation and release of hazardous transformation products has been known for some time. In 1986 Buser (Buser 1986) found formation of PBDDs/Fs through thermolysis of PBDE brominated flame retardants. Buser performed thermolysis at 630℃ wi th penta-, octa- and decaBDEs flame retardants. He confirmed the formation of PBDDs/DFs with a maximum yield of 10%, and warned:

"PBDFs and PBDDs may thus form to some degree in fires, from incineration or accidential (sic) burning of materials containing PBDPEs [the acronym historically used, now commonly replaced by PBDEs]. Formation of these hazardous compounds would pose an additional potential health risk to the public and a threat to the environment. These adverse effects should be carefully compared against the possible merits of these products and should encourage re-evaluation of PBDPEs as flame retardant additives".

Thoma *et al.* (Thoma, Rist *et al.* 1986) carried out similar thermal decomposition experiments on polybromophenol (PBP) and TBBPA at 700, 800 and 900℃, and detected PBDDs/Fs in residues of the thermal reactions, with the highest levels being formed at 800℃.

Dumler *et al.* (Dumler, Thoma *et al.* 1989) showed that a yield of PBDFs increased up to a maximum of 16% when a polymer containing decaBDE was thermally decomposed. They reported that antimony oxide has a large effect on PBDDs/Fs formation, and increases the range of temperatures over which they are formed.

Furthermore, Klusmeier (Klusmeier, Vogler *et al.* 1988) found a wide range of brominated thermal degradation products from decaBDE. Those which could be identified included tetrabromoethane; pentabromobenzene; hexabromobutadiene; hexabromobenzene; hexabromobenzofuran; hexabromoindone; octabromodiphenyl ether; heptabromodibenzofuran; heptabromodibenzodioxin; nonabromodiphenyl ether (isomer); nonabromodiphenyl ether (isomer); octabromodibenzofurann; octabromodibenzodioxin.

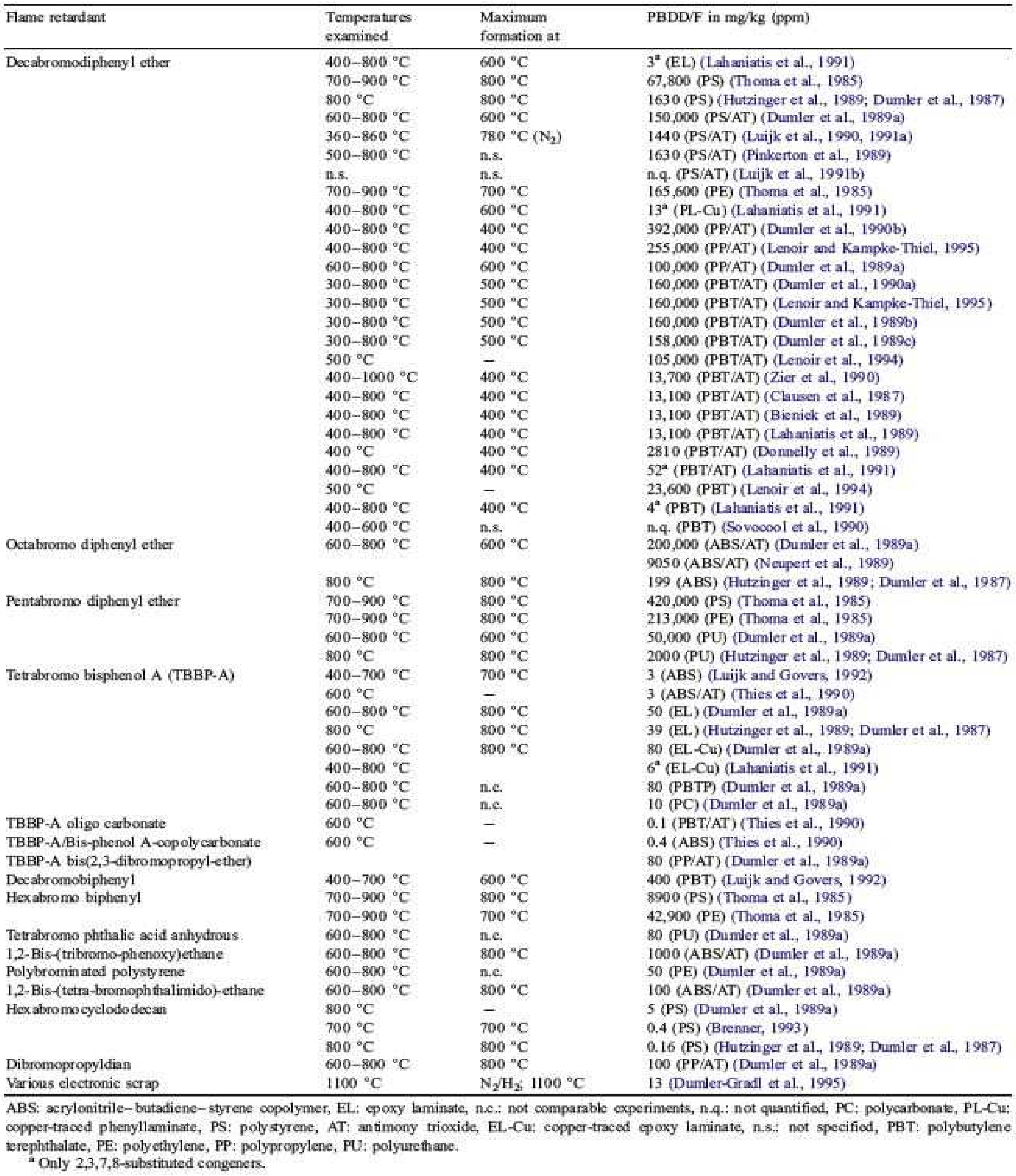
Specifically for the treatment of BFR containing printed circuit boards, Barontini (Barontini and Cozzani 2006) more recently noted that "results obtained confirm that the formation of PBDD and PBDF may be expected from the combustion of electronic scrap and of materials containing BFRs". This is further supported by evidence that treatment of such materials under conditions that mimic rudimentary recycling operations releases substantial quantities of brominated dioxin/furans (Gullett, Linak *et al.* 2007).

Formation of dioxins from 'emerging' BFRs

The potential for the formation of brominated dioxins/furans from the treatment of BFRs and BFR containing materials is not restricted to PBDEs and TBBPA. The industry has said (Pritchard 2005) that "*it is by no means inevitable*" that all brominated FRs will generate dioxins or furans when strongly heated. For example, decabromodiphenyl ethane (DBDPE) was developed many years ago by Albemarle with the specific intention of demonstrating the possibility of a 'safe' brominated FR, minimising dioxin and furan formation when processed or incinerated. It was introduced to the market in 1992 as an alternative to deca-BDE. It has been claimed that this "safe incineration" with regard the formation of transformation substances arises because of its chemical structure which, "unlike the polybromodiphenyl ethers (PBDEs), has two aromatic rings bridged by an ethane bridge" (Pritchard 2005). It is also claimed that DBDPE produces no polybrominated dibenzop-dioxins and only "minor quantities" of 2,3,7,8-tetrabromodibenzo-p-furan under pyrolysis conditions (Kierkegaard, Bjorklund *et al.* 2004).

This argument, however, is too simplistic and ignores certain mechanisms by which brominated dioxins can be formed during the thermal degradation of BFRs. These processes, including de novo formation in cooling gases released during thermal degradation of BFRs or BFR treated materials, are demonstrated by the formation of brominated dioxins from the thermal degradation of aliphatic BFRs such as HBCD, as well as the formation of mixed brominated-chlorinated dioxins from e-wastes containing both chlorinated substances and brominated substances, as discussed below. These processes demonstrate that the formation of halogenated dioxins is not dependant on the specific characteristics of a BFR, and that therefore all BFRs have the potential to act as precursors for the formation of brominated and mixed dioxins/furans.

Ebert and Bahadir (2003) compiled published data on the formation of PBDD/Fs after thermal degradation of various BFRs at temperatures above 300℃, as reproduced in the table below. These data included the identification of brominated dioxins/furans from HBCD treated polystyrene, as well as the ‘emerging’ BFR BTBPE.



Flame retardant	Temperatures examined	Maximum formation at	PBDD/F in mg/kg (ppm)
Decabromodiphenyl ether	400–800 °C	600 °C	3[a] (EL) (Lahaniatis et al., 1991)
	700–900 °C	800 °C	67,800 (PS) (Thoma et al., 1985)
	800 °C	800 °C	1630 (PS) (Hutzinger et al., 1989; Dumler et al., 1987)
	600–800 °C	600 °C	150,000 (PS/AT) (Dumler et al., 1989a)
	360–860 °C	780 °C (N_2)	1440 (PS/AT) (Luijk et al., 1990, 1991a)
	500–800 °C	n.s.	1630 (PS/AT) (Pinkerton et al., 1989)
	n.s.	n.s.	n.q. (PS/AT) (Luijk et al., 1991b)
	700–900 °C	700 °C	165,600 (PE) (Thoma et al., 1985)
	400–800 °C	600 °C	13[a] (PL-Cu) (Lahaniatis et al., 1991)
	400–800 °C	400 °C	392,000 (PP/AT) (Dumler et al., 1990b)
	400–800 °C	400 °C	255,000 (PP/AT) (Lenoir and Kampke-Thiel, 1995)
	600–800 °C	600 °C	100,000 (PP/AT) (Dumler et al., 1989a)
	300–800 °C	500 °C	160,000 (PBT/AT) (Dumler et al., 1990a)
	300–800 °C	500 °C	160,000 (PBT/AT) (Lenoir and Kampke-Thiel, 1995)
	300–800 °C	500 °C	160,000 (PBT/AT) (Dumler et al., 1989b)
	300–800 °C	500 °C	158,000 (PBT/AT) (Dumler et al., 1989c)
	500 °C	–	105,000 (PBT/AT) (Lenoir et al., 1994)
	400–1000 °C	400 °C	13,700 (PBT/AT) (Zier et al., 1990)
	400–800 °C	400 °C	13,100 (PBT/AT) (Clausen et al., 1987)
	400–800 °C	400 °C	13,100 (PBT/AT) (Bieniek et al., 1989)
	400–800 °C	400 °C	13,100 (PBT/AT) (Lahaniatis et al., 1989)
	400 °C	400 °C	2810 (PBT/AT) (Donnelly et al., 1989)
	400–800 °C	400 °C	52[a] (PBT/AT) (Lahaniatis et al., 1991)
	500 °C	–	23,600 (PBT) (Lenoir et al., 1994)
	400–800 °C	400 °C	4[a] (PBT) (Lahaniatis et al., 1991)
	400–600 °C	n.s.	n.q. (PBT) (Sovocool et al., 1990)
Octabromo diphenyl ether	600–800 °C	600 °C	200,000 (ABS/AT) (Dumler et al., 1989a)
			9050 (ABS/AT) (Neupert et al., 1989)
	800 °C	800 °C	199 (ABS) (Hutzinger et al., 1989; Dumler et al., 1987)
Pentabromo diphenyl ether	700–900 °C	800 °C	420,000 (PS) (Thoma et al., 1985)
	700–900 °C	800 °C	213,000 (PE) (Thoma et al., 1985)
	600–800 °C	600 °C	50,000 (PU) (Dumler et al., 1989a)
	800 °C	800 °C	2000 (PU) (Hutzinger et al., 1989; Dumler et al., 1987)
Tetrabromo bisphenol A (TBBP-A)	400–700 °C	700 °C	3 (ABS) (Luijk and Govers, 1992)
	600 °C	–	3 (ABS/AT) (Thies et al., 1990)
	600–800 °C	800 °C	50 (EL) (Dumler et al., 1989a)
	800 °C	800 °C	39 (EL) (Hutzinger et al., 1989; Dumler et al., 1987)
	600–800 °C	800 °C	80 (EL-Cu) (Dumler et al., 1989a)
	400–800 °C		6[a] (EL-Cu) (Lahaniatis et al., 1991)
	600–800 °C	n.c.	80 (PBTP) (Dumler et al., 1989a)
	600–800 °C	n.c.	10 (PC) (Dumler et al., 1989a)
TBBP-A oligo carbonate	600 °C	–	0.1 (PBT/AT) (Thies et al., 1990)
TBBP-A/Bis-phenol A-copolycarbonate	600 °C	–	0.4 (ABS) (Thies et al., 1990)
TBBP-A bis(2,3-dibromopropyl-ether)			80 (PP/AT) (Dumler et al., 1989a)
Decabromobiphenyl	400–700 °C	600 °C	400 (PBT) (Luijk and Govers, 1992)
Hexabromo biphenyl	700–900 °C	800 °C	8900 (PS) (Thoma et al., 1985)
	700–900 °C	700 °C	42,900 (PE) (Thoma et al., 1985)
Tetrabromo phthalic acid anhydrous	600–800 °C	n.c.	80 (PU) (Dumler et al., 1989a)
1,2-Bis-(tribromo-phenoxy)ethane	600–800 °C	800 °C	1000 (ABS/AT) (Dumler et al., 1989a)
Polybrominated polystyrene	600–800 °C	n.c.	50 (PE) (Dumler et al., 1989a)
1,2-Bis-(tetra-bromophthalimido)-ethane	600–800 °C	800 °C	100 (ABS/AT) (Dumler et al., 1989a)
Hexabromocyclododecan	800 °C	–	5 (PS) (Dumler et al., 1989a)
	700 °C	700 °C	0.4 (PS) (Brenner, 1993)
	800 °C	800 °C	0.16 (PS) (Hutzinger et al., 1989; Dumler et al., 1987)
Dibromopropyldian	600–800 °C	800 °C	100 (PP/AT) (Dumler et al., 1989a)
Various electronic scrap	1100 °C	N_2/H_2; 1100 °C	13 (Dumler-Gradl et al., 1995)

ABS: acrylonitrile–butadiene–styrene copolymer, EL: epoxy laminate, n.c.: not comparable experiments, n.q.: not quantified, PC: polycarbonate, PL-Cu: copper-traced phenyllaminate, PS: polystyrene, AT: antimony trioxide, EL-Cu: copper-traced epoxy laminate, n.s.: not specified, PBT: polybutylene terephthalate, PE: polyethylene, PP: polypropylene, PU: polyurethane.

[a] Only 2,3,7,8-substituted congeners.

Formation of PBDD/Fs after thermal degradation of BFRs above 300^{o}C, reproduced from Ebert and Bahadir 2003.

Whilst there is less published research on the newer flame retardants, there are already indications that use of these does not avoid the problem of brominated and mixed dioxins/furans. In addition to the data summarised in the table above, Balabanovich (Balabanovich, Luda *et al.* 2003) also reported that "*Polybrominated dibenzodioxins (PBDD) and dibenzofurans were found in amounts from one ppm to some hundred ppms on combustion of ABS containing 18% BTBPE and 7%* Sb_2O_3". They found a wide range of emissions from extended pyrolysis of BTBPE (such as may be expected in smouldering fires).

Balabanovich also demonstrated that brominated phenoxyphenols and brominated dioxins can be produced by the condensation of phenolic -OH and aromatic bromine in conditions in which secondary reactions take place (Balabanovich, Luda *et al.* 2003).

The formation of brominated dioxins from bromophenols has been intensively studied: Borojovich*et al.* (Borojovich and Aizenshtat 2002) indicated that short-term exposures of brominated phenols to pyrolysis conditions yielded brominated dibenzodioxins and some furans. Evans and Dellinger (Evans and Dellinger 2005) investigated the mechanism of brominated dioxin formation from the pyrolysis of 2-bromophenol. Evans and Dellinger (Evans and Dellinger 2005) also demonstrated the formation of mixed dioxins and furans from the pyrolysis of a chlorophenol and bromophenol mixture. Sidhu*et al.* (Sidhu, Maqsud *et al.* 1995) further indicated a maximum yield of 25% for the gas phase formation of tetra-brominated dioxin isomers from 2,4,6-tribomophenol.

These studies demonstrate that non-aromatic BFRs, therefore, could generate PBDD/Fs if they produced bromophenols on heating. Desmet (Desmet, Schelfaut *et al.* 2005) investigated this with hexabromocyclododecane (HBCD) used as flame retardant in polystyrene and found that various bromophenols were formed upon combustion. The authors concluded "*this formation seems to be inherent to the flame retardant mechanism of HBCD". Crucially the data presented "suggest that the use of halogenated flame retardants should not only be scrutinised from their inherent ability to form halogenated dioxins in thermal decomposition reactions, but that an interaction with the polymer breakdown products which could lead to the formation of well known dioxin precursors such as halogenated phenols should also be taken into account when evaluating the impact of BFR-treated materials on the environment.*". This is consistent with the data summarized by Ebert and Bahadir (2003) in the table above that demonstrates the formation of brominated dioxins/furans from thermal degradation of HBCD treated polystyrene.

Brominated dioxins and furans as contaminants of BFRs

Concerns about contamination by brominated dioxins/furans are not limited to the generation of these compounds by combustion of BFR containing materials during the end of life period. Ever since Thoma (Thoma, Rist *et al.* 1986) found brominated furan (PBDFs) contamination in TBBPA at ppb concentrations in 1986[10] concerns have also included the contamination of BFRs with brominated dioxins/furans during BFR production.

The World Health Organisation (WHO) warned in 1998 that *"PBDDs/PBDFs have been found as contaminants in brominated organic chemicals (e.g. bromophenols) and, in particular, in flame retardants, such as polybrominated diphenyl ethers (PBDEs), decabromobiphenyl (decaBB or DBB), 1,2-bis(tribromophenoxy)ethane, tetrabromobisphenol A (TBBPA), and others"* (WHO 1998).

In addition to the direct contamination of BFR formulations by brominated dioxins/furans, there also appear to have been other relevant contaminants including brominated hydroxybiphenyls as reported by Timmons (Timmons and Brown 1988), which are obvious precursors for the formation of brominated dioxins in fires.

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[10] Buser having already established the formation of brominated dioxins from Firemaster BP-6 (mainly 2,4,5,2',4',5'-hexabromobiphenyl) in 1978 (See page 119: Buser, H. R., H.-P. Bosshardt,*et al.* (1978). "Formation of polychlorinated dibenzofurans (PCDFs) from the pyrolysis of PCBs." Chemosphere **7**(1): 109-119).

Other more recent work has confirmed the contamination of materials containing PBDEs with PBDD/Fs. Sakai (Sakai, Watanabe *et al.* 2001) reported high levels of contamination, particularly on circuit boards containing percent level of PBDEs, as shown below in the table reproduced from Sakai, Watanabe*et al.* 2001:

Analytical item	Samples			
	PBDEs/PE	**TBBP-A/ABS**	TV casing materials	Printed circuit boards
Chlorine (Cl) (%)	ND < 0.025	2.0	0.021	1.1
Bromine (Br) (%)	8.8	8.8	3.7	2.2
Flame retardant PBDEs (μg/g)	20,000	–	6300	11,000
Flame retardant TBBP-A (μg/g)	–	420	2.4	500
PBDDs/DFs (ng/g)	3100	0.62	3000	130,000
PCDDs/DFs (ng/g)	–	0.04	0.69	0.31
PCDDs/DFs (ng-TEQ/g)	–	0.002	0.0008	0
Br_1 Cl_yDDs/DFs (ng/g)	–	–	ND	ND
Br_2 Cl_yDDs/DFs (ng/g)	–	–	ND	ND
$Br_x Cl_1$DDs/DFs (ng/g)	–	–	ND	9.5
Bromobenzene(PBBz) (ng/g)	–	–	5800	95,000
Bromophenol (PBP) (ng/g)	–	–	79,000	20,000

Significant levels of PBDDs/Fs have also been detected in waste television cabinets and other flame-retarded plastics (Watanabe and Sakai 2003). Furthermore, Tasaki (Tasaki, Takasuga *et al.* 2004) reported high, and increasing, levels of brominated dioxins in the rear covers of TV sets in Japan, as reproduced in the table below:

Contents of PBDDs/DFs in rear covers of TV sets in Japan

	Content (μg/kg) ($n = 1^a$)			Quantitation limit
	1987–1989	1990–1993	1995–1998	
MonoBDDs	<0.005	0.005	<0.005	0.005
DiBDDs	<0.005	0.089	0.049	0.005
TriBDDs	<0.005	1.3	0.36	0.005
TetraBDDs	0.13	200	39	0.005
PentaBDDs	<0.01	0.094	1.3	0.01
HexaBDDs	<0.05	<0.05	2.3	0.05
HeptaBDDs	<0.5	0.76	3.5	0.5
OctaBDD	<5	<5	<5	5
MonoBDFs	0.32	0.77	9	0.005
DiBDFs	3.1	5	46	0.005
TriBDFs	8.6	13	310	0.005
TetraBDFs	38	59	120	0.005
PentaBDFs	140	250	500	0.01
HexaBDFs	1,000	2,400	5,300	0.05
HeptaBDFs	1,500	3,000	6,600	0.5
OctaBDF	99,000	230,000	500,000	5
PBDDs/PBDFs	101,678	235,910	512,566	–
as Br	81,000	180,000	410,000	–

[a] Nine TV sets were mixed and measured.

The authors reported that for PBDEs, TBBPA and PBDDs/DFs, the analysed contents in TV covers *"varied widely"* and that this *was "probably due to the differences in manufacturing companies, production processes, or manufacturing year. Information obtained from the manufacturers revealed that manufacturing companies have changed the type of BFRs used [over time]"* and therefore the authors analysed components based on a range of years for which the products were manufactured, as shown in the table.

More recently, Schlummer (Schlummer, Gruber *et al.* 2007) reported that contamination of all samples (n=4) of mixed WEEE plastics tested exceeded the German limit value of 1 ppb for brominated dioxin/furan contamination (sum 4[11]), and two of the four samples exceeded the sum 5[11] limits, as reproduced below from Schlummer, Gruber*et al.* 2007. Of these plastic samples, all four contained PBDEs, three contained TBBPA and two contained BTBPE.

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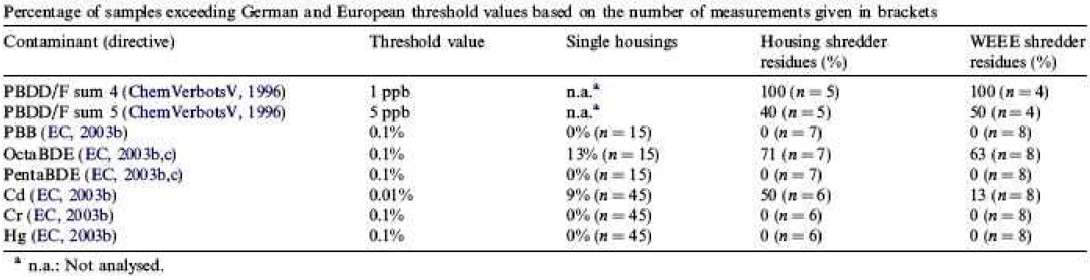
[11] the sum of 2,3,7,8-TeBDF, 2,3,7,8-TeBDD, 2,3,4,7,8-PeBDF and 1,2,3,7,8-PeBDD, as well as in terms of PBDD/F. Sum 5 is the sum of sum 4 plus 1,2,3,7,8-PeBDF, 1,2,3,6,7,8-HxBDD, 1,2,3,4,7,8-HxBDD and 1,2,3,7,8,9- HxBDD.

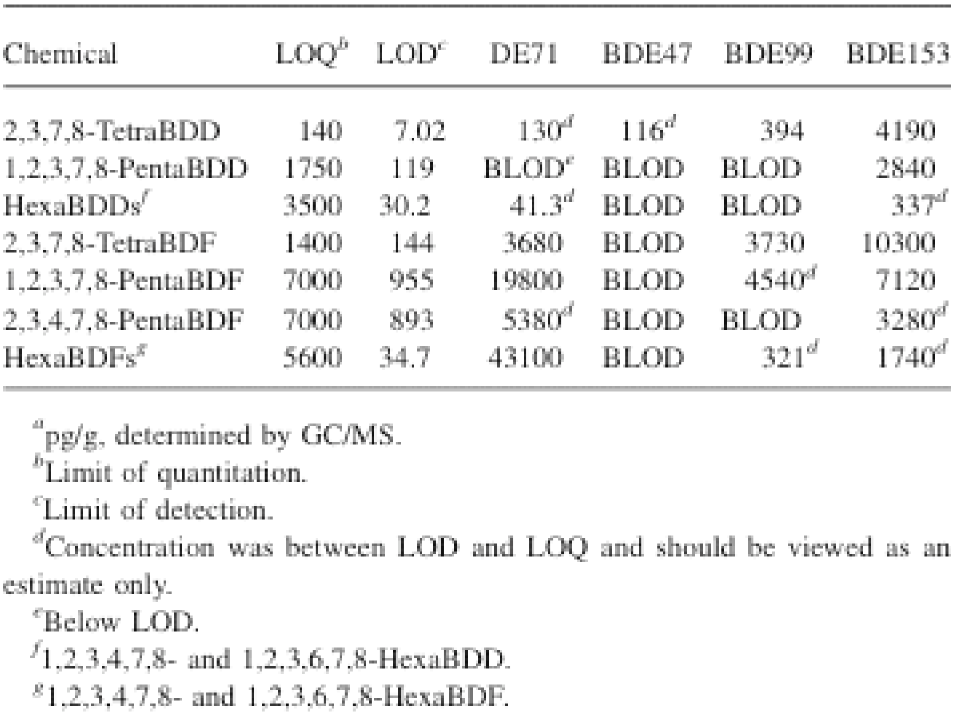


Percentage of samples exceeding German and European threshold values based on the number of measurements given in brackets

Contaminant (directive)	Threshold value	Single housings	Housing shredder residues (%)	WEEE shredder residues (%)
PBDD/F sum 4 (ChemVerbotsV, 1996)	1 ppb	n.a.[a]	100 ($n = 5$)	100 ($n = 4$)
PBDD/F sum 5 (ChemVerbotsV, 1996)	5 ppb	n.a.[a]	40 ($n = 5$)	50 ($n = 4$)
PBB (EC, 2003b)	0.1%	0% ($n = 15$)	0 ($n = 7$)	0 ($n = 8$)
OctaBDE (EC, 2003b,c)	0.1%	13% ($n = 15$)	71 ($n = 7$)	63 ($n = 8$)
PentaBDE (EC, 2003b,c)	0.1%	0% ($n = 15$)	0 ($n = 7$)	0 ($n = 8$)
Cd (EC, 2003b)	0.01%	9% ($n = 45$)	50 ($n = 6$)	13 ($n = 8$)
Cr (EC, 2003b)	0.1%	0% ($n = 45$)	0 ($n = 6$)	0 ($n = 8$)
Hg (EC, 2003b)	0.1%	0% ($n = 45$)	0 ($n = 6$)	0 ($n = 8$)

[a] n.a.: Not analysed.

Commercial PBDE mixtures tested by Hanari and his co-workers (Hanari, Kannan *et al.* 2006) were recently found to contain both polybrominated biphenyls (PBBs) and brominated furans (PBDFs), as impurities, at concentrations in the range of several tens to several thousands of nanograms per gram. Concentrations of total PBDFs were generally greater than those of total PBBs and, unlike a slightly earlier study by Sanders (Sanders, Burka *et al.* 2005), PBDDs were not detected at levels above the limit of detection:



Chemical	LOQ[b]	LOD[c]	DE71	BDE47	BDE99	BDE153
2,3,7,8-TetraBDD	140	7.02	130[d]	116[d]	394	4190
1,2,3,7,8-PentaBDD	1750	119	BLOD[e]	BLOD	BLOD	2840
HexaBDDs[f]	3500	30.2	41.3[d]	BLOD	BLOD	337[d]
2,3,7,8-TetraBDF	1400	144	3680	BLOD	3730	10300
1,2,3,7,8-PentaBDF	7000	955	19800	BLOD	4540[d]	7120
2,3,4,7,8-PentaBDF	7000	893	5380[d]	BLOD	BLOD	3280[d]
HexaBDFs[g]	5600	34.7	43100	BLOD	321[d]	1740[d]

[a] pg/g, determined by GC/MS.

[b] Limit of quantitation.

[c] Limit of detection.

[d] Concentration was between LOD and LOQ and should be viewed as an estimate only.

[e] Below LOD.

[f] 1,2,3,4,7,8- and 1,2,3,6,7,8-HexaBDD.

[g] 1,2,3,4,7,8- and 1,2,3,6,7,8-HexaBDF.

Concentrations of PBDDs and PBDFs in certain PBDEs (pg/g), reproduced from Sanders, Burkaet al. 2005

Hanari reported that the profiles of PBB and PBDF congeners varied with the degree of bromination of the commercial PBDE mixtures (i.e. more highly brominated mixtures of PBDEs contained heavily brominated homologues of PBBs and PBDFs).

Sanders (Sanders, Burka *et al.* 2005) suggested that PBDFs and PBDDs may be responsible for most, if not all, dioxin-like properties previously observed for PBDEs and that *“The presence of these minor components should be considered in future studies and in risk characterization of products containing PBDEs.”* It seems particularly anomalous, therefore, that most of the testing of PBDE congeners (such as in the EU supported FIRE[12] project) has been carried out after having stripped the brominated dioxins and furans from the chemicals. This will not give the true environmentally relevant impacts of PBDE formulations– in the real

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[12] The Flame retardants Integrated Risk assessment for Endocrine effects project http://www.rivm.nl/fire/

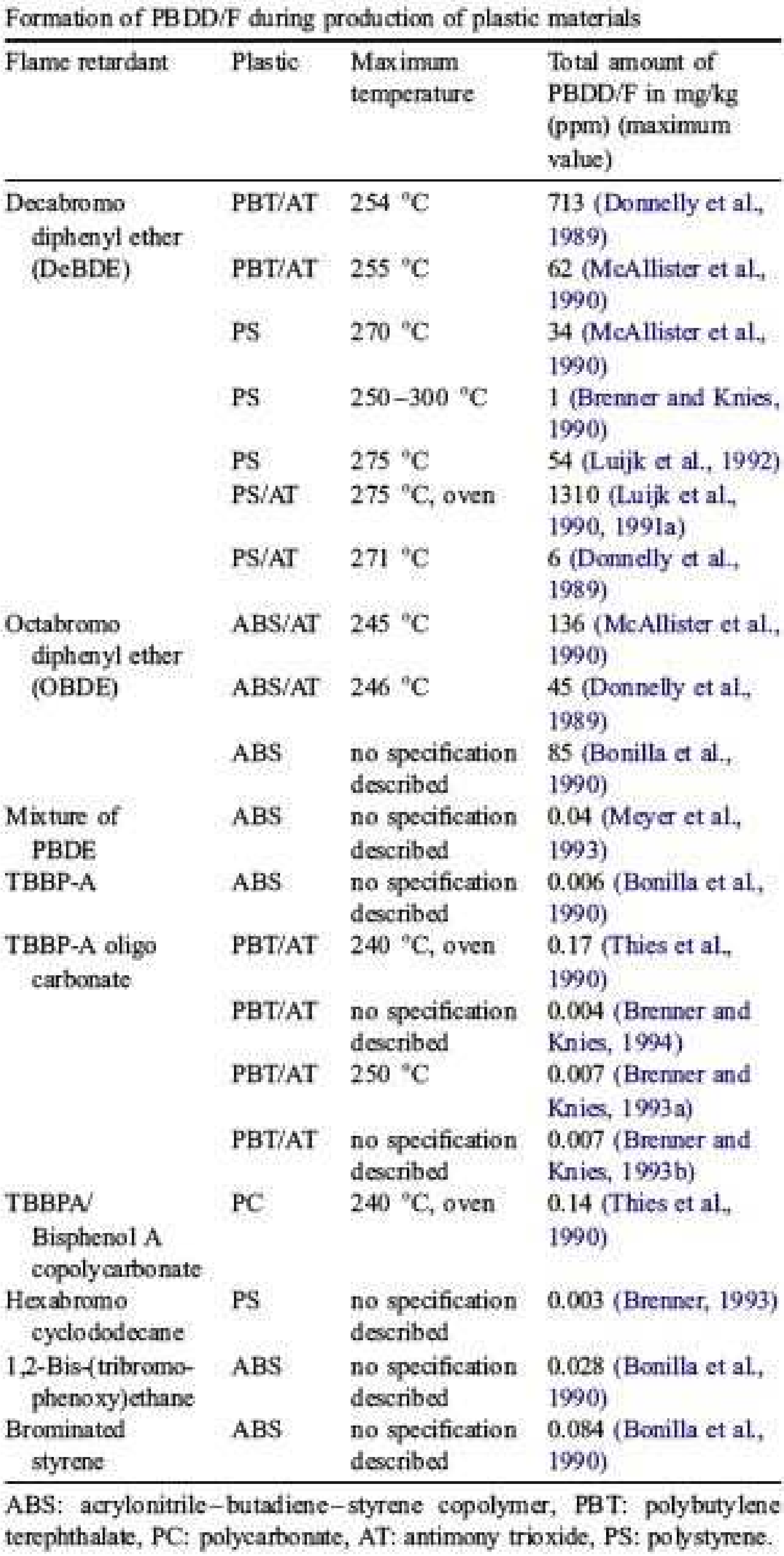
world these chemicals will be applied and released together with the associated PBDFs. If congeners are ‘cleaned’ in this way then it is vital that this is made very clear in the results, so that the impression is not given that the toxicity data reflects the technical mixtures when that is not the case.

On the basis of the production/usage of commercial PBDE mixtures in 2001, Hanari calculated that the potential global annual emissions of PBBs and PBDFs were 40 and 2300 kg, respectively. The content of PBBs and PBDFs in the PBDEs formulations used in Europe in 2001 was calculated to be 315 kg – mainly as a contaminant of Deca-BDE (Hanari, Kannan *et al.* 2006).

Additionally, PBDD/Fs may be formed from PBDEs during use by photolytic degradation (Soderstrom, Sellstrom *et al.* 2004). Hagberg (Hagberg, Olsman *et al.* 2006) reported substantial formation of PBDF congeners during photolytic decomposition of decaBDE in toluene. Twenty-seven mono- to hexasubstituted polybrominated dibenzofurans (PBDFs) were detected in toluene solutions of decabromodiphenyl ether (decaBDE) after irradiation with UV-A, UV-AB and UV-ABC. It is not yet clear to what extent these accelerated degradation experiments reflect conditions experienced by BFRs in actual applications.

PBDD/Fs can also be formed from BFRs by thermal stress (Ebert and Bahadir 2003), during extrusion of plastics containing PBDEs (Luijk, J.*et al.* 1992), in domestic fires (Zelinski, Lorenz *et al.* 1993), or under pyrolysis (Luijk and Govers 1992).

Much of the evidence for the contamination of BFRs with PBDD/Fs, as well as for the formation of PBDD/Fs from BFRs under various conditions, is associated with the use of PBDEs. However, there is also evidence for these for other BFRs, including TBBPA, HBCD, as well as certain ‘emerging’ BFRs, for example BTBPE. Examples for BFRs other than PBDEs are given in the tables below reproduced from Ebert and Bahadir 2003.

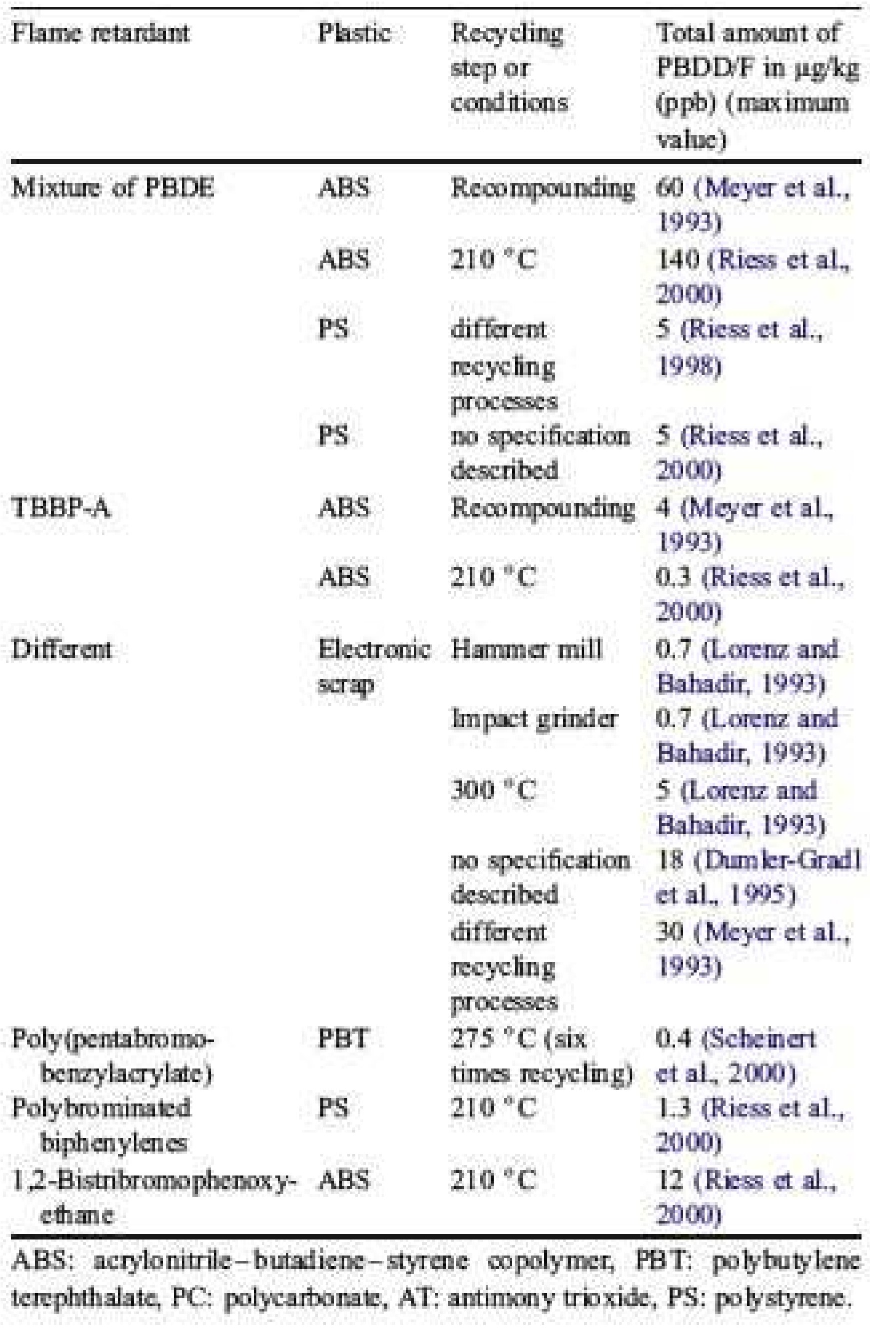


Formation of PBDD/F during production of plastic materials

Flame retardant	Plastic	Maximum temperature	Total amount of PBDD/F in mg/kg (ppm) (maximum value)
Decabromo diphenyl ether (DeBDE)	PBT/AT	254 °C	713 (Donnelly et al., 1989)
	PBT/AT	255 °C	62 (McAllister et al., 1990)
	PS	270 °C	34 (McAllister et al., 1990)
	PS	250–300 °C	1 (Brenner and Knies, 1990)
	PS	275 °C	54 (Luijk et al., 1992)
	PS/AT	275 °C, oven	1310 (Luijk et al., 1990, 1991a)
	PS/AT	271 °C	6 (Donnelly et al., 1989)
Octabromo diphenyl ether (OBDE)	ABS/AT	245 °C	136 (McAllister et al., 1990)
	ABS/AT	246 °C	45 (Donnelly et al., 1989)
	ABS	no specification described	85 (Bonilla et al., 1990)
Mixture of PBDE	ABS	no specification described	0.04 (Meyer et al., 1993)
TBBP-A	ABS	no specification described	0.006 (Bonilla et al., 1990)
TBBP-A oligo carbonate	PBT/AT	240 °C, oven	0.17 (Thies et al., 1990)
	PBT/AT	no specification described	0.004 (Brenner and Knies, 1994)
	PBT/AT	250 °C	0.007 (Brenner and Knies, 1993a)
	PBT/AT	no specification described	0.007 (Brenner and Knies, 1993b)
TBBPA/ Bisphenol A copolycarbonate	PC	240 °C, oven	0.14 (Thies et al., 1990)
Hexabromo cyclododecane	PS	no specification described	0.003 (Brenner, 1993)
1,2-Bis-(tribromo-phenoxy)ethane	ABS	no specification described	0.028 (Bonilla et al., 1990)
Brominated styrene	ABS	no specification described	0.084 (Bonilla et al., 1990)

ABS: acrylonitrile–butadiene–styrene copolymer, PBT: polybutylene terephthalate, PC: polycarbonate, AT: antimony trioxide, PS: polystyrene.

Formation of PBDD/F during production of plastic materials, reproduced from (Ebert and Bahadir 2003)



Flame retardant	Plastic	Recycling step or conditions	Total amount of PBDD/F in µg/kg (ppb) (maximum value)
Mixture of PBDE	ABS	Recompounding	60 (Meyer et al., 1993)
	ABS	210 °C	140 (Riess et al., 2000)
	PS	different recycling processes	5 (Riess et al., 1998)
	PS	no specification described	5 (Riess et al., 2000)
TBBP-A	ABS	Recompounding	4 (Meyer et al., 1993)
	ABS	210 °C	0.3 (Riess et al., 2000)
Different	Electronic scrap	Hammer mill	0.7 (Lorenz and Bahadir, 1993)
		Impact grinder	0.7 (Lorenz and Bahadir, 1993)
		300 °C	5 (Lorenz and Bahadir, 1993)
		no specification described	18 (Dumler-Gradl et al., 1995)
		different recycling processes	30 (Meyer et al., 1993)
Poly(pentabromobenzylacrylate)	PBT	275 °C (six times recycling)	0.4 (Scheinert et al., 2000)
Polybrominated biphenylenes	PS	210 °C	1.3 (Riess et al., 2000)
1,2-Bistribromophenoxyethane	ABS	210 °C	12 (Riess et al., 2000)

ABS: acrylonitrile–butadiene–styrene copolymer, PBT: polybutylene terephthalate, PC: polycarbonate, AT: antimony trioxide, PS: polystyrene.

Formation of PBDD/Fs during recycling operations (which do not involve burning or incineration) (Ebert and Bahadir 2003)

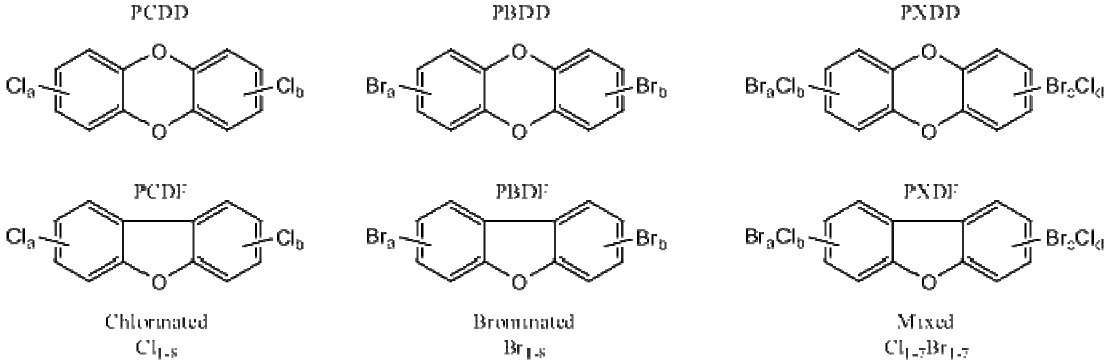
Properties of brominated and mixed brominated-chlorinated dioxins and furans

Polybrominated dibenzo-p-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) are almost planar tricyclic aromatic compounds. Theoretically, 75 brominated dioxins and 135 brominated furans are possible – as for the more well known chlorinated dioxins and furans.

In addition, a very large number of mixed halogenated congeners can potentially be formed from materials containing sources of both bromine and chlorine, with 1,550 brominated/chlorinated dibenzo- p-dioxins (PXDDs) and 3,050 brominated/chlorinated dibenzofurans(PXDFs) being theoretically possible.

The most toxic congeners are those substituted at positions 2, 3, 7, and 8. There are a total of seventeen 2,3,7,8- substituted brominated dioxins and furans (seven 2,3,7,8-substituted PBDDs and ten 2,3,7,8-substituted PBDFs), with the same number of 2,3,7,8- substituted chlorinated analogues. In contrast, there are a far greater number of 2,3,7,8- substituted mixed dioxins and furans, 337 possible 2,3,7,8-substituted PXDDs and 647 possible 2,3,7,8-substituted PXDFs, making a total of total of 984 congeners.

In total, therefore, there are a possible 5,020 dioxins and furans containing chlorine, bromine or both (mixed congeners), of which 1,700 are dibenzodioxins and 3,320 are dibenzofurans.

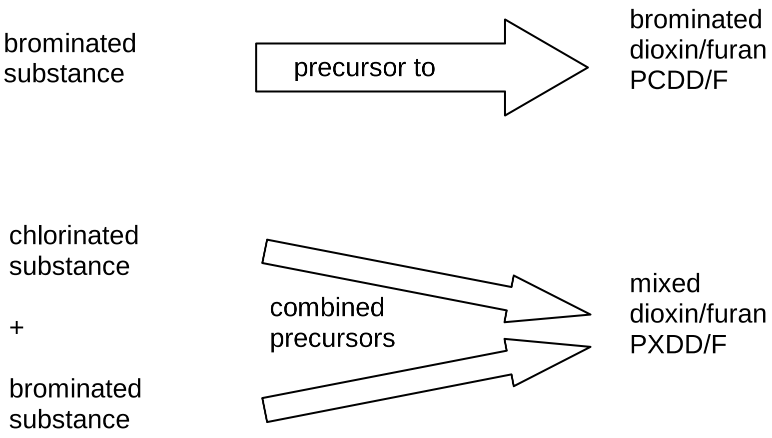


Three main subgroups of halogenated dioxins and furans; chlorinated (PCDD/Fs), brominated (PBDD/Fs) and mixed brominated-chlorinated (PXDD/Fs)

Until recently, BHCs (brominated hydrocarbons) have received relatively little attention compared to closely related chlorinated compounds, primarily because of difficulties of analysis, lack of available analytical standards, and a paucity of health effects data (Cormier, Lomnicki *et al.* 2006). However, recent findings indicate that many BHCs, particularly certain brominated dioxins and furans (PBDD/Fs), which can be produced from the transformation of brominated flame retardants, as well as some of the brominated flame retardants themselves, are highly toxic (Simonsen and Stavnsbjerg 2000).

Mixed dioxins/furans have been far less studied than other halogenated dioxins and furans, and are currently not subject to any specific monitoring requirements or regulatory controls. Furthermore, for the limited number of studies that have analysed mixed dioxins, it has been possible to characterise and determine only a small number of these compounds. Therefore, assessments of halogenated dioxin and furan emissions, and their levels in the environment, which have largely excluded mixed congeners may have significantly underestimated total levels.

Halogenated substances used in EEE are predominantly either chlorinated substances or brominated substances, and not mixed chlorinated/brominated substances (i.e. a single substances containing both chlorine and bromine). Studies have highlighted the formation of mixed halogenated dioxins/furans from waste EEE in significant quantities (Xiezhi, Zennegg*et al.* 2008), indicating that their formation involves multiple precursor halogenated substances, not single precursor substances (see Figure below). Any investigation into halogenated dioxin/furan formation from a single substance would, therefore, be unable to assess adequately the potential for formation of all halogenated dioxins/furans (including mixed congeners) in situations in which both bromine and chlorine precursors are commonly present, such as in many waste disposal and recovery situations. Furthermore, as mentioned above, all BFRs, including so called 'emerging' BFRs, have the potential to act as sources of bromine for the formation of brominated and mixed dioxins/furans.



Formation of mixed dioxins/furans from multiple precursor substances

Other dioxins and dioxin-like compounds:

Halogenated dioxins/furans can theoretically be formed by all halogens, although it is generally recognised that the iodated and fluorinated dioxins/furans are less persistent and hazardous than chlorinated and brominated analogues (Weber, Schrenk *et al.* 1995; Weber and Hagenmaier 1997; Weber, Schmitz *et al.* 1997), and therefore iodated and fluorinated compounds are not addressed in this document.

The latest draft of the Basel Convention guidelines on the treatment of mobile phones after they have entered the waste stream still warns, however (Basel Convention 2009):

“Fluorine compounds are used in lithium ion batteries. These halogens are of concern because of the possibility that dioxins and furans may be created and released under inadequately controlled burning or smelting operations”.

Toxicity of brominated and mixed brominated-chlorinated dioxins and furans

The potential for the formation of brominated and mixed dioxins and furans could be very serious. Research carried out to date suggests that brominated (PBDDs/Fs) and mixed (PXDDs/Fs) dioxins/furans have similar – and for some mixed congeners possibly greater - toxicity compared to their chlorinated homologues (Mennear and Lee 1994; Behnisch, Hosoe*et al.* 2003; Birnbaum, Staskal*et al.* 2003;Olsman, Engwall *et al.* 2007; Samara, Gullett *et al.* 2009).

Animal studies have shown that exposure to PBDD/Fs and mixed chlorinated-brominated dioxins and furans can result in toxicity to the immune system, the reproductive system and the developing foetus during pregnancy and that they should be considered as being capable of causing cancer in humans (Allsopp, Santillo *et al.* 2006).

The testing of mixed congeners, however, remains limited to only a few compounds, with no data available for the vast majority of the 984 possible 2,3,7,8-substituted mixed dioxins/furans.

Human exposure to brominated and mixed brominated-chlorinated dioxins and furans

Kotz (Kotz, Malisch *et al.* 2005) reviewed brominated and mixed dioxin levels in human milk samples in 2005 and found there were few previous studies, with only two studies investigating levels of brominated (PBDD/Fs) and mixed (PXDD/Fs) congeners in human milk samples. These were by Ohta (Ohta, Okumura *et al.* 2004) and Wiberg (Wiberg, Rappe *et al.* 1992).

Ohta (Ohta, Okumura *et al.* 2004) had reported some brominated (PBDDs/Fs) and mixed (PXDD/Fs) congeners in breast milk, but at relatively small contributions, and none were detected in cows milk, as shown below in the Figure below reproduced from (Ohta, Okumura *et al.* 2004).

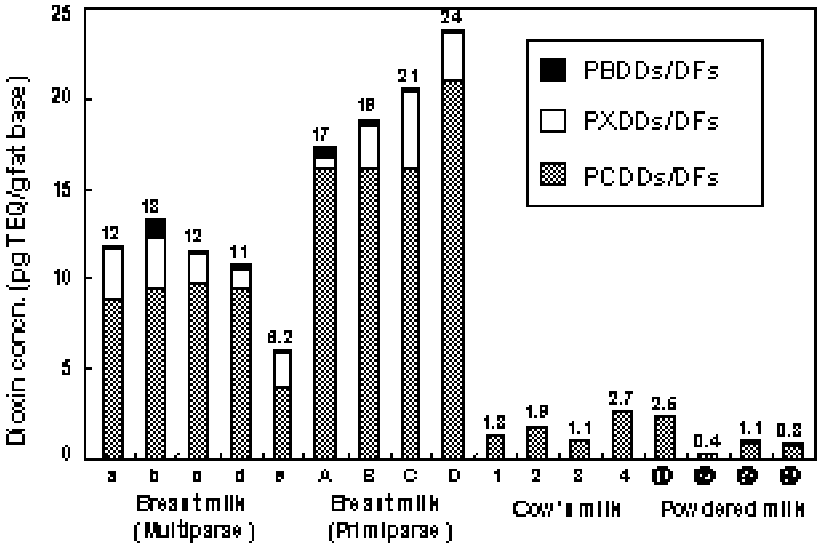


Fig.1 Levels of three kinds of dioxin concn. (TEQ) in mother's milk, cow's milk and powdered milk

Wiberg (Wiberg, Rappe *et al.* 1992) found no cases where brominated (PBDD/F) or mixed (PXDD/F) congeners were detected despite low limits of detection, < 1 ppt in most cases.

As a follow-up to the 3rd round of the WHO-coordinated exposure studies, Kotz (Kotz, Malisch *et al.* 2005) quantified PBDEs, PBDD/Fs and PXDD/Fs in pooled human milk samples from 17 countries. The aim was to compare levels of PBDE in human milk from countries worldwide, to investigate a possible correlation between PBDD/F, PXDD/F and PBDE levels, and to determine their relative contribution to total TEQs. Brominated dioxins/furans (PBDD/Fs) were identified in almost all the pooled human milk samples, including 2,3,7,8-TBDF, though total levels of PBDD/Fs were at considerably lower concentrations than chlorinated analogues (PCDD/Fs).The toxicologically most interesting tetra- and penta-substituted PXDD/Fs congeners were selected for analysis but they could not be detected in any sample. The limit of quantification of 0.05 pg/g fat for the TXDD/F and PeXDD/F congeners was comparable to those of PBDD/Fs. Similarly, mixed dioxins/furans were not detected in a subsequent study of a single pooled sample of human milk collected from 197 Belgium women in 2006 (Colles, Koppen *et al.* 2008). However, the studies of mixed dioxins/furans in human milk were of samples collected from general populations. No data is publicly available for individuals likely to have higher levels of exposure to mixed dioxins and furans due to their occupation such as informal e-waste recycling, or those living in the vicinity of such activities.

A few studies demonstrating human body burdens of brominated dioxins/furans have been reported for other types of human samples, including PBDD/Fs in human adipose tissue. Choi reported PBDD/Fs in samples collected in Japan in 1970 and 2000 (Choi, Fujimaki *et al.* 2003). Brominated furans, though not dioxins, have also been recently detected in all ten samples of human adipose tissue samples collected from the general population in Sweden in 2007, at levels up to15% of the total dioxin TEQ (Ericson Jogsten, Hagberg *et al.* 2010). These data, though limited, do confirm human exposure to, and bioaccumulation of, brominated dioxins/furans.

In spite of their chlorinated dioxin-like toxic potency and many potential sources, however, the information available on environmental levels and human exposure regarding to PBDDs/Fs remains quite limited (Takahashi, Sakai *et al.* 2006).

In 2006, the UK Committee on Toxicity (COT) (UK Committee on Toxicity of Chemicals in Food and Consumer Products and the Environment 2006) advised that *"TEFs (Toxic Equivalency Factor) developed for the chlorinated dioxins could be used as an indication of the dioxin-like activity of the PBDDs, PBDFs and dioxin-like PBBs. The TEQs (International Toxicity Equivalents) for the brominated contaminants could be combined with the TEQs for the chlorinated dioxins to provide an indication of the total intake of chemicals with dioxin-like properties as this would be more protective of public health than to view the chemicals separately".* The Committee highlighted that there are still uncertainties and that this was tentative advice but it is probably the most realistic approach currently available.

When the TEFs are calculated as proposed by COT then the UK total diet study results (Food Standards Agency 2006)(Stanmore 2004; Fernandes, D'Silva *et al.* 2006) show dietary intakes for adults of brominated dioxins/furans of 0.4 pg/kg bw day through to 0.8 ng/kg bw day, with the largest contribution coming from dairy milk. Human breast milk exposures were not addressed in this work. For children aged 1.5 to 2.5 years dietary intake rises to up to 3.0 pg/kg for high-level consumers. To these dietary intakes must be added intakes of brominated substances through the ingestion of dusts, as these are not included in total diet studies (Santillo, Labunska *et al.* 2003; Jones-Otazo, Clarke *et al.* 2005; Webster, Vieira *et al.* 2005; Gevao, Al-Bahloul *et al.* 2006; Suzuki, Takigami *et al.* 2007; Wu, Herrmann *et al.* 2007; Harrad, Ibarra *et al.* 2008; Stapleton, Allen *et al.* 2008; Fromme, Körner *et al.* 2009). In these circumstances it is certainly possible for young children to significantly exceed the WHO Tolerable Daily Intake, taking into account both chlorinated and brominated dioxins

The World Health Organisation (WHO) (van den Berg, Birnbaum *et al.* 2006) reviewed the TEF scheme in 2006 and concluded that, based on mechanistic considerations "*PBDDs, PBDFs, PXCDDs, PXCDFs, PCNs, PBNs and PBBs undoubtedly belong in the TEF concept*". Because of the lack of human exposure data, WHO proposed that preliminary exposure assessments should be done in the near future to indicate if these compounds are relevant for humans with respect to TEQ dietary intake. WHO said "*if the presence of PBDDs and PBDFs in human food as well as in people is more extensively demonstrated there will be a clear need for assigning TEFs to these compounds. ….In addition, it was concluded that among all compounds proposed in this paragraph for development of WHO TEFs, the PBDDs* *and PBDFs should be given high priority*".

The process has been a slow one. WHO had already suggested more than ten years ago that development of TEFs for selected PBDDs and PBDFs is justified given their existing similarities in structure, mechanism, and potency to PCDDs and PCDFs. The further delay is disappointing in the light of the increasing evidence that PBDDs and PBDFs are present in food and given the WHO conclusions in 1998 (WHO 1998) that "*Owing to the accumulating and toxic potential of some PBDDs/PBDFs, every effort should be made to prevent exposure of humans to, and pollution of the environment by, these compounds*". In practice, global action may be delayed in relation to these compounds until official TEFs are established, although more rapid measures may be taken sooner in some regions; for example, the consideration of restricting the use of all halogenated substances in EEE as part of the current review of the EU RoHS Directive.

End of life impacts from the recycling and disposal of e-waste containing brominated and chlorinated substances

There are many environmental and human health problems associated with current methods of recycling e-waste largely due to the presence of hazardous substances within the waste, including halogenated substances. Some of these impacts relate to the formal recycling sector employed within the EU. However, in some countries, particularly in Asia and Africa, e-waste is recycled and disposed of within the informal recycling sectors, using sub-standard and often very crude processes, including the open burning of mixed e-waste for the recovery of metals contained within the waste. Under these type of conditions impacts can be far greater. There is evidence that significant quantities of e-waste arising within the EU is transported to countries outside the EU and dealt with under such conditions (Cobbing 2006; Groß, Bunke *et al.* 2008).

At informal e-waste recycling workshops in Asia and Africa, a number of methods are used to recover metals from e-waste. In some places solder is recovered from printed circuit boards using open flames or hot plates, and subsequently the electronic components are removed, either for re-use, or to be ground down to recover metals. Another technique includes burning of electrical/electronic wastes in fires to burn off plastics and recover metals. Also, in some locations, printed circuit boards are shredded and the metals separated by vibration. The burning/heating processes may result in emission to air of hazardous organic substances, including halogenated substances contained within the e-waste, or other substances generated during these processes.

Many studies have demonstrated the release of halogenated substances present in e-waste during recycling and disposal operations, particularly for additive BFRs, many of which have known hazardous properties. Studies have demonstrated contamination of the environment by PBDEs and other additive BFRs in the vicinity of informal e-waste recycling sites in China, India and Ghana (Brigden, Labunska*et al.* 2005; Brigden, Labunska *et al.* 2008). A number of studies have investigated in some detail environmental contamination as a result of e-waste recycling and disposal in Guiyu, China, an area well known for informal e-waste recycling

Leung *et al.* (Leung, Cai *et al.* 2006) conducted a detailed study of the Guiyu area to quantify the pollution levels generated from e-waste, and identify their sources. They found PBDE levels up to 1,169 ng/g (dry weight) in soils near the recycling areas, which were 10–60 times higher than PBDE contamination reported at other locations in the world. In 2007 this study was extended (Leung, Luksemburg *et al.* 2007) to surface soils and combusted residue in the Guiyu area and found total PBDE concentrations were highest in the combustion residue of plastic chips and cables collected from a residential area (33,000–97,400 ng/g, dry wt); in soils from an acid leaching site (2,720–4,250 ng/g, dry wt); and a printer roller dump site (593–2,890 ng/g, dry wt). The authors also found that DecaBDE was the dominant congener (35–82%) among the study sites. This study did not seek to identify other additive BFR known to be present in e-waste.

Widespread pollution caused by e-waste recycling is not restricted to the immediate vicinity of the recycling sites (Zhao, Qin *et al.* 2009). One study used cinnamomum camphora leaves as biomonitors and investigated the diffusion of PBDEs from an e-waste recycling area to the surrounding regions. The results showed that PBDEs diffusion resulted in a halo of contamination of at least 74 km in radius. The attenuation of PBDE congeners fitted well with a log-linear regression. Their findings of similar attenuating slopes and characteristic travel distance among congeners suggest that the transport behaviour of lower brominated congeners might not differ from that of higher brominated congeners in short-range scale.

The contamination arising from e-waste recycling and disposal can impact on humans as well as the environment. A 2007 study conducted in China (Qu, Bi *et al.* 2007) involving three groups of people (residents from an e-waste dismantling region, residents living within 50 km of the dismantling region and a control group with no occupational PBDE exposure) found significantly elevated levels of decaBDE in serum of residents from e-waste dismantling region, at levels 11–20 times higher than the control group. The BDE-209 concentration observed in this group was the highest for humans worldwide. It is likely that similar exposure patterns would exist for other additive BFRs present in e-waste, though the potential for their bioaccumulation in humans is less well known.

The release of additive BFRs, and subsequent human exposure to them, is not restricted to the informal e-waste recycling sector. There are reports of elevated body burden levels to BFRs for e-waste recycling workers within the formal recycling sector in Europe. Studies have demonstrated higher levels of PBDEs in the blood of workers employed in the formal e-waste recycling sector, at an e-waste recycling facility in Sweden (Sjődin*et al.* 1999; Thuresson, Bergman *et al.* 2006), and at one from Norway (Thomsen, Lundanes *et al.* 2001).

Elevated levels of PBDEs and other brominated flame retardants have also been reported in air samples collected at a European plant involved in the recycling of e-waste, particularly in the vicinity of shredding equipment (Sjödin *et al.* 2001). The study found extremely high concentrations of TBBPA in the indoor air with average concentrations of from 30 ngm^{-3} to 150 ngm^{-3} (Sjodin, Carlsson *et al.* 2001; Morf, Tremp *et al.* 2005; Tollback, Crescenzi *et al.* 2006). Furthermore, amongst the BFRs detected was one of the ‘emerging’ BFRs, BTBPE. Another ‘emerging’ BFR, DBDPE was also tentatively identified in air samples from an e-waste recycling facility in Sweden (Pettersson-Julander, van Bavel *et al.* 2004).

In conclusion, as well as the release of hazardous substances (such as additive BFRs) contained within the e-waste during recycling and disposal, there is considerable evidence demonstrating impacts at e-waste recycling and disposal sites that arise due to the presence of brominated and chlorinated compounds in e-waste, as they can give rise to polychlorinated dioxins and furans (PCDD/Fs) or polybrominated dioxins and furans (PBDD/Fs).

The chlorinated dioxins and furans are perhaps one of the most well known classes of environmental pollutants. They are persistent, (resist natural breakdown processes), bioaccumulative, (build up in tissues of animals and humans), and exert a wide range of toxic effects. They are formed unintentionally as by-products of various industrial processes, usually involving chlorine or chlorinated chemicals. One way that dioxins and furans can be formed is by incomplete combustion processes (Stanmore 2004) and consequently one of the sources of these chemicals over recent decades has been from incinerators (Stringer and Johnston 2001; Allsopp, Costner *et al.* 2001).

Although chlorinated dioxins and furans have dominated pollution issues because they are widespread global pollutants and are extremely toxic (hence their listing in Annex III of the Stockholm Convention on Persistent Organic Pollutants), their brominated counterparts are also produced unintentionally by some of the same processes. For instance, brominated dioxins and furans (PBDD/Fs) have been detected in incinerator emissions and in fly ash (Birnbaum, Staskal *et al.* 2003). As already discussed, data indicates that many PBDD/Fs, and mixed brominated-chlorinated dioxins/furans, exert a similar range of toxic effects to their chlorinated counterparts.

One method of recycling e-waste is by smelting and refining to recover metals – especially precious metals. However, it has been noted that a significant drawback of thermal treatment of such wastes is the likely production of halogenated dioxins and furans (Luda, Euringer *et al.* 2005). Dioxins and furans are also known to be formed during experimental fires of plastics containing brominated flame retardants and from accidental fires. The presence of bromine in a fire inhibits combustion (Evans and Dellinger 2005). Indeed, it is for this purpose that brominated flame retardants have been developed and are so widely used in electrical/electronic equipment. However, the action of brominated flame retardants in inhibiting complete combustion can in turn result in the formation of products of incomplete combustion such as PBDD/Fs. In accidental fires, the presence of bromine will be sufficient to inhibit complete combustion and thus increase the likelihood of the formation of products of incomplete combustion such as PBDD/Fs (Evans and Dellinger 2005)

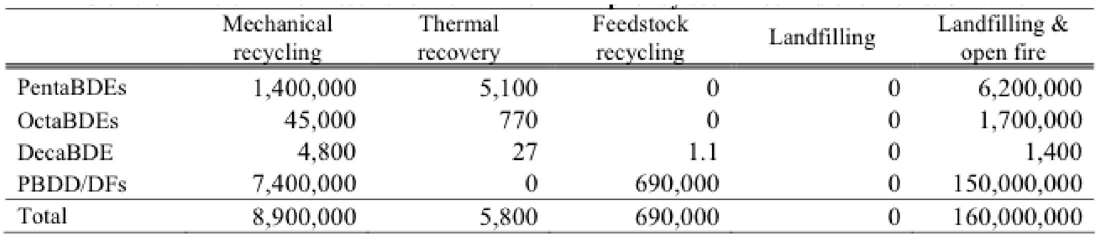
Weber and Kuch (Weber and Kuch 2003) noted that PBDD/Fs are formed in experimental fires of electrical appliances and in accidental fires. In one accidental fire, a high level of PBDD/Fs was present in the residues of a burned TV case most likely because of the combustion of brominated flame retardants in the plastic (Zelinski*et al.* 1993).

Informal treatment - Open burning and other related practices

In small workshops in India and China where open flames/hot plates are used for recovering solder from printed circuit boards, and open burning of electrical/electronic wastes is conducted, such as the burning of cables in Ghana and Nigeria, there is increasing evidence that significant quantities of PBDD/Fs and mixed chlorinated-brominated dioxins/furans are produced, with the clear potential for exposure of workers and the surrounding environment to these toxic chemicals.

Li (Li, Yu *et al.* 2007) investigated dioxins/furans present in ambient air around informal e-waste dismantling and recycling areas Guiyu in Guangdong, China and reported atmospheric concentrations of PCDDs and PCDFs were 64.9-2365 pg TEQ/m3 and 0.909-48.9 pg TEQ/m3, respectively; these are the highest documented values of these compounds found in ambient air in the world. PBDD/Fs (eight 2,3,7,8-substituted congeners) were also found at high levels (concentrations of 8.124-61 pg/m3 and 1.6-2104 pg of I-TEQ /m3).

Estimated annual damage costs of human health impacts caused by the exposure to PBDEs and PBDD/Fs from recycling and disposal alternatives are shown in the table below (Hirai, Sato *et al.* 2008). Among the five scenarios by far the highest damage cost was estimated in “landfilling and open fire”, followed by “mechanical recycling” and “feedstock recycling”. Among the four compounds, the highest human health impact was estimated to be caused by PBDD/DFs followed by PentaBDEs and OctaBDE. The estimated health impacts caused by PBDD/DFs were about 1,000 to 100,000 times higher than those by DecaBDE. The estimated health impacts caused by PentaBDEs were about 20 to 60 times higher than those by DecaBDE.



	Mechanical recycling	Thermal recovery	Feedstock recycling	Landfilling	Landfilling & open fire
PentaBDEs	1,400,000	5,100	0	0	6,200,000
OctaBDEs	45,000	770	0	0	1,700,000
DecaBDE	4,800	27	1.1	0	1,400
PBDD/DFs	7,400,000	0	690,000	0	150,000,000
Total	8,900,000	5,800	690,000	0	160,000,000

Characterisation results for estimated annual human health impact by scenarios and chemicals. Unit: Yen (1 Yen = approx 0.075 euro cents) (Hirai, Sato et al. 2008))

High concentrations of PCDD/Fs have also been found in soils and combusted residues from the e-waste recycling areas in Guiyu, China, comparable to PCDD/F levels found at other open dumping sites in Asian developing countries (Leung, Luksemburg *et al.* 2007).

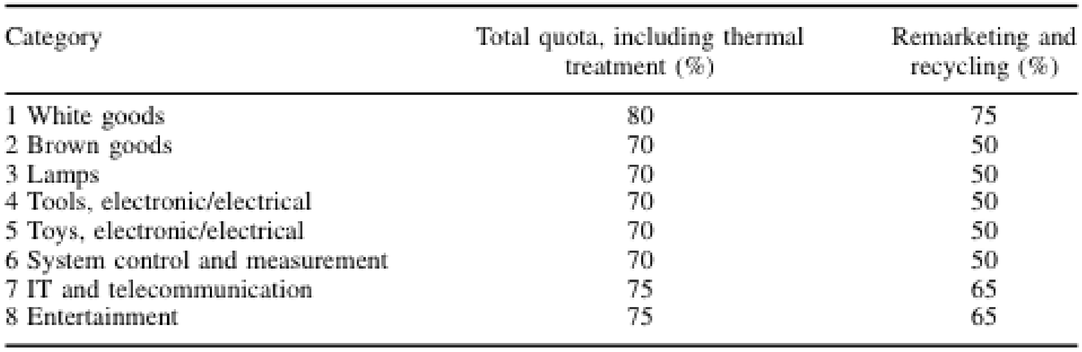
Severe contamination of the environment due to e-waste recycling has also been reported for mixed brominated-chlorinated dioxins/furans (Xiezhi, Zennegg *et al.* 2008). This study found that open e-waste burning sites were highly contaminated with dioxin and dioxin-like compounds, including chlorinated, brominated and mixed congeners. At some sites, the concentrations of mixed dioxins exceeded those of chlorinated dioxin/furans and brominated dioxins/furans, highlighting the significance of mixed dioxins for e-wastes that contain halogenated substances.

Wong (Wong, Weber *et al.* 2008) found that mothers residing at an informal e-waste site in China contained substantially higher values of PCDD/Fs (the sum of WHO-TEQ congeners) (by over 2, 3, and 6 times for milk, placenta and hair, respectively) and PBDEs (sum of congeners) in their tissues (by over 57, 19 and 31 times for milk, placenta and hair respectively), when compared with their counterparts residing at a reference site.

The *People's Daily,* the State-run newspaper, reported in 2007 that Guiyu's more than 5,500 e-waste businesses employed more than 30,000 people, and State media estimated that almost 9 out of 10 people in Guiyu suffered from problems with their skin, nervous, respiratory, or digestive systems, which may be linked to these practices (Chisholm and Bu 2007; United States Environmental Protection Agency (USEPA) 2008; United States Environmental Protection Agency (USEPA) 2008).

Disposal of e-waste to the municipal waste streams in Europe

The EU Directive 2002/96/EC on Waste Electrical and Electronic Equipment (WEEE Directive) entered into force on 13th February 2003 and required that, by December 2006, Member States must ensure that EEE producers achieve targets for recovery of e-waste collected (70-80% by weight, for different types of equipment) and for component, material and substance reuse and recycling (50-75%):



Category	Total quota, including thermal treatment (%)	Remarketing and recycling (%)
1 White goods	80	75
2 Brown goods	70	50
3 Lamps	70	50
4 Tools, electronic/electrical	70	50
5 Toys, electronic/electrical	70	50
6 System control and measurement	70	50
7 IT and telecommunication	75	65
8 Entertainment	75	65

Current recycling quotas for WEEE required that by December 2008 revised targets for recovery and reuse/recycling should be set. The current proposal from the European Commission (published December 2008) for revising these targets would increase all rates by 5% and include reuse in the quota

For WEEE from private households, adequate collection points have to be established and any 'take-back' will be free of charge for the consumer. A collection target of 4 kg per inhabitant per year was set for 31st December 2006. The European Commission's revision proposes a 65% collection rate (set as a function of the amount of EEE placed on the market in the preceding two years). This collection rate needs to be achieved annually, for the first time in 2016, by producers. Member States may have transitional arrangements granted through comitology in case they have difficulties meeting the rate, due to specific national circumstances. The proposal foresees re-examining the collection rate in 2012.

Collection targets are based on a `basket target´ i.e. measured by a mix of all WEEE, and will vary from country to country as to whether it is more or less ambitious than the 4kg/capita. Critically, a substantial fraction of e-waste generated within the EU is probably still not going to be collected. No product specific targets are proposed, this means that most likely only the heaviest and largest EEE products will be the focus of separate collection, which is problematic given the potential use of toxic substances in smaller products, for example the use of fluorescent lamps which contain mercury, and small hand held computers like PDAs containing numerous substances.

Greenpeace has summarised existing data on waste flows and the current methods used to recycle/dispose of electrical/electronic equipment, particularly mobile phones and computers (Allsopp, Santillo *et al.* 2006; Cobbing 2006). At present, a large fraction of e-waste goes into the general municipal waste stream. In some cases mobile phones and computers are reused. In others, these products and other e-wastes are being treated in modern facilities to reclaim metals and, sometimes, recycle the plastics. Some e-wastes are disposed to landfill or incinerated. The final synthesis report (United Nations University 2008) prepared as part of the EU review of the WEEE Directive confirmed the lack of data "*on the distribution of WEEE between different EoL [End of Life] options*". Prior to the WEEE Directive, the most common disposal option for e-waste was disposal to landfill, but even now there is "*no comprehensive data on the actual situation of WEEE disposal*".

As described above, all these recovery and disposal methods may be problematic because they can result in environmental contamination with hazardous substances.

Furthermore, large quantities of e-waste are also exported to countries in Asia and Africa from the EU, the US and other industrialised countries; some of it is exported for "re-use", however, much of it is unusable and ends up in the "informal" recycling sector discussed above. Whilst an EU ban on the disposal of `untreated separately collected WEEE´ to landfill is proposed, and more harmonized enforcement procedures for shipment of WEEE are foreseen, it is unlikely that this will put a stop to landfilling and incineration of unsorted WEEE, and is insufficient to prevent the flow of WEEE exports to substandard treatment. As the estimates for unaccounted flows of WEEE are between 42% and 75% (see introduction) there is a significant potential for continued impacts of hazardous substances from WEEE in the future.

In some more developed countries, metals are reclaimed at smelters/metal refineries or using mechanical separation techniques. Modern integrated smelters able to treat e-waste require investments of well above 1 billion US$. Currently, only 5-10 plants feature the technological performance necessary for the described operations. These include the plants run by UMICORE (Belgium) the Norddeutsche Affinerie AG (Germany), Boliden (Sweden/Finland), Johnson Noranda (Canada) and DOWA (Japan)(Manhart, Schmitt *et al.* 2008).

It is possible that PBDD/Fs and mixed chlorinated-brominated dibenzo dioxins and furans are produced by smelters and metal refineries that burn plastics from electrical/electronic waste. There appears to be no published scientific literature on the burning of plastics containing brominated flame retardants in smelters/metal refineries, but there are data from burning of these chemicals in other high temperature facilities, i.e. in incinerators and in test incinerators. Some, but not all of this research has shown that PBDD/Fs and mixed chlorinated-brominated dioxins and furans can potentially be emitted in the flue gas on burning of brominated flame retardants. It is, therefore, probable that these chemicals would also be released from smelters/metal refineries, albeit in quantities dependent on the design and operating conditions of the plant. The integrated smelters use very high temperature burning (1200 to 1300^{o}C) and rapid gas cooling, a method which reduces the production of chlorinated dioxins and should also decrease the production of brominated dioxins and furans. Information supplied by one company operating an integrated smelter reported that the one test carried out had shown that no PBDD/Fs were detected at detection limits in the range of <0.02 to <0.09 ng/m^3; mixed dioxins/furans were not investigated. However, since the brominated flame retardant content in the waste was described as rather moderate, and only one test was carried out, further testing during routine operations would be necessary to confirm whether brominated or mixed brominated-chlorinated dioxins and furans are produced as a result of smelting electrical/electronic waste (Allsopp, Santillo,*et al.* 2006).

Some plastics from mobile phones and computer cases are being separated and sent for recycling to be made into other plastic products. However, others are not separated and go to a smelter as part of mixed materials. Furthermore, certain mixed plastic/metal fractions from mechanical recycling may also go to a smelter or to an incinerator for metal recovery or disposal. In smelters, the plastics act as a fuel and as a substitute for coke that is normally used as a reducing agent in the smelting process, with the potential problem of formation of PBDD/Fs and mixed chlorinated-brominated dioxins from the burning of halogenated plastics.

Incineration

E-waste is often incinerated, either directly as part of the municipal waste stream, and or in the form of residual e-waste fractions that have already been through a recycling process.

There are many cases of PBDD/Fs being detected in residues and fly ashes from municipal solid waste incinerators. In many of these cases, not only PBDD/Fs but also mixed brominated-chlorinated dioxins/furans (PXDD/Fs) were found (Schafer and Ballschmiter 1986; Schwind, Hosseinpour *et al.* 1988; Sovocool, Donnelly *et al.* 1989; Chatkittikunwong and Creaser 1994; Sakai, Watanabe *et al.* 2001).

Several studies have shown efficient combustion of e-wastes containing BFRs in incinerators, with extremely low emissions of PBDDs. However, other studies using test incinerators have also shown that brominated and brominated-chlorinated dibenzo dioxins and furans can be produced in significant quantities as a result of the incineration of brominated flame retardants.

Funcke and Hemminghaus (Funcke and Hemminghaus 1997) used the same test incinerator as Vehlow *et al.* (Vehlow, Bergfeldt *et al.* 2000) and Tange and Drohmann (2004), and found that dioxins and furans were produced as a result of the combustion of brominated flame retardants. The study involved combustion of municipal waste and co-combustion of municipal waste with electrical/electronic waste containing brominated flame retardants. When the electrical/electronic waste was added, the quantity of PBDD/Fs and mixed brominated-chlorinated dibenzo dioxins and furans in the flue gas increased. The increase in brominated-chlorinated dioxins and furans correlated with the increase in bromine content of the waste.

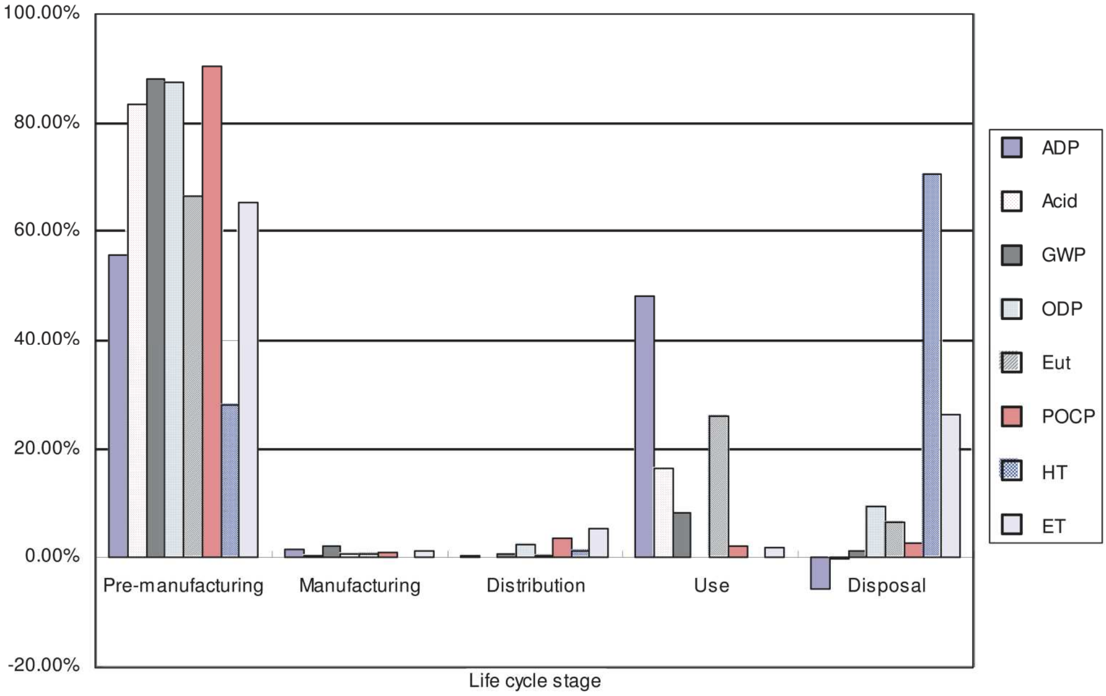
In another study, Söderström and Marklund (Soderstrom and Marklund 2002) tested the combustion of municipal waste plus PBDEs, TBBPA and HBCD in a laboratory scale incinerator. Combustion of all three types of flame retardant resulted in the production of PBDD/Fs and mixed chlorinated-brominated dibenzo dioxins and furans. Mono-, di-, tri- and tetra-brominated and chlorinated-brominated dioxins and furans were produced. It is therefore possible that during batch-wise combustion, the levels of organic bromine will increase dramatically and may well rise to match the chlorine levels, including in the residues left after electrical and electronics recycling (Soderstrom and Marklund 2002).

Recent work published by Wang *et al.* identified chlorinated and brominated dioxins/furans in ashes collected from two different municipal waste incinerators (Wang, Lee W J *et al.* 2009).

The presence of halogens in e-waste can also affect the release of other hazardous substances present during incineration. Increasing levels of bromine can increase the volatilisation of heavy metals such as copper, zinc, antimony and tin. This volatilisation is increased substantially by the presence of chlorine and bromine (Tange and Drohmann 2005) and thus the fly ash becomes more contaminated with mobile heavy metals. Tange (Tange and Drohmann 2005) suggest, rather optimistically, that this means that “they can be recovered" but in practice the majority of fly ash in Europe is disposed to landfill, mines or used for acid neutralisation. In each case, the environmental burden of leachable heavy metals can be increased by the increased levels of halogens.

Replacement of obsolete electronic products

Whilst this chapter has concentrated on end of life impacts, the environmental costs associated with replacement of electronic equipment should also be considered. Manufacturing just one 32 Mb RAM module, for example, requires 32 kg of water, 1.6 kg of fossil fuels, 700 g of gases and up to 72 g of different chemicals (Hester and Harrison 2009). Choi (Choi, Shin *et al.* 2006) found that the end-of-life stage of a personal computer was a major factor in the total human toxicity potential. This stage also greatly contributed to the ecotoxicity potential, second only to the pre-manufacturing stage:



Environmental impact assessment result for a personal computer, reproduced from (Choi, Shin et al. 2006)

The authors noted that the disposal stage included collection, disassembly, refinery processes for recycling, and incineration or landfill.

Conclusions

This document has demonstrated that human health and environmental impacts can arise during the end-of-life phase of electrical and electronic equipment containing brominated and/or chlorinated substances. These impacts arise both through the release of hazardous halogenated substances contained in the e-wastes, as well as from the generation of new hazardous substances through recycling and disposal processes, particularly chlorinated, brominated and mixed dioxins/furans.

Amongst all halogenated dioxins/furans, the chlorinated compounds have received by far the greatest attention with regard to their formation, environmental distribution and potential impacts. However, there is considerable evidence to indicate that brominated and mixed dioxins/furans are also of great concern.

The World Health Organisation concluded in 1998 (World Health Organisation 1998) that: brominated dioxins/furans (PBDD/Fs) are contaminants that are more or less similar to chlorinated dioxins/furans (PCDD/Fs) in their persistence and toxicity. Therefore humans and the environment should be protected from them, even though exposure of the general population to PCDD/Fs appears to be greater than exposure to PBDD/Fs. For e-wastes, brominated flame retardants and their precursors appear to be a main source of bromine for the formation of PBDD/Fs. All BFRs have the potential to act as sources of bromine for the formation of brominated and mixed dioxins/furans.

In response to increasing concerns about certain BFR formulations, and in some cases regulation of their use, alternative additive flame retardants are being developed and used. Many of these so called 'emerging BFRs' have already been found to be widespread in the environment, sometimes at high levels; these include BTBPE and DBDPE, substances developed and used as alternatives to PBDEs. As for all BFRs, emerging BFRs have the potential to act as precursors to brominated and mixed dioxins/furans.

Compared to their chlorinated analogues, a limited experimental database exists for PBDD/Fs and current information does not allow a quantitative risk assessment, although toxicological similarities do exist between certain PBDD/F congeners and their corresponding chlorinated homologues. On an interim basis it has been suggested that current Toxic Equivalency Factors for 2,3,7,8-substituted PCDD/PCDF congeners be applied to the comparable brominated and mixed halogenated congeners.

The fate of large quantities of e-waste generated within the EU is not known, and there is evidence that a substantial amount is recycled or disposed of using substandard processes outside the EU, with the resulting potential for environmental contamination and human exposure.

The final version of the EU synthesis report (Bio Intelligence Service for European Commission DG Environment 2006) prepared for the review of the Waste Electric and Electronic Equipment Directive (2002/96/EC) concluded:

"Detailed calculation of WEEE amounts is almost impossible due to the lack of reliable data e.g. on which of the two main sources, industry or households, produces most WEEE. Since the official waste statistics normally do not include separate estimates of WEEE from households, offices and industry there is a lack of information on where WEEE presently ends up and the environmental fate of the waste streams. The extensive uncontrolled and unrecorded transboundary movements of these end-of-life goods or their components make tracking of WEEE and its final disposal routes difficult."

Although Guiyu in China is one of the most studied areas impacted by informal e-waste disposal and recycling – and is the area with the highest reported concentrations of chlorinated dioxins/furans in air - it is not alone in being so heavily polluted. Li concludes (Li, Yu *et al.* 2007) that "*many EW [e-waste] dismantling regions exist in China, and dioxin pollution in these areas may be similar to or even higher than that found in GY [Guiyu]*".

A recent review by the United Nations University and EMPA[13] (Sepulveda, Schluep *et al.* 2010) on the environmental fate and effects of hazardous substances released from e-waste during informal recycling operations in China and India concluded that the data, which were described as "*alarming*", suggests *"a causal relationship between the release of Pb [lead], PBDEs and dioxins/furans and the determined concentrations in environmental components (e.g. soil and air), biota and humans".* They said that comparison with national and international standards *"leads us to the assumption that emissions originated from these recycling operations cause serious detrimental effects on humans and to the environment".*

The data currently available on the toxic potential of brominated and mixed dioxins/furans indicate that every effort should be made to prevent exposure of humans to these compounds and pollution of the environment by them. Therefore the following recommendations are made and research needs are specified:

As a priority, brominated flame retardants should not be used where suitable replacements are available and future efforts should encourage the development of further substitutes. Similar measures are required for the use of chlorinated polymers, including PVC. This is particularly important for the use of brominated and chlorinated substances in electrical and electronic equipment due to the extensive use of substandard recycling and disposal operations employed for large fractions of e-waste arising in the EU and elsewhere. The phase out of both PVC and BFRs in many electronic products is technically possible, as demonstrated by leading manufacturers of electronics[14].

In order to achieve the greatest protection to human health and the environment associated with substances used in EEE, restrictions on hazardous substances need to recognise the extent of the use of substandard recycling and disposal practices, and include all halogenated substances, with restriction on a halogen group basis rather than using a substance-by substance approach,

Appropriate precautions, including monitoring, should be taken both to protect workers from exposure to halogenated dioxins/furans, including brominated and mixed congeners, and to prevent their release into the environment in emissions and effluents.

Disposal of industrial wastes, fire residues and consumer products containing brominated and chlorinated compounds should be controlled to minimise the formation of, and environmental contamination by chlorinated, brominated and mixed dioxins/furans their precursors. All products that have been flame retarded with brominated compounds should be labelled and disposed of in the most appropriate way to avoid the formation and release of brominated and mixed dioxins/furans. Labeling should also be required for the use of PVC plastic.

Selected brominated and mixed congeners should be included in ongoing monitoring programmes of environmental distributions of halogenated dioxins to enhance the existing database. As part of this, analytical methods, including screening techniques, should be improved. Inter-laboratory comparisons should be undertaken to validate methodologies.

As the experimental database is limited, comparative toxicological and ecotoxicological studies with selected brominated and mixed dioxins/furans should be performed with respect to both, identifying appropriate adverse- and no-adverse-effect levels and improving the interim TEF recommendation.

These measures are required as it is currently not possible to ensure that all, or even the majority, of e-waste that is generated is recycled or disposed of in the most appropriate manner. Even if such controls were possible, the potential for impacts through recycling and disposal operations would persist as long as the presence of halogenated substances in e-

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[13] Swiss Federal Laboratories

[14] http://www.greenpeace.org/international/campaigns/toxics/electronics/how-the-companies-line-up

waste continues, (including PVC and BFRs), and therefore the phase out of these substances should be a matter of urgency for all manufacturers and regulators.

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