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Summary

This report contains a review of the current knowledge regarding the sources and distribution of brominated dioxins in the environment. The report focuses on the situation in Sweden, but it includes a comprehensive review of studies and data from the whole world. Furthermore, the report includes a tentative estimation of the total amount of PBDD/Fs that is present and potentially may be emitted from products and materials in the Swedish society, as well as a discussion on how these emissions can be minimized. The report show that PBDD/Fs are emitted from a wide range of sources in our society, including combustion processes, various high temperature processes and directly from all BFR treated materials we are surrounded with. This has resulted in a widespread distribution of PBDD/Fs in the environment, also including animals and humans. An important exposure route for humans seem to be the unintentional ingestion and inhalation of indoor dust that has been contaminated with PBDD/Fs from BFR treated materials in these environments. To eliminate these emissions, the materials would have to be removed and subsequently destructed. However, to avoid that the emissions are enhanced in these processes it is important that the BFR containing material can be efficiently identified and separated from other materials. When this is done, the BFR containing material can be destructed in authorized incineration facilities or metal smelters with highly developed flue gas treatment systems and adequate treatment of the ashes, also including the bottom ashes.

Summary

This report deals with brominated dioxins (PBDD/Fs); how they are formed and emitted and what that leads to in terms of levels in the environment. The report focuses on the situation in Sweden, but it includes a comprehensive review of studies and data from the whole world. Furthermore, the report includes a tentative estimation of the total amount of PBDD/Fs that is present and potentially may be emitted from products and materials in the Swedish society, as well as a discussion on how these emissions can be minimized.

The PBDD/Fs is a group of unintentionally produced contaminants that are analogous to the more well-known chlorinated dioxins (PCDD/Fs), but that contain bromines instead of chlorines. There are also mixed brominated-chlorinated dioxins (PBCDD/Fs), although these are only touch upon briefly in this report. Due to the structural similarities, the PBDD/Fs, PCDD/Fs and PBCDD/Fs share many properties with each other, including low water solubility and volatility and long environmental half-lives. This means that PBDD/Fs will stick to particles in the environment and stay there for a long time, usually several years. The similarities also apply to the toxicity, which generally is very high, and according to the current recommendations the toxic equivalency factors (TEFs) developed for the PCDD/Fs can also be used for the PBDD/Fs.

Like the PCDD/Fs, PBDD/Fs may be formed in all kinds of combustion processes provided that bromine is present in some form, which today usually is the case. The bromine content in materials, waste and fuels has thus increased drastically since brominated flame retardants (BFRs) were introduced on the market in the 1970s. In the combustion process, the PBDD/Fs can either be formed from basic elements such as carbon, hydrogen and bromine, or from small precursor molecules. While the former '*de novo*' pathway often is the dominating process for PCDD/Fs, the precursor pathway seems to be more important for the PBDD/Fs. This is because many BFRs, and especially the polybrominated diphenylethers (PBDEs), constitute far advanced precursors of PBDD/Fs, and especially of polybrominated dibenzofurans (PBDFs). As a result, mainly PBDFs are formed in most incineration processes, and the yields increase during poor combustion conditions when the density of precursors is high.

Furthermore, PBDD/Fs may also be formed during thermal stress of BFR mixtures or BFR containing materials and products. This means in practice that PBDD/Fs are formed already when the BFR mixture is produced and that the PBDD/F content steadily increases as the BFRs are mixed into polymers, when the polymers are refined into materials and products, and when the products are disposed of and recycled by various processes. In addition, PBDD/Fs may also be formed through photolytic transformation of BFRs, which may occur as BFR treated products are exposed to sunlight for instance. In all these processes, the transformation of PBDEs to PBDFs is by far the most important pathway, and when PBDEs are present all other formation pathways are negligible. However, recently it has been recognized that PBDD/Fs, and in this case mainly polybrominated dibenso-p-dioxins (PBDDs), may be formed naturally in some marine environments via biological and photolytical pathways.

The emission from incineration processes are both a result of the release of PBDD/Fs that already are present in the material being combusted and of the formation of PBDD/Fs in the actual process. Both these processes are favored by poor combustion conditions, which are more prominent during open

burning activities than during controlled incineration in large scale facilities. As a consequence the emissions measured from incineration facilities are relatively low, while the emissions measured in connections to open burning activities and accidental fires can be extremely high. However, the emissions also depends on the fuel and its content of BFRs. Higher emission have therefore been measured from industrial (IWI) and hazardous waste incinerators (HWI) and from metallurgical processes using electronic waste as one of its feed stocks, as compared to municipal solid waste incinerators (MSWI). Furthermore, extremely high PBDD/F emissions have been measured during open burning of electronic waste (e-waste), which is carried out as a recycling activity in some developing countries, and also may occur during accidental fires in e-waste recycling facilities for instance.

Relatively large emissions of PBDD/Fs have been measured in connection to production facilities for BFRs and facilities that are using BFRs to treat products, although there are no such data available for Swedish facilities. Nevertheless, high PBDD/F levels have been measured in PBDE mixtures as well as in materials treated with PBDEs, both in Sweden and in other countries. These PBDD/Fs constitute a threat to human health and the environment as the materials are used, disposed of and recycled since the PBDD/Fs may be emitted during the whole life cycles of the materials. Not least the recycling may lead to large emissions of PBDD/Fs, and especially during informal e-waste recycling activities. However, large emissions have also been measured in controlled recycling facilities, and in these cases the emissions seem to be connected to the dust released from the interior of the e-waste during the dismantling processes. This may lead to extensive exposure of the recycling workers at least.

As a result of the great number of sources of PBDD/Fs, these contaminants are nowadays more or less ubiquitous in the environment. PBDD/Fs have been found in air, soil, sediments, sewage water, sludge, various animal and plant species, food and feed, indoor dust and humans. In air, the PBDD/F levels are usually lower than the PCDD/F levels, but in some urban and industrial environments the reverse profile can be seen. The highest PBDD/F levels in air are found outside e-waste recycling facilities and at informal e-waste recycling sites. The levels are usually correlated with the PBDE levels and the profiles are dominated by PBDFs. In Sweden, the air levels reported from urban environments are usually lower than those reported from urban environments in Asia, but for rural sites the levels are more similar. In fact, the levels in urban environments in Sweden are not that different from the levels in Swedish rural environments.

In soil the highest PBDD/F levels are generally found at informal e-waste recycling sites as mentioned previously. However, similar levels have actually been found in connection to a Swedish recycling facility that had been subject to an accidental fire. Otherwise, soil levels are generally elevated in urban environments in comparison to rural and agricultural environments. Like for air, the PBDD/F levels are generally correlated with the PBDE levels, and the profile is dominated by PBDFs, indicating that the PBDD/Fs originate from PBDE treated materials. Lake sediments principally follow the same trend as soil, with higher levels in urban and PBDE exposed areas and with a dominance of PBDFs. However, marine sediments sometime show a different pattern. Hence, in shallow coastal waters with high biological productivity and sunshine penetration, the levels of PBDDs may sometimes be extremely high. This is because of natural formation of PBDDs in these environments.

When it comes to biota, food and feed, the PBDD/F levels are generally higher in fatty samples, such as fatty fish, mussels, eggs, liver and carcass fat. However, the levels in fish and shellfish seem also to be highly influenced by the presence of local sources in their living habitat, with natural sources giving rise to the largest variations. Some fish and mussel populations along the Swedish coastline have thus been found to contain extremely high levels of PBDDs. However, local PBDE related sources may also give rise to elevated levels, which overall may result in mixed PBDD/F profiles in some marine fish populations. Apart from these locally influenced fish and mussels, the PBDD/F levels in marine species are generally lower than the PCDD/F levels. Still, the PBDD/Fs have been found to contribute significantly to the total dioxin-like toxicity in these species, which is serious considering that some of them already contain close to acceptable levels of other dioxin-like compounds.

For indoor environments, PBDD/Fs have mainly been measured in dust. The levels vary considerably, which is believed to be connected to a varying presence of PBDE containing materials in different indoor environments. However, this correlation is not always easy to discern. Overall, somewhat higher PBDD/F levels have been found in dust from public buildings, such as hotels and offices, than in dust from residential houses. However, the highest PBDD/F levels reported for dust have been found in a residential house in USA. In this house the levels were even higher than those recorded for workshop floor dust at an e-waste recycling site in China. Nevertheless, the PBDD/F levels are usually correlated with the PBDE levels which support the theory that they have the same sources. In addition, the PBDD/F profiles are usually dominated by PBDFs. In most cases the PBDD/F levels in dust are higher than the PCDD/F levels, and when it comes to the total dioxin-like toxicity the PBDD/Fs contribute significantly. The levels measured in Swedish dust are approximately at the same levels as in other countries.

In humans, PBDD/Fs have been measured in mother's milk, adipose tissue and blood. In mother's milk the levels are in the same range all over the world, even when including mothers from an e-waste site in Vietnam and mothers from USA with much higher PBDE levels in their milk. This, together with the fact that the PBDF profiles in mother's milk generally are different from those observed in dust, indicates that the uptake and metabolism of PBDD/Fs in humans are somewhat selective. However, overall the PBDD/F levels in mother's milk are lower than the PCDD/F levels and their contribution to the total dioxin-like toxicity seem to be fairly low. PBDD/Fs have also been measured in human adipose tissue from Sweden and Japan. The levels seem to be somewhat lower in Sweden than in Japan, but the PBDD/Fs were detected in all Swedish samples as well, verifying their widespread distribution. The PBDD/F profiles where generally similar to those found in the milk samples, supporting the theory of a selective uptake and metabolism. However, contribution of the PBDD/Fs to total dioxin-like toxicity seems to be higher in the adipose tissue than in the milk samples. Finally, PBDD/Fs have been found in relatively high levels in blood from two fire fighters in San Francisco.

The data summarized in this report suggest that most PBDD/Fs that we are exposed to, apart from the naturally produced PBDDs, originate from the BFR treated materials we have in our society, and particular those that are treated with PBDEs. A rough estimate, performed in the report, suggests that such materials could hide several tons of PBDD/Fs only in Sweden. Furthermore, we are adding some hundreds of kilos of new PBDD/Fs every year in BFR containing products we are importing. This mainly includes electrical and electronic equipment (EEE), vehicles and construction materials. At the

same time BFR containing materials are constantly removed from the society as they reach their end-of-life stage. When this happens the materials are either recycled, destructed or put on landfill, with each process constituting a certain risk for further emissions.

Today in Sweden, most of the BFR containing waste is incinerated, but some may also end up on landfills. This may for example be the case for the shredder light fraction (SLF) from the vehicle fragmentation process, since this fraction is somewhat complicated to incinerate. It is estimated that up to 0.5 tons of PBDD/Fs may end up on Swedish landfills every year, and that these landfills may hide several tons of PBDD/Fs in total. For the waste fraction that is incinerated in authorized facilities the destruction efficiency of the PBDD/Fs is relatively high, at least when considering the stack emissions and the levels in the fly ashes. However, when it comes to the bottom ashes the PBDD/F levels can still be relatively high, indicating that all PBDD/Fs in the original waste is not destroyed or alternatively that new PBDD/Fs are formed in the process. It is estimated that the bottom ashes produced in Swedish MSWIs every year contain almost 6 kg of PBDD/Fs.

Besides all PBDD/Fs that are hidden in products, materials and waste in our society, there is an even larger amount of not-yet-formed PBDD/Fs in all BFRs (and particularly PBDEs) that are present in the same and similar products, materials and waste in the society. If all this material would be subject to some kind of incomplete combustion process, as a worst case scenario, it could potentially give rise to an additional 200 tons of PBDD/Fs that would be emitted. To eliminate this risk, these materials will have to be removed and subsequently destructed. However, in this context it should be noted that the risk for emission often will increase as the material is removed from its original placement and when it is being recycled and destructed.

To minimize the emissions of PBDD/Fs from waste material a key factor would be the implementation of efficient and sensitive identification and separation technologies that are capable of separating BFR containing materials from non-BFR-containing materials, so that each fraction can be treated appropriately. There are several spectroscopic technologies available for this purpose, and also technologies based on differences in density and electrostatic properties. However, none of these technologies are alone capable of screening out the BFR containing materials, but need to be used in combinations. Still, a 100% separation will not be achieved, and usually around 5% will end up in the wrong fraction. As a consequence, recycled materials should never be used for sensitive applications, such as toys and household products, and when it comes to the BFR containing fraction, it should not be recycled at all. It could perhaps be used to make basic chemicals (like bromine) or fuel for the industry, but otherwise it should be destructed.

Destruction of BFR containing materials may be accomplished in authorized incineration facilities. The mixing ration of the BFR materials in other wastes/fuels should however be kept low (<5%) in order to limit the amount of PBDD/F precursors and corrosive HBr in the combustion zone and the flue gases. The incinerators should also have highly developed flue gas cleaning systems and plans for how ashes (not least bottom ashes) should be handled. Other high temperature processes, such as cement kilns and metal smelter may also be used to destruct BFR containing materials provided that these have similar emission control systems as the authorized incinerators. If these demands are fulfilled, metals smelters are preferably used for the metal containing BFR waste, e.g. PC-boards, since these facilities are capable of recovering the metals.

As an alternative to a complete destruction of the BFR containing materials it may also be possible to extract the bromine or the intact BFRs from the materials, after which the materials can be recycled or treated as non-BFR materials and the bromine reused in the industry. A couple of such technologies have been suggested and described for BFR containing plastics, but none have so far been applied in full-scale.

The very last option for BFR containing waste, as with other organic waste fractions, is landfilling. Normally it should not be used at all, but if it for some reason has to be chosen as an alternative it has to be done under certain controlled conditions to minimize leakage, emissions and exposure of humans and animals. The landfills also have to be secured from accidental fires and be able to maintain a high security even if the surrounding and the climate are changing. The short-term risks mentioned above, e.g. risk for leakage and fire, also have to be considered when BFR containing materials are stored temporarily, while waiting for other treatments for instance. In such situations, it would perhaps also be wise to limit the amount of BFR containing materials/wastes that can be stored in the same area in order to minimize the damages caused if an accidental fire still would occur.

Sammanfattning

Den här rapporten handlar om bromerade dioxiner (PBDD/F); hur de bildas och sprids och vad detta leder till iform av halter i miljön. Rapporten har ett fokus på Sverige, men innefattar en grundlig genomgång av studier och data från hela världen. Rapporten innehåller även en preliminär uppskattning av den totala mängden PBDD/F som finns gömd och potentiellt kan emitteras från material och produkter i det svenska samhället. Vidare innefattar rapporten en diskussion angående hur dessa emissioner kan minimeras.

PBDD/F är en grupp oavsiktligt bildade föroreningar som är analoga med de mer välkända klorerade dioxinerna (PCDD/F), men som innehåller brom istället för klor. Det finns också blandade brom-klor dioxiner (PBCDD/Fs), även om dessa bara behandlas översiktligt i denna rapport. På grund av sina strukturella likheter delar PBDD/Fs, PCDD/Fs och PBCDD/Fs många egenskaper med varandra, vilket inkluderar låg vattenlöslighet och flyktighet samt lång halveringstid. Detta betyder att PBDD/Fs i miljön i stor utsträckning kommer att vara bundna till partiklar, samt att dom kommer att stanna där en lång tid framåt, vanligtvis många år. Likheterna inbegriper även giftigheten, som generellt är mycket hög för dioxiner, och i enlighet med rådande rekommendationer kan därför de toxiska ekvivalensfaktorerna (TEFs) som utvecklats för PCDD/Fs också användas för PBDD/Fs.

I likhet med PCDD/Fs kan PBDD/Fs bildas i all typer förbränningsprocesser förutsatt att brom finns närvarande i någon form, vilket idag oftast är fallet. Brominnehållet i material, sopor och bränsle har ökat drastiskt sedan de bromerade flamskyddsmedlena (BFRs) började användas på 1970-talet. I förbränningsprocesser bildas PBDD/Fs antingen från fria grundämnen, dvs kol, väte och brom, eller genom sammanslagning av små molekyler, s.k. prekursors. Medan den första ”*de novo*”-bildnings-vägen många gånger dominerar för PCDD/Fs, så verkar den senare *prekursor* -bildningsvägen vara viktigare för PBDD/Fs. Detta beror på att många BFRs, och särskilt de polybromerade difenyletrarna (PBDEs), utgör mycket långt gångna prekursorer till PBDD/Fs och framförallt då till polybromerade dibensofuraner (PBDFs). Till följd av detta bildas framförallt PBDFs i de flesta förbränningsprocesser, och utbytena ökar vid dåliga förbränningsförhållanden när mängden av prekursorer ökar.

PBDD/Fs kan också bildas när BFR innehållande material och tekniska BFR-blandningar utsätts för mer försiktaga temperaturhöjningar. Detta betyder i praktiken att PBDD/Fs bildas redan när BFR blandningarna produceras, och att PBDD/F innehållet sedan stadigt ökar när BFR blandningen blandas i polymerer, när polymeren förädlas till material och produkter, samt när produkten återvinns eller destrueras. PBDD/Fs kan dessutom även bildas genom fotolytisk omvandlig av BFRs, vilket exempelvis kan inträffa när BFR innehållande produkter exponeras för solljus. Gemensamt för alla dessa processer är att omvandlingen av PBDEs till PBDFs är den överlägset dominerande bildningsvägen, och att denna kommer att överskugga alla andra bildningsvägar så fort PBDEs finns närvarande. Dock har det nyligen blivit känt att PBDD/Fs, och i det här fallet huvudsakligen polybromerade dibenso-p-dioxiner (PBDDs), kan bildas naturligt i vissa havsmiljöer via biologiska och fotolytiska processer.

PBDD/F-emissionerna från förbränningsprocesser är en kombination av ett frisläppande av PBDD/F-molekyler som fanns med i materialet redan från början och ett bildande av nya PBDD/F-molekyler under själva förbränningen. Båda dessa processer gynnas av dåliga förbränningsbetingelser, vilka är mer framträdande vid öppen, okontrollerad eldning jämfört med kontrollerad förbränning i

storskaliga anläggningar. Till följd av detta uppmäts oftast relativt låga utsläppsnivåer från förbränningsanläggningar, medan utsläppen från öppna eldar och olycksbränder kan vara extremt stora. Utsläppsmängderna beror dock även på bränslet och dess innehåll av BFRs. Högre PBDD/F utsläpp har därför uppmäts från förbrännings-anläggningar för industriavfall (IWI) och farligt avfall (HWI) samt från metallurgiska processer som använder elektronikavfall (e-avfall) som en av sina råvaror, jämfört med anläggningar för hushålls-avfall (MSWI). Extremt höga PBDD/F utsläpp har också uppmätts i samband med öppen eldning av e-avfall, vilket utförs som en metallåtervinnings-metod i vissa u-länder, och som också kan förekomma vid olycksbränder i återvinningsanläggningar för e-avfall till exempel.

Relativt stora utsläpp av PBDD/Fs har också konstaterats kring produktionsanläggningar för BFRs och anläggningar som använder BFRs för att flamskydda produkter, även om inga sådana data finns för svenska anläggningar. Dock har höga PBDD/F-halter uppmätts i tekniska PBDE-blandningar och material behandlade med PBDEs, både i Sverige och andra länder. Dessa föroreningar utgör en miljö- och hälsofara när materialen används liksom när dom senare kasseras och återvinns. PBDD/Fs kan, liksom PBDEs, således emitteras under hela materialets livscykel. Inte minst materialåtervinningen kan leda till stora utsläpp av PBDD/Fs, och då framförallt när e-avfall återvinns under okontrollerade former. Stora emissioner har dock även uppmätts i kontrollerade återvinningsanläggningar, och då framförallt i det damm som frigörs när e-avfall demonteras. Detta kan, om inte annat, leda till höga exponeringar för personalen som jobbar i anläggningarna.

Som ett resultat av det stora antalet källor för PBDD/Fs återfinns idag dessa föroreningar i princip överallt i miljön. PBDD/Fs har således återfunnits i luft, jord, sediment, avloppsvatten, slam, olika djur och växter, mat och djurfoder, inomhusdamm och människor. I luft är PBDD/F-halterna oftast lägre än PCDD/F-halterna, men i vissa stads- och industrimiljöer är bilden den omvända. De högsta PBDD/F-halterna i luft har återfunnits utanför återvinningsanläggningar för e-avfall samt på platser där okontrollerad återvinning av e-avfall sker. Halterna är oftast korrelerade med PBDE-halterna, och PBDD/F-profilerna domineras av PBDFs. För Sverige ligger halterna för stadsluft något lägre än motsvarande data från asiatiska städer, men i landsbygden verkar lufthalterna vara mer lika. I Sverige är halterna uppmätta i stadsluft faktiskt inte så mycket högre än de uppmätta i landsbygdsluft.

För jord uppmäts generellt de högsta PBDD/F-halterna på platser där e-avfall återvinns under okontrollerade former. Men faktum är att likartade halter har uppmätts intill en svensk återvinningsindustri som utsatts för brand. Bortsett från dessa ”hot-spots”, uppmäts generellt högre PBDD/F-halter i stadsmiljö jämfört med landsbygd och jordbruksområden. I likhet med luften domineras PBDD/F-profilerna i jord vanligtvis av PBDFs och halterna är oftast väl korrelerade med PBDE-halterna. Detta bekräftar att föroreningarna härstammar från samma källa. Sjösediment uppvisar ungefär samma mönster som jord med högre PBDD/F-halter i stadsmiljö och områden med PBDE påverkan. Föroreningsprofilen domineras av PBDFs. I marina sediment kan dock bilden se annorlunda ut med extremt höga PBDD-nivåer. Detta ses huvudsakligen i grunda, kustnära miljöer med hög biologisk aktivitet och effektiv solinträngning och beror på naturlig bildning av företrädesvis PBDDs i dessa miljöer.

När det gäller biologiskt material, mat och djurfoder återfinns oftast de högsta PBDD/F-halterna i fettrika prover, som t.ex. fet fisk, musslor, ägg, lever och djurfett. Dock verkar halterna i fisk och skaldjur också vara starkt påverkade av förekomsten av lokala källor i de områden där de levt och

fångats, och i det sammanhanget verkar de naturliga källorna ge upphov till störst variationer. Vissa fisk- och musselpopulationer längs den svenska kusten har således setts innehålla extrema halter av PBDDs. Lokala källor relaterade till PBDE kan dock också ge upphov till förhöjda PBDD/F-halter i marina arter, vilket kan resultera i blandade PBDD/F-profiler i vissa miljöer och arter. Bortsett från dessa lokalt påverkade fiskar och musslor så uppvisar marina arter generellt lägre PBDD/F-halter än PCDD/F-halter. Dock bidrar ändå ger PBDD/Fs med en betydandel del av den totala dioxin-lika toxiciteten. Detta är allvarligt med tanke på att många av dessa arter, i alla fall i våra svenska hav, redan innehåller andra dioxin-lika ämnen i mängder nära de acceptabla gränserna.

I inomhusmiljö har förekomsten av PBDD/Fs huvudsakligen undersökts i damm. Halterna varierar avsevärt vilket antas hänga ihop med mängden PBDE-innehållande material som finns närvarande i lokalerna. Dock har detta samband inte alltid varit så lätt att urskilja. Generellt uppmäts något högre halter i allmänna lokaler, som t.ex. hotell och kontor, än i bostadshus, vilket är i linje med teorin. Men de högsta PBDD/F-halterna som har rapporterats för damm har faktiskt uppmätts i ett bostadshus. I detta hus, i USA, var halterna till och med högre än de som uppmätts i golvdammet från en verkstad i ett område för okontrollerad återvinning av e-avfall i Kina. PBDD/F-halterna i inomhusdamm uppvisar ändå vanligtvis en tydlig korrelation med PBDE-halterna, vilket tyder på att föroreningarna har samma källa. PBDD/F-profilerna domineras oftast också av PBDFs. Vidare är PBDD/F-halterna i damm oftast högre än PCDD/F-halterna, och bidraget till den total dioxin-lika toxiciteten är också betydande. Halterna som uppmätts i damm från svenska inomhusmiljöer ligger på liknande nivåer som i andra länder.

När det gäller prover från människa har PBDD/Fs undersökts i bröstmjölk, fettvävnad och blod. I bröstmjölk har liknande halter uppmätts över hela världen, även när man inkluderar mammor från återvinningsplatser för e-avfall i Vietnam samt mammor från USA, vilka har betydligt högre PBDE-halter i sin mjölk. Detta i kombination med att PBDF-profilerna i bröstmjölk skiljer sig ganska mycket från profilerna i inomhusdamm antyder att upptaget och metabolismen av PBDD/Fs i människa är delvis selektivt. PBDD/F-nivåerna i bröstmjölk är dock generellt lägre än PCDD/F-nivåerna och bidraget till den total dioxin-lika toxiciteten ser än så länge ut att vara gansk lågt. PBDD/Fs har även undersökts i fettvävnad från människor i Sverige och Japan. Generellt verkar halterna vara något lägre i Sverige, men föroreningarna har ändå återfunnits i samtliga prover som analyserats vilket bekräftar deras utbredda spridning. PBDD/F-profilerna i fettvävnadsproverna var överlag lik dom i bröstmjölksproverna vilket stödjer teorin om ett selektivt upptag och metabolism. Dock verkar PBDD/Fs ge ett större bidrag till den total dioxin-lika toxiciteten i fettvävnaden jämfört med i bröstmjölken . Slutligen har PBDD/Fs återfunnits i relativt höga halter i blod från två brandmän i San Francisco.

Datat som sammanfattas i denna rapport talar för att huvuddelen av de PBDD/Fs vi exponeras för, bortsett från de naturligt bildade PBDDs, har sitt ursprung i alla BFR-behandlade material vi har i vår omgivning, och framförallt då alla PBDE innehållande material. Enligt dom uppskattningar som gjorts i rapporten innehåller sådana material och produkter flera ton PBDD/Fs bara i Sverige. Till detta tillför vi också några hundra kilo varje år genom de varor vi importerar från andra länder. Detta innefattar framförallt elektrisk och elektronisk utrustning (EEE), fordon och byggmaterial. Samtidigt avlägsnas ständigt BFR-innehållande material från samhället när de har blivit uttjänta. När detta sker kan materialen antingen återvinnas, destrueras eller deponeras.

I Sverige förbränns det mesta BFR-innehållande materialet nuförtiden, men en del kan också läggas på deponi. T.ex. kan ibland den lätta fraktionen från fragmenterade bilar (SLF) läggas på deponi då denna är mer komplicerad att bränna. Uppskattningsvis hamnar upp till 0.5 ton PBDD/Fs på svenska deponier varje år och totalt innehåller dessa deponier troligtvis flera ton PBDD/Fs sedan tidigare. I avfallsfraktionen som går till förbränning sker en effektiv destruktion av PBDD/Fs, i alla fall om man ser till vad som kommer ut från skorstenen och vad som hamnar i flygaskan. Dock kan bottenaskan fortfarande innehålla relativt höga halter PBDD/F vilket antyder att alla PBDD/Fs i det ursprungliga avfallet ändå inte förstörs, och att en viss nybildning av PBDD/F också kan ske. Uppskattningsvis finns det närmare 6 kg PBDD/Fs i de bottenaskor som genereras vid svenska sopförbränningsanläggningar varje år.

Förutom alla de PBDD/Fs som är gömda i produkter, material och avfall i vårt samhälle, finns det en ännu större mängd PBDD/Fs som inte ännu bildats i alla BFRs (och framförallt PBDEs) som återfinns i samma och liknande produkter, material och avfall. Om alla dessa material, som ett värsta scenario, skulle utsättas för någon typ av dålig förbränning skulle uppskattningsvis ytterligare 200 ton PBDD/Fs kunna bildas och emitteras. För att helt elimnera denna risk måste dessa material avlägsnas från samhället och därefter destrueras. Här ska man dock komma ihåg att emissionsrisken många gånger ökar när material rivs bort från sin ursprungliga funktion samt när de återvinns och destrueras.

En av de viktigaste faktorerna för att minimera PBDD/F-emissionerna vid hanteringen av BFR-innehållande avfall är att effektivt och med hög noggranhet kunna identifera och separera det BFR-innehållande materialet från icke BFR-innehållandematerial så att varje fraktion kan behandlas på tillbörligt sätt. Det finns flear spektroskopiska tekniker som kan användas för detta ändamål och även tekniker baserade på skillnader i densitet och elektrostatiska egenskaper. Ingen av dessa tekniker kan dock ensamt klara av att separera ut allt BFR-innehållande material, utan kombinationer av metoder måste användas. Trots detta uppnås aldrig en 100%-ig separation utan vanligtvis hamnar runt 5% i fel fraktion. På grund av detta ska återvunnet plastmaterial aldrig användas i känsliga produkter såsom leksaker och hushållsartiklar, och när det gäller den BFR-innehållande fraktionen så ska denna inte återvinnas alls. Den kan möjligen användas till att göra baskemikalier (som brom) och bränsle till industrin, men annars bör den destrueras.

Destruktion av BFR-innehållande material görs företrädesvis i godkända förbränningsanläggningar. Inblandningen av BFR-material i övrigt avfall/bränsle skall dock hållas lågt (<5%) för att hålla ner mängden PBDD/F-prekursorer och korrosiv HBr i ugnen och förbränningsgaserna. Anläggningarna måste också ha ett väl utvecklat reningssytem för rökgaserna och en plan för hur askorna (inte minst bottenaskorna) ska tas om hand på ett säkert sätt. PBDD/F-innehållande material kan även destrueras med hjälp av andra högtemperaturprocesser som t.ex. brännugnar för cement och metallsmältverk. Det är dock viktigt att dessa har samma krav på rökgasrening och askhantering för att undvika stora utsläpp härifrån. Om dessa krav uppfylls kan metallsmältverk med fördel användas för destruktion av metallinnehållande BFR-avfall, t.ex. kretskort, då detta gör att metallerna kan återvinnas.

En alternativ sätt att ta hand om BFR-innehållande material är att genom extraktion eller pyrolys först avskilja bromet eller de intakta BFR-ämnena från basmaterialet varefter detta kan återvinnas eller behandlas som ett ett BFR-fritt material. Bromet kan i sin tur tas om hand och återanvändas i

industrin. Ett antal sådana här processer har utvecklats för BFR-innehållande plaster, men ingen har än så länge använts i stor skala.

Det absolut sista alternativet för BFR-innehållande avfall, liksom för annat organiskt avfall, är deponering. Detta ska egentligen endast användas i undantagsfall, men om det ändå av någon anledning måste användas så måste det göras under mycket kontrollerade former för att undvika läckage, emission och exponering av människor och djur. Deponin måste också skyddas från olycksbränder samt vara anpassad för att upprätthålla en hög säkerhet även om klimat och omgivning förändras. De mer kortsiktiga riskerna ovan, t.ex. läckage- och brandrisk, bör också beaktas vid tillfällig lagring av BFR-innehållande material, t.ex. i väntan på annan behandling. I sådana situationer skulle det också vara lämpligt med en begränsning angående hur mycket BFR innehållande material/avfall som får lagras på samma plats för att minska skadorna om t.ex. en brand ändå skulle inträffa.

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List of abbreviations

ABS	Acrylonitrile butadiene styrene
AhR	Aryl hydrocarbon receptor
ASR	Automotive shredder residue
Br, Br_2	Bromine
BFR	Brominated flame retardant
C	Carbon
Cl	Chlorine
DR-CALUX	Dioxin responsive-Chemical Activated Luciferase Expression (bioassay)
EAF	Electric arc furnace
EEE	Electrical and electronic equipment
EF	Emission factor
ELV	End-of-life vehicle
ES	Electrostatic separation (of plastics)
GC/MS	Gas chromatography coupled to mass spectrometry
HBCD	Hexabromocyclododecane
HBr	Hydrogen bromide
HWI	Hazardous waste incinerator
IWI	Industrial waste incinerator
IVL	Swedish Environmental Institute
MSWI	Municipal solid waste incinerator
NaBr	Sodium bromide
NIR	Near infrared spectroscopy
OH-PBDEs	Hydroxylated polybrominated diphenylethers
PBDEs	Polybrominated diphenylethers
TetraBDE	Tetrabrominated diphenylether
decaBDE	Decabrominated diphenylether, also called BDE#209
PBDDs	Polybrominated dibenzo-p-dioxins
PBDFs	Polybrominated dibenzofurans
PBDD/Fs	Polybrominated dibenzo-p-dioxins and furans
HexaBDF	Hexabrominated dibenzofuran
PBCDD/Fs	Mixed polybrominated/chlorinated dibenzo-p-dioxins and furans
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzofurans
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and furans
PC	Polycarbonate
PC-board	Printed circuit board
PC-CRT	Personal computer-cathode ray tube
PE	Polyethylene
PP	Polypropylene
PPO	Polyphenylene oxide
PS	Polystyrene
PVC	Polyvinyl chloride (plastics)

REP	Relative potency factor
Sb_2O_3	Antimony trioxide
S/F	Sink and float technologies (used to separate plastics)
SLF	Shredder light fraction ("fluff" from fragmented cars)
STP	Sewage treatment plant
SSS	Sliding spark spectroscopy
TBBPA	Tetrabromo bisphenol A
TEF	Toxic equivalency factor
TEQ	Toxic equivalent
WEEE	Waste electrical and electronic equipment
WHO	World Health Organization
XRF	X-ray fluorescence spectroscopy
XRT	X-ray transmission spectroscopy

1 Introduction

In recent years the brominated dioxins (PBDD/Fs) has emerged as a new type of environmental contaminants of great concern. These compounds may be emitted from the same sources as the closely related, but much more well-known chlorinated dioxins (PCDD/Fs), i.e. combustion processes and various industrial processes, as long as bromine is present in some form. The presence of bromine in materials, products and waste has increased dramatically since brominated flame retardants (BFRs) was introduced on the market in the 1970s, and now bromine containing material can be found everywhere in the society, in e.g. plastics of electrical and electronic equipment (EEE), construction material, furniture upholstery and textiles. Many brominated compounds added in products, including most BFRs, are to some extent toxic in themselves and may pose a hazard as they are emitted from the products or processes in which the materials are treated or destructed, but there is also a concern that the added BFRs may give rise to emissions of other brominated compounds, such as PBDD/Fs, which are even more toxic and hazardous. Such emissions have been observed, and there are also an increasing number of studies showing that the environment and the populations in many countries are exposed to significant levels of PBDD/Fs. Based on the observed contaminant profiles, it looks like the primary sources of these PBDD/Fs are BFR treated materials and products, at least in urban environment. In more rural environments a significant share of the PBDD/Fs may instead come from long range transport and, in some marine environments, even from natural sources.

1.1 Objectives

The objective of this report is to provide a comprehensive overview of the PBDD/F load in the Swedish environment, as well as to summarize the current knowledge concerning the main sources for these contaminants, and also how these can be reduced. More specifically, the following aspects have been explored:

- The occurrence and levels of PBDD/Fs in the environment, with a focus on Sweden and its population
- Possible sources of PBDD/Fs in the environment and the principal distribution pathways, also here with a focus on the Swedish society and environment.
- The amount of PBDD/Fs that may be present in BFR-mixtures, materials and products in use or in stock, and how much that can be formed when these materials and products are refined, used, recycled or disposed/destroyed.
- To what extent and in which situations it would be possible to limit the formation and emission of PBDD/Fs from BFR containing material that we already have in our society.

The focus in the report has been directed towards anthropogenically formed and emitted PBDD/Fs since previous studies strongly indicate that these are the main sources in urban environments. Natural formation of PBDD/Fs seems only to be significant in certain marine environments, and it gives rise to a completely different dioxin pattern. Furthermore, the formation and emission of mixed brominated and chlorinated dioxins (PBCDD/Fs) that can be observed in incineration facilities for instance, is only touch upon briefly.

2 Background

2.1 Brominated dioxins - structures, properties and toxicity

The brominated dioxins (PBDD/Fs) are, like the closely related chlorinated dioxins (PCDD/Fs), composed of two subgroups of compounds; the polybrominated dibenzo-p-dioxins (PBDD) and the polybrominated dibenzofurans (PBDF). These subgroups are in turns composed of 75 and 135 individual substances or congeners, respectively, which structurally only differ in the number and positions of the bromine atoms attached to the carbon backbone (Figure 1). Like the chlorinated dioxins, the PBDDs and PBDFs are, for the sake of simplicity, often collectively referred to as just brominated dioxins or PBDD/Fs. However, in this report the PBDDs and PBDFs will often be discussed separately since they are formed to a different extent in the processes that are considered important for the topic treated in the report. In addition to the pure PBDD/Fs and PCDD/Fs, containing only bromine and chlorine, respectively, there are also mixed dioxins with both bromine and chlorines in the molecules. This compound group is even larger and contains an additional 1550 dibenzo-p-dioxins (PBCDDs) and 3050 dibenzofurans (PBCDFs). (WHO 1998)

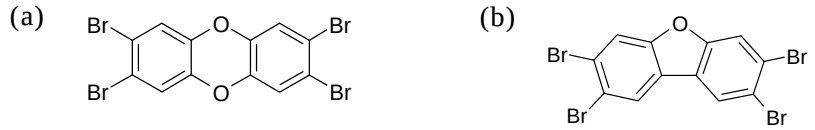

Figure 1. *Molecular structures for the a) polybrominated dibenzo-p-dioxin (PBDD) 2,3,7,8-TeBDD, and the b) polybrominated dibenzofuran (PBDF) 2,3,7,8-TeBDF.*

In general, the PBDD/Fs (and the PBCDD/Fs) are, like the PCDD/Fs, highly lipophilic compounds with low water solubility and volatility. However, these properties depend on the degree of bromination so that the highly brominated congeners are less water soluble and volatile than the congeners with fewer bromines (Table 1). This also affects the mobility and degradability of the PBDD/Fs since the highly brominated congeners will be more strongly adsorbed to particles and thereby less available to leaching and degradation processes (WHO 1998). Thus adsorbed to particles, such as soils and sediments, the PBDD/Fs are highly persistent and have long half-lives. However, as free, non-adsorbed molecules, in the atmosphere or in solution, they are rather easily debrominated by photolysis (Buser 1988; Chatkittikunwong and Creaser 1994). Furthermore, PBDD/Fs may be thermolytically debrominated via substitution reactions, e.g. with chlorine (WHO 1998).

The degree of bromination and the position of the bromines also affect the toxicity of the PBDD/Fs. Like the PCDD/Fs, the PBDD/F congeners with bromines in the 2,3,7,8-positions (Figure 1) are considered to be the most toxic ones, and even if the PBDD/Fs have been far less studied than the PCDD/Fs, the current knowledge indicates that the toxicity pattern is similar for the two compound groups (Ao et al. 2009; Birnbaum et al. 2003; Olsman et al. 2007; WHO 1998). Consequently, it has been suggested, by a WHO expert panel, that the toxic equivalency factors (TEFs) originally

developed for human risk assessment of PCDD/Fs, also should be used for human risk assessment of PBDD/Fs until further knowledge has been acquired (van den Berg et al. 2013). When it comes to environmental risk assessment of aquatic environments however, it is recommended to consider the use of a set of relative potency factors (REPs) compiled by the same expert panel (van den Berg et al. 2013).

Like the PCDD/Fs, and other dioxin-like compounds, the PBDD/Fs give rise to a wide range of toxic and negative biological effects such as lethality, wasting, thymic atrophy, teratogenesis, reproductive disorders, chloracne, immunotoxicity, enzyme induction, decrease in thyroxin and vitamin A levels and increase in hepatic porphyrins (Birnbaum et al. 2003; D'Silva et al. 2004). Most effects, if not all, are mediated by the Ah receptor (AhR), which is a soluble intracellular ligand-activated transcription factor. Dioxin-like compounds that binds to the receptor activates the AhR signaling pathway, which leads to alterations in gene expressions and subsequent toxic effects. The binding affinity to the Ah-receptor is structure dependent, which explains why PCDD/Fs and PBDD/Fs have similar toxic profiles (D'Silva et al. 2004; van den Berg et al. 2013). However, due to the differences in size and reactivity between the bromine and chlorine atoms, some PBDD/Fs seem to be more toxic than the corresponding PCDD/Fs, while in some cases it seem to be the reverse (Birnbaum et al. 2003; D'Silva et al. 2004; van den Berg et al. 2013).

Table 1. *Physical and chemical properties of some PBDDs and PBDFs.*

	MW (amu)	Boiling p. (°C)	Vapor press. (Pa)	Water sol. (mol/L)	Log Kow
137-TriBDD	420.9		*5.7×10^{-5}	*4.3×10^{-10}	7.0
2378-TeBDD	499.8	438.3	6.4×10^{-7}	*2.0×10^{-11}	7.9
12378-PeBDD	578.7		*7.2×10^{-7}	*9.2×10^{-13}	8.8
123467-HxBDD	657.6		*8.3×10^{-8}	*4.3×10^{-14}	9.7
1234678-HpBDD	736.5		*9.4×10^{-9}	*2.0×10^{-15}	10.6
OBDD	815.4	523.2	4.1×10^{-11}	*9.2×10^{-17}	11.5
238-TriBDF	404.9		*4.9×10^{-5}	*1.9×10^{-9}	6.4
2378- TeBDF	483.8		*4.7×10^{-6}	*8.9×10^{-11}	7.3
12378-PeBDF	562.7		*8.1×10^{-7}	*2.1×10^{-12}	8.5
123467-HxBDF	641.6		*6.4×10^{-8}	*1.9×10^{-13}	9.1
1234689-HpBDF	720.5		*7.2×10^{-9}	*8.9×10^{-15}	9.9
OBDF	799.4				

*Calculated values using EPI Suite™ v.3.12 (US-EPA), retrieved from Report 5736 from Naturvårdsverket (2007).

2.2 Formation of PBDD/Fs

Like PCDD/Fs, PBDD/Fs have never been produced intentionally, other than for scientific purposes, but are generated as undesired by-products in various processes in the society. These include incineration processes, various high temperature processes, processes used to produce other brominated compounds (e.g. BFRs), and thermal and photochemical processes acting on BFR containing materials during their use, disposal and recycling (Weber and Kuch 2003). Furthermore, it has recently been recognized that PBDD/Fs may be formed naturally in some marine environments via biological and photolytical pathways (Arnoldsson et al. 2012a, b; Haglund et al. 2010).

2.2.1 PBDD/F formation in high temperature processes

PBDD/Fs are formed in incineration processes and other high temperature industrial processes with similar mechanisms as PCDD/Fs (Huang and Buekens 1995), provided that bromine is available in the fuel (Söderström 2003). This availability has however been limited before the BFRs were seriously introduced on the market in the 1970s (Alaee et al. 2003; Söderström and Marklund 2002), although ethylene dibromide was present as an additive in gasoline long before that, giving rise to a limited PBDD/F formation in vehicle engines (Haglund et al. 1988). However, since the introduction of BFRs, the amount of bromine circulating in our society, and finally reaching our municipal solid waste incinerators (MSWI), has increased dramatically, and thereby the conditions for PBDD/F-formation (D'Silva et al. 2004; Kawamoto 2009; Söderström and Marklund 2002, 2004). The correlation between the bromine content in the fuel and the amount and proportion of PBDD/Fs and PBCDD/Fs formed has been shown in several studies (Funcke 1997; Schüler and Jager 2004; Söderström and Marklund 2002; Söderström 2003).

Like the PCDD/Fs, PBDD/Fs and PBCDD/Fs may be formed both from precursors, such as brominated and chlorinated phenols and benzenes, during conditions of incomplete combustion, and from basic elements, i.e. carbon, hydrogen, oxygen, bromine and chlorine, via so-called *de novo* synthesis (Sidhu et al. 1995; Söderström 2003; Weber and Kuch 2003). Both processes are favored by moderate temperatures, i.e. 250-500 °C, and the presence of active surfaces (e.g. copper) on which the reactions can take place. However, the precursor pathway also require spots of pyrolytic conditions in the combustion zone in which the precursors can survive, while the *de novo* process only require survival of carbon fragments that can take part in dioxin formation at later stages in the process, e.g. when the flue gases are cooled down (Söderström and Marklund 2004). In most incinerators, the *de novo* formation in the cooling zones is the dominating mechanism for the PCDD/Fs, since the chlorine mainly is introduce as inorganic chloride (Huang and Buekens 1995). However, for the PBDD/Fs the precursor pathway is probably more important, since most of the bromine is introduced as BFRs, and usually in the form of brominated aromatic compounds that can act as direct PBDD/F-precursors in the process (Weber and Kuch 2003).

Another possible formation pathway for PBDD/Fs and PBCDD/Fs is that bromine atoms replace chlorine substituents in existing PCDD/F molecules (Kawamoto 2009). However, in reality, the reverse scenario is generally more likely to happen, i.e. that bromines in PBDD/Fs are replaced by chlorines, resulting in PBCDD/Fs and PCDD/Fs, which is because the Cl-C-bond is stronger than the Br-C-bond (Schüler and Jager 2004; Weber and Kuch 2003). Consequently, at higher temperatures (within the interval for dioxin formation 250-500 °C) and longer residence times the proportion of chlorine will normally exceed that of bromine in the formed dioxin molecules, provided that chlorine and bromine are present in equal proportions in the fuel (Söderström and Marklund 2004; Weber and Kuch 2003). On the other hand, if the residence time is short and/or the temperature is in the lower end of the formation interval, the proportion of bromine may exceed that of chlorine in the formed dioxin molecules, which is because the bromination reaction is faster than the chlorination reaction (Söderström and Marklund 2004; Weber and Kuch 2003).

2.2.2 Formation during incomplete combustion of BFRs

Generally, the formation and emissions of dioxins and other organic contaminants increase during poor combustion conditions which is due to the increased presence of precursors that can give rise to dioxins directly, and soot that can contribute in *de novo* synthesis (Hedman 2005). If BFRs are present, the situation is even worse since many of these compounds constitute, or may give rise to, far advanced precursors of PBDD/Fs (Weber and Kuch 2003). Particularly the polybrominated diphenylethers (PBDEs) are easily transformed into PBDFs, which is obvious when comparing the molecular structures of the two compound classes (Figure 2). Thus, the PBDEs only require an intra-molecular elimination of molecular bromine (Br_2) or hydrogen bromide (HBr) followed by a cyclization to form PBDFs. In these reactions, the elimination of HBr is energetically favored in comparison to the elimination of Br_2, which results in a decreased dioxin formation potential from penta-, octa- to decabrominated diphenylethers (pentaBDEs > octaBDEs> decaBDE) (Buser 1986; Luijk et al. 1991; Thoma et al. 1987). The reactions are, on the other hand, always enhanced by the presence of a polymer matrix and antimony trioxide (Sb_2O_3), which both often are present when flame retarded material is combusted. This is because polymeric materials constitute the main materials that are treated with BFRs, and because Sb_2O_3 often is added in these materials to enhance the function of the BFRs (Weber and Kuch 2003). The polymer matrix is here acting as a hydrogen donor in the initial debromination process, which give rise to less brominated and more reactive PBDEs (see above), and Sb_2O_3 as a catalyst in the debromination process as well as in the elimination of HBr/Br_2 during the subsequent cyclization (Dumler et al. 1990; Luijk et al. 1991).

Combustion of PBDEs may also give rise to PBDDs, but generally in much lower yields than PBDFs. This is because the PBDDs also require a second oxygen to be inserted into the PBDE molecule before the cyclization (Figure 2), and this happens less readily (Dumler et al. 1990; Luijk and Govers 1992). Another possible formation pathway for both PBDDs and PBDFs is via smaller precursors such brominated phenols and benzenes. However, even if PBDEs may give rise to relatively large amounts of such precursors and these are rather reactive (Hutzinger et al. 1989; Weber and Kuch 2003), the amounts of PBDD/Fs (or at least PBDFs) formed via this pathway is much lower than those formed via direct cyclization of the PBDEs (Weber and Kuch 2003). On the other hand, brominated phenols and benzenes may be formed from other BFRs (e.g. TBBPA and HBCD) that lack the ability to form dioxins by a simple elimination and cyclization step. PBDD/F-formation has thus been reported during combustion of both tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD), although in much lower yields than what may be formed from PBDEs (Ortuño et al. 2014b; Takigami et al. 2014).

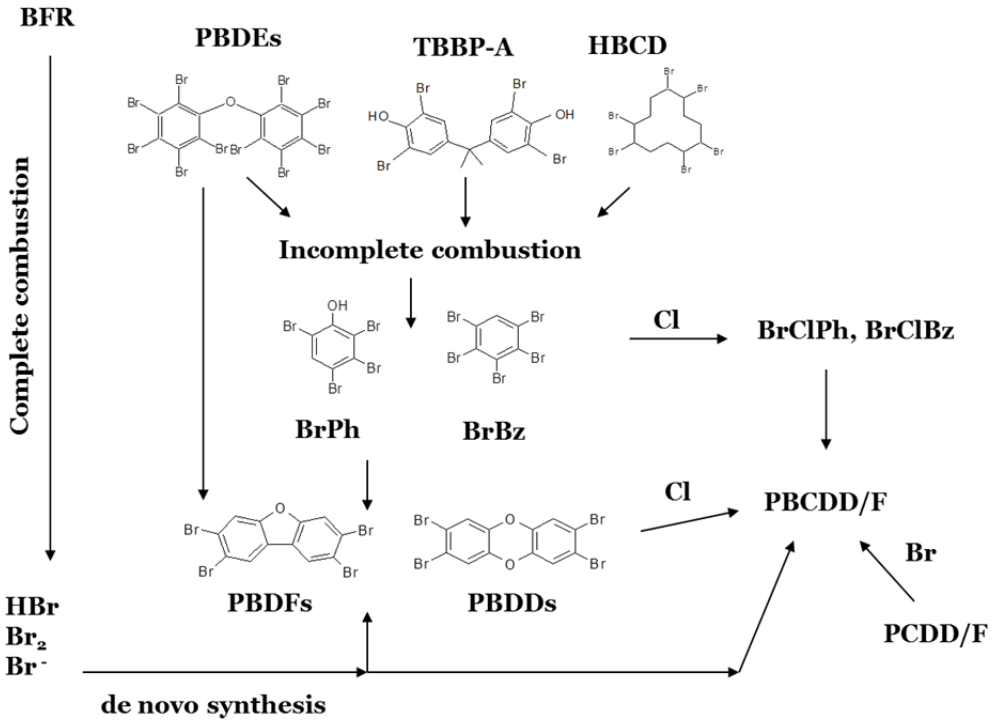

Figure 2. *Thermolytic transformation of brominated flame retardants (PBDEs, TBBP-A and HBCD) into brominated dioxins (PBDDs) and furans (PBDFs). The intermediates/precursors brominated phenols and benzenes, as well as analogues compounds containing both chlorines and bromines are also shown.*

2.2.3 Formation of PBDD/Fs during thermal stress of BFRs

PBDD/Fs may also be formed during moderate thermal stress of BFRs, which may occur during their production, when they are mixed into materials, when the materials are refined into products and when the products are used, recycled and destroyed. PBDD/Fs may thus be formed as by-products during the BFR-synthesis, resulting in relatively high levels in the final technical BFR-mixtures (Hanari et al. 2006; Ren et al. 2011), see section 3.2.1 below. The subsequent mixing of the BFRs with the polymer as well as the extrusion and moulding of plastics into products usually involve enhanced temperatures in which further PBDD/F-formation may occur (Ebert and Bahadir 2003; Luijk et al. 1992; Mcallister et al. 1990; Weber and Kuch 2003). Furthermore, when the products are used they are in some cases subject to elevated temperatures, e.g. EEE with an elevated working temperature, which possibly may give rise to PBDD/F-formation. Finally, during end-of life treatment of BFR-containing material, thermal processes such as fragmentation, grinding, melting and incineration, may be used, potentially giving rise to further formation and emission of PBDD/Fs (Duan et al. 2012; Ebert and Bahadir 2003; Weber and Kuch 2003). However, it should be noted that most of these processes are mainly (if not only) relevant for PBDEs that can be converted into PBDFs via a simple elimination/cyclization step, while for other BFRs they are less important. Factors influencing the extent of PBDD/Fs formed include temperature and duration of the process (Mcallister et al. 1990; Schlummer et al. 2007; Weber and Kuch 2003).

Formation of PBDD/Fs can potentially also occur during cooking of PBDE contaminated food. This was recently shown in a study by Vetter et al. (2014), in which salmon spiked with decaBDE was heated at 200 °C. During each minute of heating 0.5 ‰ of the BDE 209 was transformed into PBDFs, i.e. mainly hepta- and hexaBDFs. The dioxin-like toxicity, measured by the DR-CALUX assay, was also gradually increasing during the cooking process. However, interestingly when the decaBDE was heated in edible oil instead of salmon no PBDF was formed, and neither when a tetrabrominated PBDE (BDE 47) was heated in salmon, showing that both the original compounds and the matrix influence the transformation rate.

2.2.4 Formation during photolytic conversion of BFRs

PBDD/Fs may also be formed through photolytic transformation of BFRs, both during natural sunlight exposure and artificial UV-light exposure (Söderström et al. 2004; Watanabe and Tatsukawa 1987). However, like for the thermolytic processes, this is mainly relevant for PBDEs and results then almost exclusively in PBDF formation. The reaction pathways also seem to be similar to the pathways followed during the thermolytic conversion of PBDEs into PBDFs, i.e. initiated by a debromination to remove one of the ortho-bromines (the bromines adjacent to the ether bridge between the two benzene rings) from the PBDE molecule, followed by a cyclization to a PBDF (Eriksson et al. 2004). However, unlike the thermolytic pathways, the photolytic transformation mainly results in lower brominated PBDFs (Eriksson et al. 2004; Watanabe and Tatsukawa 1987), which most likely is because the PBDFs are highly photolabile themselves resulting in a continuous debromination of the formed PBDFs (Eriksson et al. 2004). The formation reactions, or at least the initial debromination of the PBDEs, seem to be faster in clear solutions than when particles, of e.g. soil and sediment, are present (Hua et al. 2003; Söderström et al. 2004), and is also decreasing with increasing polarity of the solvent used (Eriksson et al. 2004). Furthermore, the debromination is faster for highly brominated compounds than for the less brominated compounds (Eriksson et al. 2004). Nevertheless, transformation of PBDEs into PBDFs have been observed in a number of studies with different PBDEs as starting material, in different matrices and with different light sources (Christiansson et al. 2009; Eriksson et al. 2004; Hagberg et al. 2006; Hua et al. 2003; Söderström et al. 2004; Watanabe and Tatsukawa 1987), and it has also been observed in real products such as TV-plastics (Kajiwara et al. 2008) and curtain textiles (Kajiwara et al. 2013) during exposure to natural sunlight.

2.2.5 Natural formation of PBDD/Fs

Recently it has also been recognized that low brominated PBDDs may be formed by natural processes in some marine environments. This may happen through enzymatic coupling of bromophenols (mainly 2,4,6-tribromophenol; 2,4,6-triBrPh) mediated by bromoperoxidases, and through photochemical transformation of hydroxy-PBDEs (OH-PBDEs) (Arnoldsson et al. 2012a, b; Haglund et al. 2007; Haglund 2010). Both bromophenols and OH-PBDEs are abundant compounds in some marine environments, and at least the former are known to be produced naturally in organisms such as algae and cyanobacteria (Flodin and Whitfield 1999). OH-PBDEs are also suggested to be produced naturally in marine organisms (Kelly et al. 2008; Löfstrand et al. 2011), but may also originate from

anthropogenic PBDEs via metabolism, atmospheric hydroxyl radical reactions, and oxidation in sewage treatment plants (Stapleton et al. 2009; Ueno et al. 2008).

The formation from bromophenols basically involve the enzymatic coupling of two bromophenol molecules, which for the most commonly found bromophenol 2,4,6-triBrPh leads to the formation of tetra- and tribrominated PBDD, with a predominance of 1,3,6,8-TetraBDD (Arnoldsson et al. 2012b). The photolytical conversion of OH-PBDEs follows a similar pathway as described for PBDEs above, with a cyclization reaction during which HBr is eliminated. It has been shown that this reaction give rise to the most abundant 1,3,7- and 1,3,8-triBDDs from the most abundant OH-PBDEs (OH-BDE 47 and OH-BDE 68) in the environment (Arnoldsson et al. 2012a). In summary these natural formation pathways mainly give rise to tri- and tetra-brominated PBDDs, which is quite distinct from the PBDD/F pattern produced by the anthropogenic sources. As we know, these give rise to more of the highly brominated congeners, and particularly PBDFs (Tu et al. 2011; Wyrzykowska et al. 2009).

3 Emissions of PBDD/Fs from potential sources

Considering all the potential formation processes discussed above, there are clearly many possible sources for PBDD/Fs in our society and the environment. This includes all incineration processes, industrial processes that involve high temperature, production processes for BFRs and BFR treated materials, BFR-containing products as they are used, recycled and disposed of, and finally various marine environments in which PBDDs are formed naturally. In this chapter, the anthropogenic emission sources for PBDD/Fs will be discussed with the starting point in the available emission data. It should be noted though that, for some sources, the amount of available emission data is rather limited.

3.1 Incineration and high temperature industrial processes

During incineration and various high temperature processes, PBDD/Fs may be emitted both due to the release of dioxins already present in the fuel/the material being combusted, and as a result of the formation of PBDD/Fs in the actual processes. Both processes are favored by poor combustion conditions, which are more prominent during open burning activities than during controlled incineration in large scale facilities. In the following sections, both processes are discussed.

3.1.1 Incineration facilities and industrial process

The emissions of PBDD/Fs from incineration facilities and various metal processing plants have been investigated in a number of studies of which some are summarized in Table 2. Generally, it seems like the PBDD/F emissions from municipal solid waste incinerators (MSWI) are relatively low. They are for instance significantly lower than the PCDD/F emissions from the same processes, and since these generally are considered to be acceptable today (Avfall Sverige 2009), as a result of the highly optimized processes with efficient flue gas cleaning systems, the PBDD/F emissions from this source category should not be of immediate concern. However, the PBDD/F emissions seem to be highly dependent on the fuel and its content of brominated compounds. Consequently, in industrial waste incinerators (IWI), which usually use a more diverse fuel with a higher BFR content, the PBDD/F emissions are often larger (Wang and Chang-Chien 2007), and in metallurgical processes that frequently use electronic waste (e-waste) as one of its feed stocks, as well as having less sophisticated flue gas cleaning systems, the PBDD/F emissions are even further elevated (Du et al. 2010b).

Du et al. (2010b) compared the stack emissions of PBDD/Fs in several large-scale incinerators and metal processing plants in China, including MSWI, hazardous waste incinerators (HWI), crematories, sinter facilities, electric arc furnaces (EAF) and secondary smelters (for lead, aluminum, copper and zinc). They found markedly higher PBDD/F-levels in the flue gases from the metallurgical processes than in those from general combustion processes, and concluded that the former may constitute an important source of these compounds to the atmosphere. Likewise, Wang and Chang-Chien (2007) found higher levels of PBDD/Fs in the flue gases from IWI than in those from MSWI, while the PCDD/F-levels were more similar for the two incinerator types.

Table 2. *Levels of PBDD/Fs, PCDD/Fs and PBDEs in stack flue gases from municipal solid waste incinerators (MSWIs), crematories (Crem), industrial waste incinerators (IWIs), a hazardous waste incinerator (HWI), and various metallurgical processes (Metal). Both total levels and toxic equivalents (TEQs) are given for PCDD/Fs and PBDD/Fs.*

	Σ PBDD/F (ng/Nm^3)	**Σ PBDD/F (pg TEQ/Nm^3)**	**Σ PCDD/F (ng/Nm^3)**	**Σ PCDD/F (pg TEQ/Nm^3)**	**Σ PBDE (ng/Nm^3)**	**Reference**
MSWI, China	0.025	12	8.6	690		Du et al. (2010b)
MSWIs, Taiwan	0.00045-0.012	0.12-2.9	0.34-216	17-10200		Wang and Chang-Chien (2007)
MSWIs, Taiwan	0.065-0.088	1.9-3.1	1.8-3.1	73-120	26-109	L-C Wang et al. (2010a)
MSWI, Taiwan	0.021-0.17	0.22-14			5.4-9.3	Tu et al. (2011)
MSWIs, USA	0.0045-7.2				1.6-289	Wyrzykowska et al. (2008)
Crem., China	0.040-0.075	10-23	8.3-31	940-3000		Du et al. (2010b)
IWIs, Taiwan	0.0045-0.077	1.1-16	0.32-4.2	13-900		Wang and Chang-Chien (2007)
HWI, China	0.15	54	4.9	350		Du et al. (2010b)
Metal, China	0.56-5.8	140-1500	0.59-4300	30-120000		Du et al. (2010b)
Metal, Taiwan	0.020-3.0	0.21-29	0.15-21	16-3600	5.8-92	L-C Wang et al. (2010b)
Metal, China	0.036-0.19	0.32-4.3			3.1-40	Li et al. (2015)

Du et al. (2010b) also observed that the congener profiles for PBDD/Fs are more variable than they are for PCDD/Fs, which are fairly stable within a certain process category (e.g. MSWI). The PBDD/F profile thus varies depending on the fuel, i.e. how much and what BFRs that are loaded, which can be explained by the fact that different BFRs give rise to different kinds and proportions of precursors that can take part in the subsequent PBDD/F formation (Weber and Kuch 2003). The PCDD/Fs, on the other hand, are mainly formed via de novo synthesis in these processes, which principally is dependent on operational parameters such as temperature and residence times (Huang and Buekens 1995).

However, the PBDD/F emissions are of course also dependent on the combustion conditions. This was, among others, shown in a study by Wyrzykowska et al. (2008), who studied PBDD/Fs and PBDEs in a MSWI in USA. The levels of both compound classes increased significantly during start-up and shut-down of the process as compared to steady state conditions. They also observed that the proportions of PBDFs increased (from approx. 70 to 90 %) during start up and shut down, i.e. as the combustion conditions became worse and the total levels of PBDD/Fs increased the proportions of PBDFs also increased. This could be explained by an increased proportion of PBDFs formed through direct conversion of PBDEs during poor combustion conditions. Furthermore, Wyrzykowska et al. (2008) concluded that the emissions during steady state conditions were comparable to those observed in other MSWIs, while the start-up/shut-down emissions were comparable with the emissions from IWIs.

Table 3. *Levels of PBDD/Fs, PCDD/Fs and PBDEs in fly ash (FA) and bottom ash (BA) from biofuel- and coal-fired power plants, municipal solid waste incinerators (MSWIs), hazardous waste incinerators (HWIs), and an electric arc furnace (EAF). Both total levels and toxic equivalents (TEQs) are given for PCDD/Fs and PBDD/Fs.*

	Σ PBDD/F (ng/g)	Σ PBDD/F (pg TEQ/g)	Σ PCDD/F (ng/g)	Σ PCDD/F (pg TEQ/g)	Σ PBDE (ng/g)	Reference
FA, Biofuel, Swe.	0.026-0.37	0.5-3.9	0.045-11	2.2-120		Johansson et al. (2015)
FA, Coal, Taiwan	0.0020	0.013			6.3	Tu et al. (2011)
FA, MSWIs, Swe.	0.022-0.14	0.3-6.0	5.2-350	81-4300		Johansson et al. (2015)
FA, MSWIs, Taiwan	0.023-0.16	1.3-1.5			0.44-1.8	Tu et al. (2011)
FA, MSWIs, Taiwan	0.0066-0.039	0.093-2.0	~200	~2000	0.33-26	L-C Wang et al. (2010a)
FA, HWIs, Swe.	0.30-3.0		2.3-4.8	140-240		Hagberg et al. (2005b)
FA, EAF, China	23	290	97	1600		Du et al. (2009)
BA, Biofuel, Swe.	0.010-0.049	0.3-1.6	0.0027-1.3	0.9-8.4		Johansson et al. (2015)
BA, Coal, Taiwan	0.0037	0.034			6.4	Tu et al. (2011)
BA, MSWIs, Swe	0.069-30	1.1-140	0.034-1.0	1.5-13		Johansson et al. (2015)
BA, MSWIs, Taiwan	1.6-3.1	28-61			160-300	Tu et al. (2011)
BA, MSWIs, Taiwan	0.43-2.6	8.1-52	~1	10-80	20-190	L-C Wang et al. (2010a)

When it comes to the ashes, PBDD/Fs have both been found in bottom ashes and fly ashes (Du et al. 2009; Johansson et al. 2015; Tu et al. 2011; L-C Wang et al. 2010a). However, in contrast to PCDD/Fs, the levels of PBDD/Fs (and PBDEs) are usually higher in the bottom ashes than in the fly ashes, at least in MSWIs. Thus, both L-C Wang et al. (2010a) and Tu et al. (2011) found much higher levels (and much larger total amounts) of PBDD/Fs and PBDEs in the bottom ashes as compared to fly ashes in MSWIs in Taiwan. Likewise, Johansson et al. (2015) found higher levels of PBDD/Fs in the bottom ashes as compared to fly ashes from MSWIs in Sweden. This indicates that PBDEs and PBDD/Fs in the feeding waste are not always completely destroyed in the combustion process, which could constitute a problem if the ashes should be used as construction material, for instance. Like for the flue gases, the levels in the fly ashes seem to be higher in metallurgical processes and HWIs than in MSWIs (Du et al. 2009; Hagberg et al. 2005b; L-C Wang et al. 2010a). This is different from the PCDD/Fs, which are found in similar levels in the fly ashes from all these processes.

PBDD/F data for Swedish incinerators and metal processing plants are, like for other countries, scarce, at least the data that is accessible to the public. There is this recent ash screening study performed by Johansson et al. (2015) in which fly ashes and bottom ashes from several MSWIs and biofuel-fired power plants were investigated, and the study by Hagberg et al. (2005b) in which PBDD/Fs were measured in fly ashes from two HWIs (Table 3). From these studies it can be concluded that the 1) PBDD/F levels in the Swedish ashes are similar to those found in Taiwan, 2) that the PBDD/F levels (unlike the PCDD/F levels) are higher in the bottom ashes than in the fly ashes

(just like in Taiwan), and 3) that PBDD/F levels generally increase in the order coal/biofuel< MSWIs< HWIs. Besides these studies there might be some occasional data measured by individual companies, but these are not accessible to the public. There is no data to be found on PBDD/F levels in flue gases from Swedish incinerators.

3.1.2 Open burning

Open burning, including open barrel/backyard burning, uncontrolled waste burning for metal recycling, accidental fires etc., usually involve poor combustion conditions in which dioxin formation is favored. PBDD/F-emissions during such activities, with and without a clear BFR source, have been investigated in a few studies. In Table 4, three such studies in which emission factors (EFs) have been calculated are presented together with similar data for two laboratory studies in which PC-boards have been heated, and three large-scale incineration processes, i.e. two MSWIs and one coal-fired power plant. The EF is generally defined as the mass of the compound emitted per kilogram of burnt material/fuel, but for one of the studies it has been calculated per kilogram of burnt carbon (Gullett et al. 2010).

It is evident that the open burning activities give rise to much higher emission of the contaminants than the controlled processes, and also that the presence of BFR containing e-waste increase the emissions even further. It should be noted though that the EFs presented for the large-scale processes only include what comes out from the stack, and that usually the major part of the dioxins and PBDEs are removed from the flue gases with the fly ash before reaching this point. However, even after considering this, the EFs for the open processes are much higher. When e-waste is present the levels of both brominated and chlorinated dioxins as well as the PBDEs increase, which is because e-waste usually makes the combustion conditions even worse and because it introduces precursors for both PBDD/Fs (i.e. BFRs) and PCDD/Fs (e.g. PVC) in the process (Weber and Kuch 2003). However, as evident in Table 4, the emissions of the brominated compounds increase much more than those of PCDD/Fs.

In addition to these studies, large PBDD/Fs emission have been observed in connection to accidental fires in TV-sets, e-waste and plastic recycling facilities, dump sites for household wastes, shopping malls and private houses (Lundstedt 2009, 2012; Myers et al. 2012; Organtini et al. 2014; Söderström 2003; Zelinski et al. 1993), and also in connection to combustion and heating processes used during informal recycling activities in developing countries (Naturvårdsverket 2011; Yu et al. 2008; Zennegg et al. 2009). In all these situations, larger or smaller amounts of BFRs have most likely been present, and the combustion processes that have occurred are undoubtedly examples of poor combustion conditions.

Table 4. *Emission factors (EFs) for PBDD/Fs, PCDD/Fs and PBDEs emitted during various open burning tests performed on domestic wastes, mixed e-waste and PC-boards; during laboratory burning of PC-boards and from the stack of municipal solid waste incinerators (MSWIs) and a coal-fired power plant (coal). The EFs are generally calculated as emissions per kg of material burnt (b.), but in one case per kg of carbon burnt.*

	Σ PBDD/F (µg/kg b.)	Σ PBDD/F (ng TEQ/kg b.)	Σ PCDD/F (µg/kg b.)	Σ PCDD/F (ng TEQ/kg b.)	Σ PBDE (µg/kg b.)	Reference
Open burning, dom. waste		87-1580[a]		202-1700[a]	42-1840[a]	Gullett et al. (2010)
Open burning, e-waste	28-700		6.9-122	990-17000	125-16000	Lönnemark and Blomqvist (2005)
Open burning, PC-boards	1100		11	92		Gullett et al. (2007)
Lab. burning, PC-boards	0.47-81	81-7240	0.084-0.84	18-84		Ortuño et al. (2014a)
Lab. burning, PC-boards		72-160 000		0.28-760		Duan et al. (2011, 2012)
MSWI, Taiwan	0.00069	0.016	0.014	0.55	1.5	L-C Wang et al. (2010a)
MSWI, Taiwan	0.00013-0.0013	0.0010-0.10			0.036-0.048	Tu et al. (2011)
Coal, Taiwan	0.00025	0.0025			0.063	Tu et al. (2011)

[a]µg or ng/kg carbon burnt

In the studies by Lundstedt (2009, 2012), very high PBDD/F levels (mainly PBDFs) were found in the soot collected after a TV fire. The levels were more than four orders of magnitude higher than the PCDD/F levels, and even 2-20 times higher than the PBDE levels. The latter indicates strongly that PBDD/Fs had been formed during the fire, and have not just been released from the plastics, since the proportions in the original TV plastics were the reverse, i.e. with PBDE levels 30-40 times higher than the PBDD/F levels. Furthermore, Lundstedt (2009, 2012) found high levels of PBDD/Fs in soot collected after fires in recycling facilities for e-waste and plastics, residential houses, a shopping mall and a boat garage. In some cases the PBDD/Fs dominated the contamination profile, e.g. at the e-waste recycling facility, while in some cases the PCDD/Fs or the PBDEs dominated, e.g. at the plastics recycling facility and the shopping mall, respectively. This was most likely governed by the presence of BFRs and PVC, as well as by the prevailing combustion conditions during each fire. Finally, very high levels of PBDD/Fs were found in the extinguishing water after a fire in another e-waste recycling facility. The total levels of PBDD/Fs (25-44 ng/L) were 10-70 times higher than the total PCDD/F levels (0.65-2.7 ng/L), but 40-70 times lower than the PBDE levels (1300-2000 ng/L). Nevertheless, the results indicate that the PBDD/F emissions may be extensive during accidental fires, particularly when a clear BFR source is present.

The studies by Lundstedt (2009, 2012) are all examples of Swedish cases. Besides these there are two other Swedish studies available on PBDD/F emissions from open fires. These are the study by Lönnemark and Blomqvist (2005), in which e-waste was combusted under different conditions in the laboratory, and the study by Söderström (2003) in which soot samples were collected after an accidental TV fire. In both cases, high levels of PBDD/Fs were found, significantly higher than the levels of PCDD/Fs.

3.2 Emissions during production and use of BFRs

As described above PBDD/Fs may be formed as by-products during the production and use of BFRs. Although this is mainly a case for PBDEs, it may also happen for other BFRs (Ebert and Bahadir 2003). PBDD/Fs may thus be emitted both from the processes used to produce BFRs and from the processes used to produce BFR containing materials, and this have been shown in a number of studies.

For example, Ota et al. (2009) found elevated levels of PBDD/Fs in emission gases and effluents from various industries in Japan producing or handling BFRs or BFR containing materials. This includes processing facilities for BFRs and production facilities for flame retarded plastics and textiles. The highest levels in exhaust gases were found at facilities producing flame retarded plastics, particularly from the extruder outlet (23 000 ng/m^3), and at processing facilities for BFR mixtures (8100 ng/m^3), while the highest effluent levels were found in process water from facilities producing or processing flame retardants (up to 1300 ng/L), or flame retarded plastics and textiles (up to 820 ng/L). The effluent levels can be compared with those found in municipal sewage treatment plants (STP) in Japan, in the same study, ranging between 0.11-13 ng/L in the incoming water and below the detection limit-1.4 ng/L in the outgoing water. The exhaust gas values may be compared with the levels found in stack gases from MSWI in Table 2 above, which are at least six orders of magnitude lower. However, in both cases it should be noted that the gas and water volumes in the STP and MSWI, respectively, are much larger, which will result in a dilution of the emissions. The comparison should therefore be done with care.

Similar levels as in Ota et al. (2009) were found by Sakai et al. (2005) when measuring the exhaust gas and waste water emissions from BFR production and textile processing plants in Japan. The largest emissions were found in the exhaust gases and effluents from the textile processing plants using decaBDE as flame retardant, while the emissions from similar plants using TBBPA or HBCD were lower. The study also showed that the levels in the river close to one of the textile processing plants were about 100 times higher downstream of the plant than upstream of the plant. In both this and the study by Ota et al. (2009), the PBDD/F emissions were strongly correlated with the PBDE emissions, supporting that they have a common source. In addition, the PBDD/F profiles were in both cases strongly dominated by PBDFs.

Furthermore, Tadami et al. (2008), found elevated PBDD/F-levels in ambient air, air deposition and ambient water close to facilities producing or handling BFRs. The levels in air and air deposition were 10-100 times higher than in background areas while the levels in ambient water were even more elevated, particularly in the vicinity of textile facilities using BFRs. Also Sedlak et al. (1998) found high levels of PBDD/Fs in chimney deposits from textile processing facilities using BFRs. From this it can be concluded that at least textile processing plants may constitute a significant source of PBDD/Fs to the environment.

There is no production of BFRs in Sweden, and the use of technical BFR mixtures is also relatively low. In 2010, about 40 tons of BFRs were used in the Swedish industry, which is a 10 times reduction since 2000 (KEMI 2015). There are, however, no data available regarding the emissions from these industries.

3.2.1 Occurrence in BFR mixtures and BFR treated products

Since the PBDD/Fs generated during the production and use of BFRs largely will end up in the technical BFR mixtures and the flame retarded products, these may constitute a source for further emissions. Again this is mainly valid for PBDE-mixtures and PBDE treated materials, but may occur for other BFRs as well.

Thus, Hanari et al. (2006) and Ren et al. (2011) reported the PBDD/F-levels in a number of PBDE-mixtures to range between 0.26-50 µg/g and 3.4-14 µg/g, respectively. The levels were highest in highly brominated decaBDE mixtures as compared to the less brominated octa- and pentaBDE mixtures. The PBDD/F-profiles were in all cases strongly dominated by PBDFs, i.e. octaBDF in the decaBDF mixtures, hexa-octaBDFs in the octaBDE-mixtures and tetra-pentaBDFs in the pentaBDE mixture. Based on the levels found in the mixtures and the global demand for PBDE agents in 2001, the annual distribution of PBDFs (from this source) were calculated in the two studies to be 430 and 2300 kg, respectively.

PBDD/Fs has also been found in BFR treated plastics and textiles, particularly in those where PBDEs have been used. The levels found in a number of TV- and computer screen (PC-CRT) casings, PC-boards and textiles are summarized in Table 5, and from this it can be concluded that the levels vary considerably. However, this is not surprising considering that the levels of PBDEs, which give rise to the PBDD/Fs, also vary considerably. Nevertheless, the PBDD/F levels sometime reach strikingly high values (up to 590 µg/g) indicating that PBDE plastics may constitute an important source for these compounds in the environment. In the study by Sindiku et al. (2015), it was estimated that in the 237 000 tons of TV and PC-CRT casings that are stockpiled in Nigeria (from which their samples was collected) the total amount of PBDD/Fs would range between 2-8 tons. Overall, PBDD/F levels in this study correlated well with the PBDE levels, so that the higher PBDD/F levels were found in plastics with high PBDE levels. In plastics treated with other BFRs, the PBDD/F levels were lower. Furthermore, the PBDFs dominated strongly over the PBDDs in all plastics with high PBDE levels. An interesting note was that many of the samples analyzed contained a mix of BFRs, indicating that these products had been produced from recycled plastics containing different kinds of BFRs with different amounts of accompanying PBDD/Fs. If this is true, PBDD/Fs may also be spread, via recycled plastics, to products that are not deliberately flame retarded. This is also noted in a report by Bibi et al. (2012).

When looking at all the studies in Table 5 together, it is also interesting to note that the proportion of PBDFs, in relation to the PBDEs, in most cases are significantly higher in the plastics than what have been reported for technical PBDE mixtures (see above). While the proportion in the technical mixtures ranged between 0.26-14 ppm, the proportion in the plastics frequently exceeded 1000 ppm. This supports the hypothesis that PBDD/Fs are being formed also when the BFR treated material is refined into products as well as during its use, recycling and destruction. In further support of this, Schlummer et al. (2007) and Lundstedt (2009) found higher proportions of PBDD/Fs, in relation to PBDEs, in fragmented WEEE plastics as compared to in samples from whole casings. In addition, Schlummer et al. (2007) found higher PBDD/F proportions in the smaller particle sizes of the fragmented plastics, indicating that more PBDD/Fs will be produced as the duration and impact of the shredder process is extended.

Table 5. *Levels of PBDD/Fs and PBDEs (µg/g) in casings of TVs and computer cathode ray tubes (PC-CRT), PC-boards, fragmented plastics and e-waste, as well as in a textile.*

	Σ PBDD/F (µg/g, dw)	Σ PBDE (µg/g dw)	Reference
TV-casings	100-510	36 000-91 000	Tamade et al. (2002); Tasaki et al. (2004)
TV-casing	590	18 000	Lundstedt (2009); Lundstedt et al. (2011)
TV-casing	5.3-5.6	780-1010	Ortuño et al. (2015)
TV-casings	0.00041-44	0.76-150 000	Takigami et al. (2008)
TV-casing	3.0	6300	Sakai et al. (2001)
TV-casing	23	110 000	Kajiwara et al. (2008)
TV and PC-CRT casings	0.021-350	630-306 000	Sindiku et al. (2015)
Fragmented casings	0.0030-0.035	4500-27 000	Schlummer et al. (2007)
PC-board	0.40	18	Lundstedt (2009); Lundstedt et al. (2011)
PC-boards	0.0018-1.4	2.4-22 000	Takigami et al. (2008)
PC-boards	4.3		Duan et al. (2011, 2012)
PC-board	130	11 000	Sakai et al. (2001)
Fragmented e-waste	1.3	38	Lundstedt (2009); Lundstedt et al. (2011)
Fragmented e-waste	0.0030-0.014	800-7400	Schlummer et al. (2007)
Fragmented plastics	0.38-2.0	52-121	Remberger et al. (2014)
Fragmented plastics	0.021-0.52	120-1300	Zennegg et al. (2014)
Textile	2.4	130 000	Kajiwara et al. (2013)

The actual emission of PBDD/Fs from products has not been investigated in any studies, but PBDD/Fs have indeed been found in high levels in indoor environment (see section 4.2.1 below), which indicates a certain emission from common products in our surrounding. Based on the data summarized here, it is no doubt that PBDD/Fs are present in many EEEs and textiles, but since PBDEs also have been found in various household products and cars (Chen et al. 2010; Kajiwara et al. 2011; Mandalakis et al. 2008) and even in children's toys (Chen et al. 2009), these may also constitute a source for PBDD/Fs. Although the usage of BFRs in Sweden have been relatively low over the years, the measurements performed by Lundstedt (2009); Lundstedt et al. (2011) and Ortuño et al. (2015) show that PBDD/Fs also are present in products in Sweden.

3.3 Emissions during recycling and destruction of BFR containing materials

3.3.1 Informal recycling activities

During recycling activities, such as dismantling, shredding, grinding, melting and molding, the PBDD/Fs trapped in the BFR treated products may be released to the environment along with the BFRs themselves. In addition, new PBDD/Fs may be formed from BFRs (from PBDEs in particular) during the actual recycling processes as discussed in section 2.2.3. This could be a problem at any recycling facility, but is of particular concern during the informal recycling activities carried out in countries such as Nigeria, Ghana, Vietnam, India and China. Informal e-waste recycling has been carried out in some of these countries for more than 20 years, and today there are cities that have become more or less dedicated to these activities, e.g. Guiyu and Taizhou in China (Duan et al. 2011, 2012; Yu et al. 2008). As a result, these sites and cities have become severely contaminated with a

multitude of contaminants, including dioxins and BFRs (Naturvårdsverket 2011; Sepulveda et al. 2010; Tue et al. 2013), and they are most likely also constituting a source for contaminants to the regional and global environment (Li et al. 2007; Zhang et al. 2012).

PBDD/F-emissions from e-waste sites have been investigated indirectly by sampling of various matrices in and around the sites. For example, Ma et al. (2008); Ma et al. (2009), measured PBDD/Fs, PCDD/Fs and PBDEs in e-waste shredder residues, workshop floor dust, soil and plant leaves from an e-waste recycling facility in Taizhou, China. Extremely high levels were found in soil (716-800 000 pg/g for Σ PBDD/Fs) and workshop floor dust (89 600-143 000 pg/g), much higher than the levels found in soil from a chemical-industrial complex (nd-427 pg/g), in the same study, and soil from urban, rural and agricultural areas in which no PBDD/Fs were detected (Table 7 in section 4.1.2). The PBDD/F levels in the e-waste shredder residues (392-18 500 pg/g) and leafs (113-818 pg/g) were somewhat lower, but still high. The TEQs calculated for PBDD/Fs were generally higher, and in some cases much higher, than the TEQs for PCDD/Fs. The PBDFs were found at much higher levels than the PBDDs, indicating that PBDEs and PBDE containing materials constituted the main source for the PBDD/Fs. Furthermore, the PBDD/F levels correlated strongly with the levels of both PBDEs and PCDD/Fs, suggesting that they were formed and released in the same processes.

Even higher soil levels of PBDD/Fs were found at an e-waste burning site and a PC-board smouldering site in Guiyu, China (Yu et al. 2008; Zennegg et al. 2009), (Table 7). The PBDD/F levels at these sites far exceeded those of the PCDD/Fs, even if these also were high. Besides this, mixed PBCDD/Fs were found in very high levels, which in fact exceed the highest levels measured for PBDD/Fs. Furthermore, the PBDD/Fs were found to be the most important contributor to the total dioxin-like toxicity measured by the DR-CALUX assay. Similar results were obtained by Ramu et al. (2008) when analyzing soil from informal e-waste recycling sites in Bangalore and Chennai, India (Table 7). Particularly high levels and TEQ contributions were found at a site where cable burning had been carried out.

The highly contaminated dust from the informal recycling processes, like the sample analyzed in Ma et al. (2009), may lead to extensive exposure of the recycling workers and the nearby inhabitants, especially since these usually are the same persons and since the activities are carried out in direct proximity to their homes; often in the backyards or even inside the houses. Tue et al. (2010) studied the occurrence of dioxin-like compounds, including PBDD/Fs, in settled house dust in an e-waste area in Vietnam and found just a bit lower levels (7700-63 000 pg/g for PBDD/Fs) than Ma et al. (2009) found in the workshop floor dust (89 600-143 000 pg/g), see also section 4.2.1. However, a perhaps unexpected conclusion of Tue et al. (2010) was that the PBDD/Fs in the dust were probably not a result of PBDE-transformation during the actual recycling process and neither originated directly from the plastic casings, but was more likely from dust inside the WEEE. The PBDF- and PBDE profiles of the e-waste dust were thus more similar to the profiles found in general house dust and dust inside EEE than the profiles in plastic casings and BFR-mixtures.

As mentioned above, the informal recycling activities may also lead to contamination on a regional and global scale. Thus, Li et al. (2007) and Zhang et al. (2012) found very high levels of PBDD/Fs in the air around Guiyu and Taizhou, respectively. In fact, the levels around Guiyu were the highest documented for these compounds in ambient air in the world. In both studies, evidences were found that the emissions from the recycling activities contributed significantly to the general contamination

in the surrounding environments. This was seen either as significantly elevated levels of PBDD/Fs, and other dioxins, or as distinct contaminant profiles that were similar to those at the e-waste sites but different form general urban profiles.

Activities similar to informal e-waste recycling may occur even in countries like Sweden. For example, illegal cable burning with the aim to recover copper appears to be a quite common activity (KEMI 2009), although performed in secret. However, the exact extent of these activities in Sweden is unknown, and there is no data available on the emission they are causing. Nevertheless, the actual burnings should lead to similar emissions irrespective of where they are performed, in Sweden or in China, and it is possible that they give a small but still significant contribution to the to the total PBDD/F load in Sweden.

3.3.2 Controlled recycling facilities

The emissions of PBDD/Fs from official recycling facilities have also been investigated in a few studies, although mainly in Japan and Sweden. Thus in Japan, Takigami et al. (2006) measured PBDD/Fs (and PBDEs) in air inside a dismantling hall of an e-waste recycling facility and found levels at 2400 pg/m^3. This is 2-3 orders of magnitude higher than the levels found in ambient air in Kyoto, Japan (Hayakawa et al. 2004) and almost six orders of magnitude higher than those found in Gothenburg, Sweden (Remberger et al. 2014), (Table 6, section 4.1.1). The air levels in the recycling plant were reduced ten times after a dust collector had been installed, but were obviously still high afterwards. The PBDD/F levels in the collected dust was extremely high, about 0.5 µg/g, which is even higher than the levels found in the workshop floor dust in Guyiu (Ma et al. 2009). Furthermore, Tamade et al. (2002) found high levels of PBDD/F in the exhaust gases from the molder (7500 pg/m^3 or 34 µg/h) and the incinerator (14 pg/m^3 or 0.7 µg/h) in another Japanese e-waste recycling plant, which for the incinerator are comparable to the levels found in exhaust gases from Taiwanese IWIs (Wang and Chang-Chien 2007), for instance. Finally, in a survey performed by Tadami et al. (2008) elevated levels of PBDD/Fs were found in air and water in the vicinity of various e-waste recycling facilities in Japan. Up to 50 pg/m^3 in air was measured, which almost reaches the levels found in Guiyu, and up to 100 pg/L in water, which is almost 10 times higher than the maximum levels found in the incoming water of Japanese sewage treatment plants (Ota et al. 2009).

In Sweden, the air levels measured in a recycling facility (Remberger et al. 2014) was lower (3.3-3.9 pg/m^3) than in the Japanese facility, but still much higher than in most outdoor environments. The PBDD/F levels found in dust from the Swedish facility was, on the other hand, similar or even higher (0.28-1.3 µg/g) than in the Japanese facility. This indicates that the emissions from recycling facilities mainly are connected to the dust they generate. However, it still need to be clarified where this contaminated dust originates from, i.e. whether it originates from the fragmentation processes used in the facilities or from the dust trapped inside the WEEE. The study by Takigami et al. (2006) indicates, like the previously cited study by Tue et al. (2010), that the dust inside the WEEE may be the main source. The contamination profile in the dust from the facility thus had greater resemblance with that in the dust trapped inside the WEEE than with that in the actual WEEE plastics.

There are no other studies available that have investigated the emissions of PBDD/Fs from Swedish recycling facilities, but there are some that have looked at PBDEs. Sjödin et al. (2001) compared the PBDE levels in air at a WEEE recycling facility, a PC-board factory, a computer repairing facility, various computer halls and an outdoor suburban environment, and found the highest levels in the recycling facility. Furthermore, Sjödin et al. (1999) found elevated levels of PBDEs in the blood of WEEE dismantling workers as compared to clerks working full-time in front of computer screens as well as to hospital cleaners. Although this doesn't say anything certain about the PBDD/F levels, it can be suspected that these compounds follow the PBDE levels rather well, considering how they are correlated in other situations. On the other hand, the PBDD/F levels and the PBDE levels in mother´s milk do not seem to correlate very well (Kotz et al. 2005), see section 4.2.2.

4 Occurrence of PBDD/Fs in the environment

As a result of the great number of sources, not least the diffuse ones, the PBDD/Fs are more or less ubiquitous in the environment today. Although the number of studies are limited and the data rather scattered the PBDD/Fs have been found in many different environmental compartments, including outdoor as well as indoor environments. In this chapter, the PBDD/F levels found in various environments are summarized and discussed.

4.1 Occurrence in the outdoor environment

4.1.1 Atmospheric levels

The levels of PBDD/Fs in the air have been measured in a number of studies, and often in combination with PCDD/F and PBDE measurements. The results from some of these studies are summarized in Table 6. Not surprisingly, the general trend is that the contaminant levels are higher in urban and industrial areas than in rural and remote areas. In addition, total PBDD/F levels are generally lower than the total PCDD/F levels. However, in some urban and industrial environments the levels are in the same range, and occasionally the PBDD/F- levels can be even higher, e.g. for some measurements in Kyoto and Taizhou (Hayakawa et al. 2004; Zhang et al. 2012). Still, the highest atmospheric PBDD/F-levels, besides the levels measured just outside an e-waste recycling facility in Japan (Tadami et al. 2008), have been measured in samples collected from areas were informal e-waste recycling is carried out, i.e. Guiyu and Taizhou in China (Li et al. 2007; Zhang et al. 2012), but at these places the PCDD/F levels are also very high. This suggests that both PBDD/Fs and PCDD/Fs are directly emitted from the recycling processes used at these places.

Relatively high atmospheric levels of PBDD/Fs have also been found in some Chinese and Taiwanese cities and industrial areas (Li et al. 2008; Li et al. 2011; Wang et al. 2008; M-S Wang et al. 2010), indicating that there is a diffuse emission of these compounds from such areas, probably both from incinerators and directly from products in the society. The strong dominance of PBDFs, over PBDDs, in all studies supports the theory that most PBDD/Fs in the atmosphere, even in remote areas, originate from BFR-containing materials. In some studies, the PBDD/F levels were also better correlated with the PBDE-levels than with the PCDD/F-levels, while the mixed PBCDD/Fs mainly correlate with the PCDD/Fs. This further supports that PBDD/Fs mainly are connected to PBDE handling, while PBCDD/Fs are formed in parallel to PCDD/Fs in incinerators (Hayakawa et al. 2004).

PBDD/Fs has also been found in air deposition samples in a few studies (Hayakawa et al. 2004; Remberger et al. 2014; Tadami et al. 2008), with the same overall trend, i.e. with lowest levels in remote areas, higher levels in urban areas and the highest in areas where BFRs or BFR containing material is handled.

The Swedish PBDD/F data that are available for air, i.e Råö and Gotheburg, show that the levels in rural areas are similar to those in rural areas in Asia, while the levels in Swedish urban areas are lower than urban areas in Asian. Surprisingly, the levels in the urban areas in Sweden were not significantly higher than in the rural areas (Remberger et al. 2014). Perhaps the air levels in Sweden are mainly affected by long range transport.

Table 6. *Levels of PBDD/Fs, PCDD/Fs and PBDEs in ambient air in various rural, urban and industrial environments. Both total levels and toxic equivalents (TEQs) are given for PCDD/Fs and PBDD/Fs.*

	Σ PBDD/F (pg/Nm^3)	Σ PBDD/F (fg TEQ/Nm^3)	Σ PCDD/F (pg/Nm^3)	Σ PCDD/F (fg TEQ/Nm^3)	Σ PBDE (pg/Nm^3)	Reference
Rural/Remote						
Various, China	0.0034-0.020		0.28-1.0			Wang et al. (2008)
Råö, Sweden	0.0072-0.69			0.23-31	0.49-9.8	Remberger et al. (2014)
Pallas, Finland	0.014-0.030			0.32-2.3	0.94-1.4	Remberger et al. (2014)
Guangzhou, China	0.057-0.39				110	Chen et al. (2006); Li et al. (2011)
Urban						
Gothenburg, Sweden	0.0025-0.086			0.10-23	2.9-9.2	Remberger et al. (2014)
Varoius, China	0.015-0.030		0.57-1.5			Wang et al. (2008)
Sci.park, China	0.058-0.13		0.55-0.71			Wang et al. (2008)
Shanghai, China	0.70-1.4		3.3-8.0			Li et al. (2008)
Guangzhou, China	0.14-1.7		3.6-9.9		88	Chen et al. (2006); Li et al. (2011)
Kyoto, Japan	1.8-12		1.2-7.8		4400-80000	Hayakawa et al. (2004)
Taizhou, China	3.5-81	13-310	1.5-28	51-350	41-160	Zhang et al. (2012)
Guiyu, China (e-waste site)	8.1-61		65-2400			Li et al. (2007)
Taizhou, China (e-waste)	37-155	96-690	11-80	361-910	160-540	Zhang et al. (2012)
Industrial						
Lin-hai, China	0.028-0.058		1.1-2.7			Wang et al. (2008)
Guangzhou, China	0.42-4.2		3.6-9.9		230-3700	Chen et al. (2006); Li et al. (2011)
Close to MSWI, Taiwan	0.42		0.58		52	M-S Wang et al. (2010)
Close to BFR-fac. Japan	10-1000					Tadami et al. (2008)
Air dismantling hall	2400				510 000	Takigami et al. (2006)

4.1.2 Levels in soils and sediments

There are a number of studies available in which PBDD/Fs have been analyzed in soils and sediments (Table 7). Most studies are from China, Japan and Taiwan, but there are also a few from Sweden. As mentioned in section 3.3.1, the highest soil levels have been found in areas where e-waste is recycled under rudimentary conditions, with peak levels in soil at open burning sites in the "e-waste city" Guiyu, China (Yu et al. 2008; Zennegg et al. 2009). However, high PBDD/F levels in soil have also been found in connection to more developed and controlled e-waste and plastics recycling facilities, after they have been subject to accidental fires. In fact, after one such fire in Sweden, PBDD/F levels in the same range as those found in Guiyu were measured in one hotspot outside then burnt down e-waste facility, even 2.5 years after the fire (Lundstedt 2012). In urbans soils, the PBDD/F levels are generally lower, although higher than those found in rural and agricultural areas. In most samples, the PBDFs were much more abundant than the PBDDs, indicating that the contamination mainly originates from

PBDE agents. However, in some occasional samples the PBDD-levels may be as high or even dominate over PBDFs, which indicate that there might be other bromine sources present or that the PBDD/Fs have been formed via other mechanisms, e.g. from smaller precursors and *de novo* synthesis. The PBDD/F levels in the soils correlate fairly well with the PBDE levels, which further supports that they have similar origin. However, the PBDD/F levels correlate quite well with the PCDD/F levels as well, which tells us that the processes that emits large amounts of PBDD/Fs generally emits large amounts of PCDD/Fs as well, although the starting materials may be different.

PBDD/Fs have also been found in sediments, both in the fresh water and in marine environments. The levels are generally in the same ranges for the two environments but may be elevated due to the influence of various local sources. In a study by Hagberg et al. (2005a), no clear differences was seen between the PBDD/F levels in a rural and an urban lake, while slightly higher levels were seen in an urban stream as compared to a rural lake in a study by Lundstedt (2012). In the latter study, somewhat further elevated levels were found in the sediment outside the burnt down e-waste recycling facility mentioned earlier in this section, and also in the sediments from a pond and a stream affected by a fire in a plastics recycling facility. Also in coastal sediments investigated, the differences between urban and rural environments were not dramatic. Significantly lower levels have been observed in rural areas (Takigami et al. 2005; Terauchi et al. 2009), as well as occasional peaks in sediments in the vicinity of local sources, e.g. metal smelters that use e-waste as one of its feed stocks (Dang 2009). However, overall the levels in the sediments show a quite poor correlation with the proximity to cities and industries, at least when only total levels are considered. On the other hand, in the study by Dang (2009) it was observed that, although the PBDD/F levels also may be high in rural areas, the profiles are usually different from those in urban areas. In the rural areas, the low brominated PBDDs usually dominate while in the urban and industrial areas the highly brominated PBDFs usually dominate. This is most likely because the PBDFs originate from PBDEs and other BFRs, while the PBDDs mainly originate from natural production described above. In some sediment samples we probably see a combination of these sources, resulting in similar levels of PBDDs (mainly low brominated) and PBDFs (mainly high brominated) (Ohta et al. 2002; Terauchi et al. 2009).

In the studies by Choi et al. (2003a), Takigami et al. (2005) and Dang (2009) cores of sediment from Japan and Sweden were also collected. These showed that the PBDD/F levels in the sediments decreased quite drastically with the depth saying that the PBDD/Fs emission increased between the late 1960s to the mid-1990s, which correlate fairly well with the usage of PBDEs, with some delay. Takigami et al. (2005) noted that it was mainly the PBDF levels that increased during this period while the PBDD-levels remained stable. This further supports the hypothesis that the PBDFs in sediments mainly originates from anthropogenic activities and PBDEs while the PBDDs mainly originates from natural formation.

In general, PBDD/F-levels in sediments are lower than PCDD/F levels, which most likely is because the PCDD/F sources still are more widely spread than the PBDD/F sources in our society and environment. However, close to obvious PBDE/PBDF sources and places where the natural production of PBDDs is high the situation can be the reverse (Dang 2009; Lundstedt 2012).

Overall, the PBDD/F levels in rural and urban soils and sediments seem to be similar in Sweden and the Asian countries for which data is available. Sweden may, like the Asian countries, have hot spots with very high PBDD/F levels. However, these hot spots are most likely much smaller than the hot spots in China that may be composed of whole cities that are engaged in informal e-waste recycling.

Table 7. *Total levels of PBDD/Fs, PCDD/Fs and PBDEs in soil and sediments in various environments.*

	Σ PBDD/F (ng/g, dw)	Σ PCDD/F (ng/g, dw)	Σ PBDE (ng/g dw)	Reference
Rural Soil				
Agricultural, China	nd.	0.0034-0.46	0.08-0.79	Ma et al. (2008); Ma et al. (2009)
Lanna, Sweden	0.028-0.054	0.0052-0.068	0.065-1.3	Lundstedt (2012)
Urban soil				
Umeå and Norrköp., Sweden	0.0011-0.22	0.0092-0.97	0.18-66	Lundstedt (2012)
Bangalore and Chennai, India	0.0060-0.31	0.045-1.4		Ramu et al. (2008)
Kyoto, Japan	0.28	0.54		Hayakawa et al. (2004)
Industr. area, China	nd.-0.43	0.045-0.71	2.03-269	Ma et al. (2008); Ma et al. (2009)
Industr., Thailand	0.019-0.16	0.40-1.0	1.8-13	Naturvårdsverket (2011)
Dump site, Peru	0.0086-0.32	0.031-1.3	3.6-92	Naturvårdsverket (2011)
Soil from e-waste areas				
Taizhou, China	0.19-0.44	1.4-6.6		Wang et al. (2009)
Taizhou, China	0.72-800	0.85-10.2	72-5710	Ma et al. (2008); Ma et al. (2009)
Guiyu, China	100-2500	0.21-13.9[a]		Yu et al. (2008)
Guiyu, China	1400-3900	6.0-800	36 200-44 400	Zennegg et al. (2009)
Bangalore and Chennai, India	0.27-290	0.22-170		Ramu et al. (2008)
Soil from recycling plant fires				
Ontario, Canada	8.6-180			Myers et al. (2012)
Norrköping, Sweden	0.085-1300	0.65-16	0.71-5100	Lundstedt (2012)
Lanna, Sweden	0.37-6.7	0.0096-0.64	0.42-34	Lundstedt (2012)
Eksjö, Sweden (dump site)	5.7-67	1.9-71	39-29 000	Lundstedt (2009)
Fresh water sed.				
Rural/urban lakes, Sweden	0.44-0.54	0.97-2.4		Hagberg et al. (2005a)
Rural lake Sweden	0.082-0.085	1.3-1.9	4.4-16	Lundstedt (2012)
Urban lake, China	0.00048-0.0057	0.056-0.35		Zhou et al. (2012)
Urban river, Sweden	0.41-1.7	0.31-2.0	29-62	Lundstedt (2012)
Pond and stream, Sweden (fire affec)	0.061-8.7	0.013-2.1	0.73-150	Lundstedt (2012)
Stream at dump site, Peru	0.012-0.074	0.021-0.17	3.7-6.1	Naturvårdsverket (2011)
Lake, industr. area Thailand	0.037-1.5	0.27-180	3.4-58	Naturvårdsverket (2011)
Marine sediments				
Coastal, Hong Kong/Korea	nd.-0.46	0.23-6.3		Terauchi et al. (2009)
Cores, Tokyo Bay, Japan	0.0052-0.070	0.55-36	10-78050	Choi et al. (2003a)
Coastal, Osaka, Japan	0.0041-0.077	1.98-17.4	8.0-352	Ohta et al. (2002)
Coastal, Osaka, Japan – also cores	0.0024-0.59	0.50-12	53-910	Takigami et al. (2005)
Coastal and offshore, Sweden	0.050-10			Dang (2009)

nd = not detected, [a]ng TEQ/g

4.1.3 Sewage water, sewage sludge and storm water sludge

In a recent screening of PBDD/Fs in the Sweden, performed by the Swedish Environmental Institute (IVL) (Remberger et al. 2014), samples of water and sludge from two STPs (Gothenburg and Borås) were included, as were three samples of storm water sludge from Gothenburg. The incoming sewage water showed levels (0.18-0.26 ng/L) in the same range (although in the lower end) as those previously found in various Japanese STPs (0.11-13 ng/L), (Ota et al. 2009). However, unlike these, the Swedish STPs showed similar PBDD/F-levels in the outgoing water (0.17-0.26 ng/L) as in the incoming water, which would suggest that the Swedish STPs are inefficient in removing PBDD/Fs. This is surprising considering that PBDD/Fs in sewage water mainly should be adsorbed to the suspended particles, which normally are efficiently removed in the treatment process. However, the results may also reflect the large variability among these kinds of data, as well as the fact that the Swedish data in this case only was based on four samples (two incoming and two outgoing).

The PBDD/F-levels found in the sewage sludge ranged between 0.33-0.53 ng/g d.w., which would imply that about half of the PBDD/Fs in the sewage water were removed with the sludge if the measurements above for the incoming water (0.18-0.26 ng/L) are representative. This estimation is based on the fact that sewage water contains approximately 0.2 g particles/L (Olofsson 2012), resulting in 0.066-0.11 ng particle bound PBDD/Fs per L, which corresponds to a significant fraction of the levels found in the incoming water. Still the outgoing water showed similar levels. This further shows that the variability among these kinds of data is large, and that more data is needed to elucidate the removal efficiencies for PBDD/Fs in Swedish STPs.

The PBDD/F levels found in the storm water sludge (0.14-0.40 ng/g d.w.) were similar to those found in the sewage sludge, and for both matrices they were in the high end of the levels found in surface sediments of Swedish lakes for instance (Table 7, section 4.1.2) (Hagberg et al. 2005a; Lundstedt 2012). For comparison, the total PBDE levels in one of the storm water sludge samples was 360 ng/g, which is much higher than in Swedish lake sediments (Lundstedt 2012). As in most other studies, the PBDF levels dominated strongly over the PBDD levels in all sludge and sewage water samples.

4.1.4 Occurrence in biota, food and feed

PBDD/Fs have not been studied in biota, food and feed samples to a large extent, but there are at least some data to be found. The results are not always easy to compare since they are given as total levels in some studies and as total TEQs in other. In addition, in some cases the concentrations are given based on wet weight of the sample while in some cases it is based on the fat content. Nevertheless, in Table 8 the results for a number of fish and food samples are summarized. Here the results have been calculated as TEQs using the TEFs established for PCDD/Fs according to the recommendations by van den Berg et al. (2013). Apart from the studies in Table 8, PBDD/Fs have also been found in samples of mixed food from Japan (Nomura et al. 2007), seafood from China (Miyake et al. 2008), cormorant liver and eggs and fish from China (Watanabe et al. 2003), fish and shellfish from Sweden (Haglund et al. 2007; Malmvärn et al. 2005), red algae, cyanobacteria and aquatic sponge from Sweden (Malmvärn et al. 2008; Unger et al. 2009) earthworms from an e-waste

site in China (Wang et al. 2009) and the feed additive choline chloride in the Netherlands (Traag et al. 2009).

Not surprisingly, the highest PBDD/F levels are found in fat rich samples such as fatty fish, mussels, eggs, liver and carcass fat. However, for marine samples the levels seem to be even more influenced by where the samples have been collected. Fish and shellfish thus seem to be highly influenced by local sources, with natural sources giving rise to the largest variations (Haglund et al. 2007). Haglund et al. (2007) thus found highly varying levels in fish and shellfish along the Swedish coastline, and the variation seemed to be connected to factors such as depth, temperature, nutrient status and sunshine penetration of the waters, which have a direct influence on the natural production of PBDDs. The highest levels were found in species from the littoral zone, such as mussels, perch and eel, as compared to pelagic fish such as herring. In these samples the PBDDs dominated completely over PBDFs. However, in most other food, feed and biota samples, including marine samples at places where the PBDD production is lower, the PBDFs strongly dominate over the PBDDs, which indicate that the contamination originates from BFRs from local or regional sources. Such sources may of course also give rise to spatial variations. For example, Ashizuka et al. (2008) detected PBDD/Fs, with a dominance of PBDFs, in several fish species in one region of Japan but not in any fish species from two other regions of Japan. The difference was suggested to be due to a local BFR-related source in the first region.

Fernandes et al. (2008); Fernandes et al. (2009a) also found varying levels of PBDD/Fs in shellfish from Scotland. The levels correlated quite well with the distance to industrial areas with lower levels at remote areas. In most cases the profiles were dominated by PBDFs, but in some cases very high levels of 237-TriBDD (up to 15 pg/g w.w.) were found (Fernandes et al. 2009a), especially in native oysters. These results indicate that the contamination was originated from a combination of anthropogenic and natural sources. Similar levels of PBDDs and PBDFs were also found by Miyake et al. (2008) when analyzing various fish and shellfish from China, indicating a combination of sources.

Generally, the PBDD/F levels seem to be lower than the PCDD/F levels in food and biota samples and much lower than the PBDE levels, but there are exceptions. In environments strongly affected by BFRs, the PBDD/F levels (PBDF) may thus be in the same range or even exceed those of PCDD/Fs (Naturvårdsverket 2011). In addition, in marine environments with high PBDD production, the PBDD/F levels (PBDD) may be much higher than the PCDD/F levels (Haglund et al. 2007; Malmvärn et al. 2008; Unger et al. 2009). The PBDD/Fs may also contribute significantly to the total TEQs. This has been noted by Fernandes et al. (2009a); Fernandes et al. (2009b); Haglund et al. (2007); Haglund et al. (2014) as being a cause of concern since some food products (mainly fish and seafood) already contain close to acceptable levels of other dioxin-like compounds.

Also mixed PBCDD/Fs have been found in various food products and these are most likely further contributing to the total dioxin-like toxicity (Fernandes et al. 2011; Fernandes et al. 2014). However, in this case it is probable that only a “tip of the iceberg” has been investigated so far, since the PBCDD/Fs are composed of so many individual congeners of which only a few have been studied.

It is difficult to compare the PBDD/F levels found in Swedish biota and food samples with those found in other countries since the data overall is so scattered. However, the levels found in fish seem to be at similar levels in Sweden as in other places, at least when samples that are highly affected by

natural formation (high in PBDDs) are excluded. When these are included, Sweden show some extremely elevated levels with up to 170 ng/g in mussels (Malmvärn et al. 2005), but it is possible that similar levels are found in coastal waters in other places of the world. However, this has not been investigated.

Table 8. *Levels of PBDD/Fs, PCDD/Fs and PBDEs in various fish and food samples. The levels are based on wet weight (fresh sample) or fat weight. The PBDD/F and PCDD/F levels are given as toxic equivalents (TEQs), while the PBDE levels are given as total levels.*

	Σ PBDD/F (pg TEQ/g, ww)	**Σ PCDD/F (pg TEQ/g, ww)**	**Σ PBDE (ng/g, ww)**	**Reference**
Various fish species, Japan	0.001-0.256		0.01-2.88	Ashizuka et al. (2008)
Various fish spec., Sweden	0.023-0.18	0.39-6.5		Haglund et al. (2014)
Various fish, UK	0.030-0.051	0.037-26.32	11-130	Rose et al. (2015)
Fish, Thailand	0.013-0.031	1.0-5.3	0.42-1.0	Naturvårdsverket (2011)
Shellfish, Scotland	0.022-0.23	0.09-0.45	0.12-2.74	Fernandes et al. (2008)
Shellfish, Scotland	0.01-0.23		0.04-3.2	Fernandes et al. (2009a)
Meat, Sweden	0.024	0.049		Haglund et al. (2014)
Dairy prod., Sweden	0.0055	0.050		Haglund et al. (2014)
Plants, Peru	0.0021-0.13	0.33-5.2	0.30-14	Naturvårdsverket (2011)
Milk	0.091-0.30[a]		0.31-3.1[a]	Fernandes et al. (2009b)
Egg	0.24-0.42[a]		0.87-4.4[a]	Fernandes et al. (2009b)
Carcass fat	0.15-0.38[a]		0.46-25[a]	Fernandes et al. (2009b)
liver	0.18-3.5[a]		0.75-37[a]	Fernandes et al. (2009b)
Egg, dump site, Peru	0.19-0.37[a]	0.12-4.4[a]	56-150[a]	Naturvårdsverket (2011)

[a]pg TEQ/g fat

4.2 PBDD/F is indoor environments and humans

4.2.1 PBDD/Fs in house dust

In indoor environments, PBDD/Fs have mainly been studied in dust. Most studies are from Japan but there are also some from Vietnam, USA, China and Sweden (Table 9). The levels found in dust from residential houses vary over more than two orders of magnitude but are at least within similar ranges in all studies. The occasionally higher levels found in some residential houses have in most cases been difficult to relate to specific sources, e.g. 69 ng/g in Kono et al. (2007) and 150 ng/g in Tue et al. (2013), although the 53 ng/g found in a Swedish samples was assumed to be because it had been collected in an office room loaded with EEE (Remberger et al. 2014).

The levels found in the dust from more public buildings, like hotels, offices, conference centers and schools, show similar ranges as those from residential houses, but shifted towards somewhat higher average levels for hotels and offices, at least if samples from the same studies are compared. Similarly, residential house dust from an e-waste recycling site in Vietnam showed higher average PBDD/F levels than dust from houses in a general urban Vietnamese environment, analyzed in the

same study (Tue et al. 2010). Even higher average PBDD/F levels was found in workshop floor dust collected at an e-waste recycling site in Taizhou, China as mentioned in section 3.3.1 (Ma et al. 2009). However, the maximum levels found in that study where still not higher than the maximum levels found in a residential house in USA (Tue et al. 2013), which emphasizes the large variation in the data overall.

Table 9. *Levels of PBDD/Fs, PCDD/Fs and PBDEs in ambient air in various rural, urban and industrial environments. Both total levels and toxic equivalents (TEQs) are given for PCDD/Fs and PBDD/Fs.*

	Σ PBDD/F (ng/g)	Σ PBDD/F (pg TEQ/g)	Σ PCDD/F (ng/g)	Σ PCDD/F (pg TEQ/g)	Σ PBDE (µg/g)	Reference
House dust, Japan	0.61-7.7				0.14-3.0	Suzuki et al. (2006)
House dust, Japan	0.84-69		0.36-27		0.13-8.1	Kono et al. (2007)
House dust, Japan	0.68-1.5		0.45-0.55	0.60-0.91	0.24-0.73	Takigami et al. (2009b)
House dust, Japan	1.1-12	1.8-87[a]	0.70-11	7.4-400[a]		Suzuki et al. (2010)
House dust, Vietnam	1.5-2.3		0.51-0.60			Tue et al. (2010)
House dust, USA	0.33-150	nd.-270	0.12-80	0.086-170		Tue et al. (2013)
House dust, Sweden	2.7-53	21-160		7.3-860	0.12-0.27	Remberger et al. (2014)
Hotel dust, Japan	0.74-6.3				0.0098-1.7	Takigami et al. (2009a)
Office dust, Japan	1.1-8.8				0.26-20	Suzuki et al. (2006)
Office dust, Japan	1.6-31	1.8-87[a]	0.53-19	7.4-400[a]		Suzuki et al. (2010)
Publ. Dust, Sweden	3.5-130	23-900		7.9-84	0.49-720	Remberger et al. (2014)
House dust, EWRS, Vietnam	7.7-63		1.1-4.5			Tue et al. (2010)
Workshop dust, EWRS, China	90-143	945-2020	2.6-150	1070	6.3-82	Ma et al. (2009)
Dust, recycling plant, Japan	~500				~400	Takigami et al. (2006)
Dust, recycling plant, Sweden	280-1300					Remberger et al. (2014)
TV dust, Japan	~500				~1200	Takigami et al. (2006)
TV dust, Japan	180-650	880-2600		160-340	67-560	Takigami et al. (2008)
TV dust, Japan	2100-8500				160-320	Tamade et al. (2002)
Dust from new car, Sweden	3800	14000		0.30	3600	Remberger et al. (2014)

nd = not detected, [a]based on the CALUX assay, the range include all samples from Suzuki et al. (2010)

Despite the lack of correlation, the variation in the PBDD/F levels is probably connected to the presence of potential emission sources in the houses. The sources may be various flame retarded materials such as EEE, furniture, textiles and construction materials, of which EEE is suspected to be one of the more important ones. This is supported by the very high PBDD/F levels found in dust from

recycling plants for WEEE (Remberger et al. 2014; Takigami et al. 2006), and dust from the interior of TV-sets (Takigami et al. 2006; Takigami et al. 2008; Tamade et al. 2002). As discussed above, there are indications that most of the PBDD/Fs that find their way from EEE to the indoor environment (even in recycling plants), are transferred via the dust that is temporarily trapped on and inside the EEE, and is not mainly due to plastic particles that have been teared of and released during a fragmentation process for instance (Takigami et al. 2006; Tue et al. 2010). One such indications is based on the observation that the PBDF/PBDE ratio generally seem to be higher in house dust and dust inside EEE than in the actual plastic of the same equipment (Tamade et al. 2002; Tue et al. 2010). This also suggests that PBDEs are further transformed into PBDFs during and after the migration to the dust.

Very high PBDD/F levels were also found in dust from a new car in Sweden (Remberger et al. 2014), although the PBDF/PBDE ratio in this case was somewhat lower than in house dust. The latter may be due to different sources in cars and houses, i.e. a higher proportion of flame retarded textiles in cars. Nevertheless, in dust samples overall the PBDF levels are strongly correlated with the PBDE levels, which further supports the assumption that the PBDFs and PBDEs originate from the same sources (Kono et al. 2007; Suzuki et al. 2010). In most dust samples the PBDD/F profile is also completely dominated by PBDFs

Many of the studies in Table 9 also show that the PBDD/F levels in dust usually are higher than the PCDD/F levels, and that the PBDD/Fs often contribute significantly to the dioxin-like toxicity in the dust (Suzuki et al. 2010; Tue et al. 2010; Tue et al. 2013). This demonstrates the abundance of PBDD/F sources in our indoor environment, and emphasizes the importance to reduce these sources.

PBDD/Fs have also been analyzed in samples of indoor air in a few studies, but have only rarely been detected in this matrix, apart from in the recycling facilities mentioned in section 3.3.2. Takigami et al. (2009b) thus found 0.10 pg TetraBDD/m^3 in the air of one room in one house, while in other rooms and other houses all levels were below the detection limit. In another study the same group failed to detect any PBDD/Fs in indoor air from a hotel (Takigami et al. 2009a). Finally, Mandalakis et al. (2008) detected HeptaBDFs in one out of 41 air samples from 33 cars in Greece. They determined the total level of the HeptaBDFs in this sample to 61 pg/m^3, which in fact is quite high considering that the levels in a Swedish e-waste recycling facility were 3.3-3.9 pg/m^3 (Remberger et al. 2014) and the levels in outdoor air usually are below (and often much below) 1 pg/m^3 (Table 6, section 4.1.1)

4.2.2 PBDD/Fs in humans

When it comes to humans, PBDD/Fs have been detected in human milk samples from several countries. Kotz et al. (2005) thus provide human milk data for 17 different countries, and additional data for Japan, Ireland, Belgium, Vietnam and Sweden have been provided by other studies (Table 10). All measured levels are in the same range, i.e. 0.04-1.2 pg TEQ/g lipid, also including samples from women in an e-waste area in Vietnam, which is notable (Tue et al. 2013). What is also notable is that the PBDD/F-levels in breast milk from USA also fall within this range, despite having PBDE levels that are 35-500 times higher than in samples from other countries (Kotz et al. 2005). This indicates that the uptake and/or half-life of PBDD/Fs in the human body are different from that of PBDEs, or that the PBDD/Fs mainly originate from other sources than PBDE containing material.

In many of the milk samples, the tetra and pentaBDFs dominate the PBDD/F profiles (Croes et al. 2013; Kotz et al. 2005; Tue et al. 2013). This is different from most dust samples in which more highly brominated PBDFs, i.e. hexa-heptaBDFs, dominate. This supports the theory that the uptake and accumulation in the human body is somewhat selective, considering that indoor dust probably constitutes an important PBDD/F source for humans (Lorber 2008). However, the highly brominated PBDFs are still taken up by humans to some extent, and the levels and profiles found in human milk are therefore also depending on the PBDD/F mixtures that humans are exposed to. As a consequence, in some cases the highly brominated PBDFs dominate also in milk samples (Haglund et al. 2014; Pratt et al. 2013). It should be noted though that in many cases only a few congeners of PBDD/Fs have been detected, which of course could be due to very low levels in the samples, but in some cases also to limitations in the analytical methods used. This has been pointed out in many studies. Overall, however, the PBDD/F levels in mother's milk seem to be low in relation to the PCDD/F- levels, which also is true for their TEQ contributions.

The PBDD/Fs seem to be eliminated from the breast milk in the same way as other persistent organic pollutants (POPs), i.e. through lactation and breastfeeding. Ohta et al. (2004) thus found significantly higher levels of both PBDD/Fs and PBDEs in the milk of first-time mothers (primiparae), than in the milk of mothers who have given birth to more than one child (multiparae). This means that infants may be exposed to significant amounts of PBDD/Fs via the breast milk.

PBDD/Fs have also been analyzed in samples of human adipose tissue, although only in Sweden (Ericson et al. 2008; Ericson Jogsten et al. 2010; Hagberg et al. 2011) and Japan (Choi et al. 2002; Choi et al. 2003b). On the other hand, the contaminants have been detected in all samples analyzed, confirming their widespread presence in humans and the environment. The levels seem to be somewhat higher in Japan than in Sweden, but the difference is not large. Surprisingly, the levels in Japan have not changed significantly from 1970 to 2000, at least not when the absolute levels are considered. However, in relation to the PCDD/F levels, which have decreased since the 1970s, the PBDD/F levels have increased. The absolute levels of PBDE have increased significantly during the same period (Choi et al. 2003b). In all samples of adipose tissue the PBDFs dominate the congener profile and often the 2378-tetraBDF, 12378-pentaBDF and 23478-pentaBDF seem to be the dominating congeners, further supporting the theory of a selective uptake. However, in some cases also 27/28-diBDF, 123478-hexaBDF and 1234678-heptaBDF have been detected. In the study by Ericson Jogsten et al. (2010) it was shown that the PBDD/Fs contributed with 1-15% of the total TEQ, which must be considered as a significant fraction.

PBDD/Fs, again dominated by 2378-tetraBDF, 12378-pentaBDF and 23478-pentaBDF, have also been measured in blood serum of fire fighters from San Francisco, USA (Shaw et al. 2013). Although, the PBDD/Fs were only detected in two out of twelve fire fighters the levels must be considered high. The PBDD/F levels were much higher than the PCDD/F levels in those fire fighters and dominated the contribution to the total TEQs.

Table 10. *Levels of PBDD/Fs, PCDD/Fs and PBDEs in human samples including, mother's milk, blood serum and adipose tissue. The levels are mainly based on fat weight but in some cases on wet weight (fresh sample), indicated by an asterisk. Furthermore, the PBDD/F and PCDD/F levels are both given as total levels and as toxic equivalents (TEQs), while the PBDE levels are given only as total levels.*

	Σ PBDD/F (pg /g, fat)	**Σ PBDD/F (pg TEQ/g, fat)**	**Σ PCDD/F (pg/g, fat)**	**Σ PCDD/F (pg TEQ/g, fat)**	**Σ PBDE (pg/g, fat)**	**Reference**
Mother's milk, 17 countries		0.04-0.63		4-19	0.70-370	Kotz et al. (2005)
Mother's milk, Japan	25-500	0.13-1.2	130-2300	4.1-21	2-13	Ohta et al. (2004)
Mother's milk, Ireland	1.4-6	0.58-1.2		6.32 (mean)	2.7-9.4	Pratt et al. (2013)
Mother's milk, Belgium		0.67		10.3	2.0	Colles et al. (2008)
Mother's milk, Flanders, Belgium		0.34		6.9		Croes et al. (2013)
Mother's milk, Vietnam, e-waste	nd.-1.5	nd.-0.2	1.1-117	0.22-5.9		Tue et al. (2013)
Mother's milk, Sweden		0.0036[a]		0.12[a]		Haglund et al. (2014)
Blood serum, fire fighters, USA	nd.-2778	nd.-732	183-856	1-11	48-442	Shaw et al. (2013)
Adipose tissue, Sweden	0.41-3.67	0.11-1.81		1.79-31.5	1.16-7.46	Ericson Jogsten et al. (2010)
Adipose tissue, Sweden	0.33-3.9					Hagberg et al. (2011)
Adipose tissue, Sweden	0.12-2.24					Ericson et al. (2008)
Adipose tissue, Tokyo, Japan	1.9-8.3				0.0068-2.75	Choi et al. (2002); Choi et al. (2003b)

[a]based on wet weight

5 Potential PBDD/F-emissions from materials and products in the Swedish society

The data presented in this report suggests that most PBDD/Fs we are exposed to, apart from the naturally produced PBDDs, originate from all the BFR treated materials we have in our society, and particularly those that are treated with PBDEs. As a consequence it would be interesting to estimate how much PBDD/Fs that potentially could be emitted from these materials, both when it comes to PBDD/Fs that already are present in the materials as impurities, and the PBDD/Fs that may be formed as the materials are subject to various processes. In this chapter an attempt is made to make such estimation.

5.1 PBDD/Fs in BFR mixtures

No BFRs are produced in Sweden but some are imported as raw material for the industry. In 2000 the imported amount reached 570 tons, while it had decreased to 41 tons in 2010 (KEMI 2015). The proportion of PBDEs (responsible for the majority of the PBDD/F emission) among these imported BFRs has also decrease during the same period, from 16 % in 2000 to more or less 0 % in 2010, and today the imported BFRs are mainly composed of TBBPA and various “new” BFRs such as decabromodiphenyl ethane (DBDPE) and pentabromoethylbenzene (PBEB) (KEMI 2015; Remberger et al. 2014). Consequently, the amount of PBDD/Fs accompanying BFRs in imported technical mixtures is probably fairly small today. While the PBDD/F levels in PBDE mixtures can reach 50 µg/g (Hanari et al. 2006), the levels in other BFR mixtures seldom exceeds 10 ng/g (WHO 1998). Hence, even if 10 ng/g is used as an estimate, the total amount of PBDD/Fs in the BFR mixtures imported to Sweden today would be less than 0.5 g/year. Furthermore, some of these PBDD/Fs are exported with products produced in Sweden (KEMI 2015).

5.2 PBDD/Fs in materials and products

A larger problem is all PBDD/Fs that are imported to Sweden in BFR treated products, such as EEE, vehicles and construction materials (e.g. insulation, plastics tubings, electrical switches, cables etc.). Although the exact extent of this import is difficult to estimate, since many products (not least EEE) consists of a large number of smaller components originating from many different producers, tentative estimations can still be done. Thus, KEMI (2009) has estimated that 700-800 tons of PBDEs where imported to Sweden in products during 2001, and that the amounts were 400 tons/year ten years earlier. However, after 2002 when the first version of the RoHS directive (EU 2011) came into force, which limits the use of hazardous compounds in EEE, the amounts have most likely decreased steadily, and in 2010 it was estimated to be around 170 tons in total (Bibi et al. 2012). Today it is probably even lower.

The PBDD/F amounts in these PBDE treated products can be estimated by using an average PBDD/F-PBDE ratio of 0.5 %. As discussed in section 3.2.1, the PBDD/F - PBDE ratio in products are usually significantly higher than it is in technical PBDE mixtures. Although the ratio may vary a lot, the data in Table 5 suggests that 0.5 % would be a reasonable average. This would imply that in 2010 around

0.8 tons of PBDD/Fs were accompanying products that were imported to Sweden during that year. In the early 2000, the corresponding number would be 3-4 tons/year, while today it is probably much lower.

PBDD/Fs may also accompany products that are treated with other BFRs than PBDEs, but this is most likely of less concern. The products treated with such BFRs can be assumed to contain similar PBDD/F-BFR-ratios as the BFR mixtures they have been treated with, due to lower PBDD/F conversion rates for these non-PBDE-BFRs (WHO 1998). In addition, as discussed above, these BFR-mixtures contain much less PBDD/Fs from the beginning as compared to the technical PBDE-mixtures. It can therefore be assumed that products treated with TBBPA, HBCD etc. have an average PBDD/F content of 10 ng/g BFR. This would imply that in the 1100 tons of TBBPA and 13 tons of HBCD that were imported to Sweden in products during 2010 (Bibi et al. 2012; KEMI 2015), there were only about 10 g of PBDD/F in total. This is negligible in comparison to the PBDD/F amounts in the PBDE treated products. On the other hand, these non-PBDE-BFRs are growing in importance as the PBDEs are phased out. In addition, some of the new BFRs, e.g. tetrabromophenoxyethane (TBPE), have been suggested to contain more PBDD/Fs than TBBPA and HBCD (Riess et al. 2000; Sindiku et al. 2015), which until now have constituted the main replacement products for PBDEs.

Even more difficult is it to estimate the PBDD/F amounts present in products and materials we already have in our society. Besides the uncertainty about which products and materials that actually contain BFRs as well as what type and levels of BFRs they contain, there is also a large variation and uncertainty regarding the products estimated lifetime, i.e. for how long they are present in our society. EEE is known to have a lifetime of about 5-10 years (Bibi et al. 2012), and cars about 10-12 years (SSC 2012). However, some construction materials in buildings for instance may be around for much longer time than this (Sundqvist et al. 2013), and there are also products with significantly shorter lifetimes.

Nevertheless, assuming that the import of PBDD/Fs in PBDE treated products has decreased linearly from 2000, through 2010 (using the numbers above), until today, the total amounts of these unintentionally imported PBDD/Fs would add up to around 27 tons. Even if it is not realistic to believe that all of this still is present in our society, a large fraction of it probably is, which in any case would mean several tons of PBDD/Fs. In addition, there are also large amounts of PBDD/Fs in older products and materials that are still in use and the levels (of both PBDEs and PBDD/Fs) in those are probably even higher.

5.3 PBDD/Fs in waste

When products and materials have reached their end-of-life stage and are disposed of they may either be recycled into new products, put on landfills or destructed through incineration. This is of course also true for BFR containing materials. In the fraction that is incinerated, the PBDD/Fs are at least partly destroyed (although some may be formed as well), while the PBDD/Fs in the fractions that are recycled or landfilled will continue to be present in the society, with the accompanying risks for emissions this involve. According to KEMI (2009), BFR containing wastes have had a somewhat higher tendency to end up on landfills than other waste fractions. This is because the recycling of BFR containing materials is complicated and restricted, and because the capacity for incineration of such

waste in Sweden has been limited so far. However, the incineration capacity for BFR containing waste is constantly increasing and today a very small part of it is actually landfilled (KEMI 2009).

In the waste chain, BFR containing materials are mainly found in e-waste, construction waste and disposed cars, i.e. end-of-life vehicles (ELV). According to Bibi et al. (2012), KEMI (2009) and Avfall Sverige (2015), Sweden produces 140 000-170 000 tons of e-waste every year of which 2000-4000 tons are BFR containing plastics. Most of these plastics are incinerated in authorized incineration facilities. When it comes to construction waste, the figures are more uncertain. It is known that most of the BFRs are found among the plastics, even in this case, and also that the total amount of plastic waste from this sector is around 43 000 tons/year (Sundqvist et al. 2013). However, no numbers have been found regarding the size of the BFR containing fraction. Nevertheless, even for this fraction the major part is incinerated, although some are ending up on landfills (Bibi et al. 2012). Finally, disposed cars contribute with relatively large amounts of BFR-containing waste. The cars are usually fragmented and separated in a metal fraction and a lighter fraction called “shredder light fraction” (SLF) or, in Sweden, “fluff”. The SLF contain a lot of plastics and textiles and are rich in BFRs and other hazardous compounds. As the SLF has been problematic to incinerate, due to high content of chlorine and bromine that are causing corrosion in the incinerators and also due to its relatively high content of heavy metals, it has previously mainly been put on landfill. However, today the major part of it is incinerated, although there is a need for a larger capacity for this kind of waste in Sweden (Aae Redin et al. 2001; Jensen et al. 2012).

From this it can be summarized that the majority of the BFRs, and thereby the PBDD/Fs, that we have in our landfills originate from SLF from fragmented cars, but also that construction waste may contribute with a significant share. There is no numbers on the amount of such waste in our landfills, but an estimate from 2009 (KEMI 2009) say that 200 000-300 000 tons of organic waste is put on landfills every year, and that this may contain 50-100 tons of decaBDE. Using the same PBDD/F-PBDE ratio as above, this would correspond to 0.25-0.5 tons of PBDD/Fs. The calculations behind the estimated 50-100 tons decaBDE was based on the assumption that all of the organic waste landfilled contained decaBDE in the same level as those measured in Japanese SLF in a study by Sakai et al. (2006). Perhaps this is an overestimation, but it gives at least a hint of the amounts that may be added every year, and it would imply that we probably have several tons of PBDD/Fs stored in our landfills.

Although the properties of the PBDD/Fs (Table 1) suggest that they are strongly sorbed to the waste and the soil at landfills, there is always some leakage occurring. It has been estimated that in the 8-12 miljon m^3 of drainage water that are leaching from landfills in Sweden every year, there is total decaBDE content of 10 kg (KEMI 2009). If the PBDD/Fs are leaching to the same extent there should be a leakage of about 50 g/year of these contaminants.

5.4 PBDD/Fs in incineration residues

As discussed earlier in this report, the PBDD/Fs in BFR containing material that is incinerated may be destroyed to a smaller or greater extent depending on the prevailing combustion conditions. High temperatures and sufficient oxygen supply facilitate high degradation efficiency, while poor combustion conditions may lead to less efficient degradation. In addition, slow flue gas cooling may result in the formation of new PBDD/Fs (Söderström and Marklund 2004). The surviving PBDD/Fs as

well as the ones formed in the process may end up in the flue gases, the fly ashes or the bottom ashes.

The amounts PBDD/Fs emitted to air from MSWIs in Sweden is most likely quite small, based on the fact that the PBDD/F levels in flue gases usually are at least 100 times lower than the PCDD/F levels (Table 2, section 3.1.1), and the current estimation that less than 1 g of PCDD/F is emitted from Swedish MSWI stacks every year (Avfall Sverige 2009). This would imply that only a few mg of PBDD/Fs are emitted through this route every year. Also the amount of PBDD/Fs ending up in fly ashes seems to be fairly small. Based on the assumption that the average PBDD/F level in fly ashes is 0.1 ng/g (or 2 pg TEQ/g, Table 3) and the fact that 250 000 tons of fly ashes are produced in Sweden every year (Avfall Sverige 2015), the total amount of PBDD/Fs in these fly ashes would reach 25 g (or 0.5 g TEQ). This should be compared to 38 kg PCDD/Fs (480 g TEQ) calculated from a PCDD/F content of 150 ng/g (1900 pg TEQ/g, Table 3). On the other hand, larger amounts of PBDD/Fs seem to be stored in the bottom ashes. According to Johansson et al. (2015), the average PBDD/F levels in Swedish bottom ashes is around 6 ng/g (30 pg TEQ/g). This corresponds to 5.7 kg (29 g TEQ) of PBDD/Fs totally in the 954 000 tons of bottom ashes produced at Swedish MSWIs every year (Avfall Sverige 2015), which can be compared to 380 g PCDD/Fs (5.7g TEQ) calculated from an average PCDD/F level of 0.4 ng/g (6 pg TEQ/g).

5.5 PBDD/Fs that may be formed

The BFRs (and particularly the PBDEs) present in products and materials may also be considered as a stock of not-yet-formed PBDD/Fs as discussed above. However, the amount of PBDD/Fs that may be formed from these BFRs depends of course on the processes the materials are subjected to. The largest amounts of PBDD/Fs seem to be formed during incomplete combustion and various smouldering processes. As a worst case scenario it can thus be estimated how much PBDD/Fs that could be formed and released if all BFRs (PBDEs) stockpiled in Sweden where subjected to some kind of incomplete combustion process, e.g. an accidental fire. Assuming that we have around 2000 tons of PBDEs stockpiled in Swedish products and material (see above), this could potentially give rise 200 tons of PBDD/Fs in such smouldering process (Ortuño et al. 2015). This is indeed a worst case calculation for this amount of PBDEs, but on the other hand the total amount of PBDE in Sweden may be significantly higher.

6 How to minimize the emissions of PBDD/Fs in our society?

Considering the large amounts of PBDD/Fs that are hidden in products, materials and waste in our society, and the even larger amounts of precursors of PBDD/Fs that are present in the form of PBDEs, it would be relevant to work out a strategy how these materials should be handled in order to minimize the emissions of PBDD/Fs and the subsequent risks for exposure. The PBDD/Fs have already been identified as a risk for human health and the environment, which has led to a ban and phase out of the usage of most PBDEs in both Sweden and Europe (SSC 2012), leading to drastically reduced import levels. However, we still have to deal with the PBDD/Fs and the PBDE containing materials we already have within our borders.

PBDD/Fs are indeed emitted from PBDE containing materials during their whole life cycles, and to completely eliminate these emissions, the materials would have to be removed from the society and subsequently destructed once and for all. This may not be realistic on a short-term view, but should perhaps be a goal on a long-term view. At the same time, it has to be taken into account that the risks for emissions usually will increase as materials are subject to end-of-life treatments such as recycling, destruction and disposal, and especially if it involves methods that are not fit for purpose. A key factor in the work to reduce the PBDD/F emissions is therefore the implementation of efficient and sensitive separation technologies that are capable of isolating BFR containing material for subsequent destruction (Gallen et al. 2014). If BFR containing material end up in the wrong waste fraction it may be treated with inappropriate methods resulting in large emissions, and it is also a risk that the PBDEs and PBDD/Fs are uncontrollably spread to recycled materials and thereby end up in new products.

Apart from efficient and accurate identification and separation technologies, it is also important that the BFR containing fractions can be treated appropriately after being isolated. Safe destruction technologies need to be available and if possible with some kind of bromine recovery system included. As a last alternative, it must also be possible to safely landfill BFR containing materials that for some reason are impossible to destruct or recycle. These issues are further discussed below.

6.1 Identification and separation of BFR containing materials

Today in Sweden, the identification and separation of BFR containing materials is often performed manually, and it is mainly based on the experience and training of the personal doing the job, supplemented by spot checks with handheld bromine detection instruments (Retegan et al. 2010; SSC 2012). However, this leads to a limited sorting capacity and also a certain percentage of error since it is difficult to achieve a complete separation on such grounds. Laboratory analyses using advanced techniques such as gas chromatography coupled to mass spectrometry (GC/MS) would give more accurate and reliable results but are far too slow and costly to be used in the running separation process. There are indeed faster screening GC/MS instruments available, based on thermo-desorption and pyrolysis and with a total analysis time of 15 minutes, but even those are too slow for practical separation applications (Riess et al. 2000). Faster methods that can be automatized

to accurately identify and efficiently separate different materials would be needed. In the sections below, various methods that are used or potentially can be used for this purpose are summarized.

6.1.1 Spectroscopic technologies

The spectroscopic technologies are all based on the measurement of wavelength specific light (radiation) that is emitted or absorbed after atoms in materials have been excited by radiation such as X-ray or laser or by a spark. The emitted light is element specific, and can be used to determine the content of bromine for instance, even quantitatively. The X-ray fluorescence (XRF) technology (Kalnicky and Singhvi 2001) can thus detect bromine down to the 10 ppm range, and is used in many recycling facilities to detect BFRs in plastics. However, the XRF needs direct contact with the material being scanned, which may limit its use in automated processes. It also needs a fairly long scanning time, up to a minute, and the equipment is also quite expensive (SSC 2012).

The sliding spark spectroscopy (SSS) technology (Golloch and Siegmund 1997) is both faster and cheaper than the XRF technology. However, the SSS is less sensitive and can only detect bromine down to the 1000 ppm range, which in practice means that it can distinguish materials with more than 1 % bromine from those with less than 1 % bromine. This will screen out most BFR treated plastics, since these usually has bromine contents between 3-20 % (SSC 2012). However, foreign plastics with polymers originating from recycled BFR plastics may be missed by this technique, due to lower final levels. Like the XRF, the SSS needs direct contact with the equipment being scanned, which limits its use in automated applications. As a consequence, only handheld XRF and SSS instruments are available today and they are based on manual scanning (SSC 2012).

A more suitable technology for large automated systems is the X-ray transmission (XRT) technology (Schlummer 2014). A full scale XRT has been installed in a recycling facility in Switzerland, and it is said to be able to sort up to 1 ton of scrap per hour (SSC 2012). Besides being able to separate BFR and BFR free plastics, it is also claimed to be able to separate other waste fractions, e.g. lead vs. lead-free, combustible waste from metal, glass and PVC etc. The equipment is however very expensive. Other promising technologies are Laser and Raman spectroscopy (SSC 2012; Tsuchida et al. 2009). Both of these are mainly developed to distinguish between different types of plastics and polymers, but can potentially also be used to separate plastics with and without BFRs. Besides, separation of different types of plastics it may also constitute an important step in the isolation of the BFR containing materials.

Another technology that is already widely used for the separation of different plastic types, but that are unable to distinguish between BFR containing and BFR-free plastics, is the Near Infrared (NIR) spectroscopy (Beigbeder et al. 2013). NIR is thus capable of separating a wide range of plastics, including polystyrenes (PS), acrylonitrile butadiene styrene (ABS), polycarbonates (PC), polyphenylene oxide (PPO), polypropylene (PP), polyethylene (PE) and polyvinyl chloride (PVC), based on reflectance. However, a drawback is that it is unable to separate black plastics since these are uable to reflect light (Beigbeder et al. 2013).

The spectroscopic technologies may be used on whole plastic details, such as TV and computer casing, which often is the case when handheld XRF and SSS instruments are used during manual sorting. However, spectroscopic techniques may also be used on fragmented materials, which may be more relevant during automated processes. The plastic waste is then often fragmented into small

pieces, after which metallic components are removed by magnets or other techniques. NIR may then be used to separate the plastics in different types after which XRT, Laser or Raman spectroscopy may be used to isolate the BFR containing plastics. The actual separation in these processes may be achieved by air jets that blow the pieces to the right containers, directed by the result from the spectroscopic screening (Tsuchida et al. 2009).

6.1.2 Sink and float technologies

The sink and float technologies (S/F) separates materials according to their densities and since the density of plastics increases when BFRs are added to them, S/F may be used in the separation of such plastics (Menad et al. 2013). In the right liquid media, BFR containing plastics will sink while BFR-free plastics float. The density of the liquid media (normally water) can be altered by the addition of different salts in order to separate different plastics (SSC 2012). One drawback with this technique is that it may have limited capacity to screen out BFR-containing plastics in a mix of different polymers, which may have different intrinsic densities. The density of the liquid media also has to be calibrated to the specific polymer being processed. However, for specific input fractions the sink and float technology may give very clean and well separated output fractions with respect to BFR content. For example, for TV-casings, which are mainly made of high density polystyrene (HIPS) but of which only 30 % contain BFRs (in Europe) the sink and float technology is very useful (Schlummer and Maeurer 2006). The S/F technology can also produce bromine free fractions from more mixed WEEE plastics. However, the large share of black plastics in the low bromine fractions makes the downstream polymer separation with NIR difficult, which results in a mixed, low quality polymer as the final products, which may be difficult to find a market for. This inhibits the use of the S/F technology on a wider scale (SSC 2012).

6.1.3 Electrostatic separation

Electrostatic separation (ES) technologies are based on the fact that plastics have different electrostatic properties depending on their type (Atroune et al. 2015; Inculet et al. 1998; SSC 2012). Some plastics take on a negative charge while others take on a positive charge when subject to a Corona discharge, induction or friction. The charged particles can then be separated in a high tension field according to their charges. Since the ES distinguishes between positive and negative charges, it works best for binary mixtures. The plastics also have to be dry to be able to be electrostatically charged. Furthermore, the ES technology is mainly useful for separating different types of polymers and less for separating BFR plastics from non-BFR plastics. It is however available on industrial scale (SSC 2012).

6.1.4 Choice of technology

It should be noted that none of the technologies above are alone capable of screening out the BFR-containing plastics, and at the same time produce a clean polymer fraction with sufficient quality for

making new plastics. Therefore combinations of technologies usually need to be used in practice. An example of such combination is: 1) manual dismantling including rough separation, 2) fragmentation, 3) online NIR to separate polymers, 3) ES of the dark fraction containing both PS and ABS, 4) S/F of especially the PS and ABS fractions that contain the majority of the BFRs. This combination would be possible to automate to a large extent, with the advantages that would involve. However, in some cases it might be more efficient to screen out the BFR containing material already during the dismantling process, using handheld SSS and XRF instruments, even if it is more labor intensive. It should also be noted that even with combination of techniques, a 100 % separation will not be achieved. Normally, at least 5 % of the plastics will end up in the wrong fraction (SSC 2012). Because of this, recycled plastics, including the "BFR-free" fraction, should never be used for sensitive applications, such as toys and household products. When it comes to the BFR-containing fraction, it should not be recycled at all to avoid spreading of the BFRs and PBDD/Fs. It could perhaps be used for making raw material for the industry or fuel (see section 6.4 below), but otherwise it should be destructed or as a last choice put on landfills

6.2 Destruction of BFR and PBDD/F containing materials

6.2.1 Incineration

BFRs and PBDD/Fs are mainly found in materials with high calorific values, e.g. plastics, polyurethane foam and textiles. Because of that, incineration with energy recovery is an attractive way of destructing them and at the same time gain energy from the process (Tange and Drohmann 2005). However, it has to be done with care to avoid corrosion of the incinerators and emissions of toxic compounds, including PBDD/Fs (Rademarkers et al. 2002; Wyrzykowska et al. 2008). Normally, authorized incineration facilities, including larger MSWIs or HWIs, have to be used and the mixing ratio of the BFR-containing material (in other fuels) have to be kept low, normally below 5 % (SSC 2012). A too high BFR load will lead to poorer combustion conditions (due to the properties of the BFRs) and more precursors in the combustion zone, which will lead to higher emissions of PBDD/Fs. Large loads of bromine (from BFRs) and chlorine (from PVC) will also lead to high levels of HBr and HCl in the flue gases which will cause corrosion of metal parts in the incinerator, particularly in the energy recovery system (Rademarkers et al. 2002). The acids can however be removed from the flue gases by scrubbers, and test have been performed with co-combustion of both WEEE plastics and SLF with acceptable emissions as a result (SSC 2012). However, as mentioned above, the bottom ashes from incinerators may contain significant levels of PBDD/Fs (Johansson et al. 2015), and if SLF has been incinerated they may also contain high levels of heavy metals. This has to be taken into account considering that bottom ashes may be used as raw materials in constructions. Perhaps the control and monitoring of bottom ashes need to be improved.

6.2.2 Cement kilns

The possibility of co-combusting BFR and PBDD/F-containing material in cement-kiln have been suggested but not yet fully investigated (Fink 1999; Reijnders 2007). The destruction efficiency may depend on how the waste is fed in the kiln. If the kiln is not optimized for solid fuel, like the BFR-containing material, the residence time in the combustion zone (above 1100 °C) might be too short.

This has to be assessed for each kiln that may come into question and the emissions have to be monitored (SSC 2012).

6.2.3 Metal smelters

The metal containing fractions of WEEE and fragmented vehicles (ASR) often end up in metal smelter, since this waste is a valuable material for metal recovery. The levels of precious metals in WEEE may for example be very high with an average PC-board containing 15-20 % copper, 200-500 ppm gold, 1000 ppm silver and 80-100 ppm palladium (Hageluken 2006). This is much higher levels than in virgin ore. However, the metal containing fractions also contain significant amounts of plastics, which often contain BFRs and PBDD/Fs. To avoid releases of these compounds, the materials have to be treated in an environmentally sound manner(SSC 2012).

Usually the WEEE and the ASR fractions are mixed with other primary (ore concentrates, anode slimes etc.) or secondary materials (e.g. industrial residues and catalysts) in the smelters to remove the combustible parts and recover the metals. However, this may lead to large emissions of dioxins (PBDD/Fs, PCDD/Fs and PBCDD/Fs) depending on the design of the smelter and how the scrap is fed (Du et al. 2010a; Du et al. 2010b; Odabasi et al. 2009; SSC 2012; L-C Wang et al. 2010b). While the temperature in the molten bath is high (above 1100 °C) and appropriate for BFR and PBDD/F destruction, the charging of the waste and fuel may involve some periods and spots with lower temperatures where the degradation may be lower and dioxin formation may occur. To avoid significant emissions of PBDD/Fs (and other dioxins) from metal smelters, efficient afterburning of the off-gases followed by sophisticated flue gas cleaning systems, similar to those in modern MSWIs, should be required for processing WEEE and ASR materials. The emissions of PBDD/Fs and PBDD/Fs, and not only PCDD/Fs, should also be monitored regularly (SSC 2012).

6.3 Landfilling of BFR and PBDD/F containing materials

Organic waste in general should only be put on landfills temporarily or as a last alternative if all other end-of-life treatments for some reasons are unsuitable. This also holds for BFR containing waste (SSC 2012). There is always a risk that contaminants may leach or be emitted from the waste during long term storage, and especially if it’s done under uncontrolled conditions. Furthermore there is a risk that even larger amounts of contaminants are spread during events of accidental fires at the landfills. Such events, with smouldering of waste, are also ideal for the formation of new PBDD/Fs. Elevated levels and emissions of PBDD/Fs and PBDEs have thus been observed at landfills subjected to accidental and uncontrolled fires (Lundstedt 2009; Naturvårdsverket 2011). Furthermore, PBDEs have been seen to leach from landfills in several studies (Danon-Schaffer et al. 2013; Osako et al. 2004; Weber et al. 2011), and even if there is no such data available for PBDD/Fs it is likely that they behave similarly. PBDEs have also been detected at elevated levels in soils adjacent to landfills (Danon-Schaffer 2010) indicating an atmospheric release with subsequent deposition.

Consequently, in cases when BFR containing materials have to be landfilled it has to be done under certain, controlled conditions (SSC 2012), which basically is similar to landfilling of other hazardous waste fractions.

- The landfills should not be located in proximity to residents or other sensitive receptors, such as groundwater reservoirs or surface water. Neither should they be located where there is a risk for flooding or erosion.
- They should be fenced to prevent people and animals from entering.
- They should, as far as possible, be secured from accidental fires through appropriate compaction, coverage etc., but should also be designed so that fires that still break out can be isolated efficiently.
- They should use state-of-the-art bottom liners to minimize leakage.
- They should be designed and capped to minimize infiltration of rain water.
- They should collect, control and treat leachates and landfill gases.
- There should be a plan for a long-term aftercare, including control and monitoring programs.

Considering the climate change, landfills for hazardous waste like this should also take into account the possibilities of higher precipitation, infiltration and erosion rates, since this may enhance the leachate production, the mobilization of larger waste fractions, the degradation of the liners and the volatilization rates (Laner et al. 2009; Weber et al. 2011).

Most of these requirements, listed above for landfills, should also be taken into account when BFR containing material is stored while waiting for other treatments, long term or short term. For example, fragmented WEEE destined for metal recovery and BFR plastics that are about to be destructed may sometimes be stored in big piles, which potentially could emit and leak BFRs and PBDD/Fs. In addition, such piles may run the risk of catching fire and thereby emit enormous amounts of contaminants. In order to limit the overall emissions of PBDD/Fs these risks would have to be minimized, both by measures similar to those listed above, and through limitations in the amount of BFR-containing material that can be stored in the same place.

6.4 Separation of BFRs and PBDD/Fs from polymers

Instead of destructing or landfilling BFR-containing plastics, a conceivable alternative would be to extract the bromine or the intact BFRs from the material, after which the polymers could be safely recycled or treated as a non-BFR polymer. A number of such technologies have been suggested (SSC 2012) but none has so far reached full-scale usage, which probably is due to the lack of economic incentives in going further with such treatments.

6.4.1 Separation of BFRs or Br from polymers by dissolution

One alternative is to separate the bromine from the BFR containing material by dissolution. The material is then dissolved in a suitable solvent after which the bromine is recovered either as intact BFRs or as bromide (e.g. as HBr or NaBr). This has been suggested by a number of researchers (SSC 2012), but have only been fully developed in the so called CreaSolv® process (Schlummer and Maeurer 2006; Schlummer et al. 2006). In this processes a range of dissolution, filtration and precipitation steps are used to separate styrenic polymers from other polymers and to purify them from BFRs and other materials. The styrenics, being the most important WEEE-polymers, are thus

considered to be the targets in the CreaSolv® process. In a first step, the BFR containing material is treated with a proprietary solvent that will dissolve the styrenic polymers while keeping the non-styrenic polymers and non-polymeric materials in solid state. This will allow the latter to be filtered off. In a second step, the styrenic polymers are precipitated, by the addition of another proprietary solvent, while the BFRs and the PBDD/Fs are kept in solution. The purified, precipitated styrenes are then filtered off, dried and pelletized, while the solvent is recycled within the process and the bromine collected in a residual slurry. From the slurry it is then possible to recover both bromine and antimony (which often are present together with BFRs), for reuse in the industry. Furthermore, the CreaSolv® process allows separation of different types of styrenic polymers, as a result of different precipitation behaviors, and which is an advantages if the polymers are to be used for producing new plastics. Some styrene polymers are thus incompatible and will give the plastics impaired properties when blended (Schlummer et al. 2006).

6.4.2 Pyrolytic recovery of bromine

Another alternative is to separate the BFRs and PBDD/Fs from the plastics in a pyrolytic process in which the polymer simultaneously is converted into a gaseous, liquid or solid fuel. At least two such technologies have been suggested (SSC 2012). In the Haloclean process, two gas-tight rotary kilns was used to convert WEEE polymers into oils, which then were dehalogenated in a third reactor using melted polypropylene as a hydrogen source. During the polypropylene treatment the bromine was driven off as HBr. Although the bromine-free oil was not pure enough to be used for production of new plastics, due to the large variety of polymers in the original WEEE, it could be used to produce methanol. Furthermore, the residues from the process could be used to recover precious metals (Hornung et al. 2003).

In another process, called staged-gasification, the pyrolysis was performed in two stages; first the actual pyrolysis at 550 °C followed by a high temperature gasification at more than 1230 °C (SSC 2012; Tange and Drohmann 2005). The HBr was recovered from the syngas by “wet” alkaline scrubbing. Such HBr recovery by scrubbing can of course also be performed on gases from ordinary incinerators after the BFR containing materials have been destructed (Vehlow et al. 2002), but the pyrolytic gasification processes also offers a possibility to produce a homogenous fuel or raw materials for other chemical processes (SSC 2012).

7 Conclusions

- PBDD/Fs are emitted from a wide range of sources in our society, including combustion processes, various high temperature processes and directly from all BFR treated products and materials we are surrounded with. In addition, there is a diffuse emission of naturally produced PBDDs in some marine environments.
- Practically all anthropogenic sources are related to BFRs, and especially PBDEs, but the combustion and high temperature processes enhance the emissions by releasing PBDD/Fs that already are present in the material and by causing formation of new PBDD/Fs from the BFRs. These processes are strongly favored by poor combustion conditions and smouldering.
- It is difficult to say for sure which of the anthropogenic sources that is dominating on a global scale, but on a local and regional scale open burnings, accidental fires and thermal stress processes acting on BFR containing materials may be very important. This is because of the large amounts of such materials in our society.
- In indoor environments, direct emissions from PBDE treated products, e.g. EEE and textiles, transferred via dust may be the largest exposure route for humans, although exposure via food is also important. PBDE treated material may thus contain very high levels of PBDD/Fs.
- Metal smelters that are using WEEE as one of their feed stocks and poorly optimized incinerators (MSWIs, HWIs or IWIs) may be important for the global emissions of PBDD/Fs, although modern facilities emit fairly low PBDD/F amounts.
- PBDD/Fs are ubiquitous in the environment today. Background levels in air, soil/sediments and biota are generally relatively low, usually lower than the levels of PCDD/Fs, but elevated levels may be found in some urban and locally contaminated environments. In some environments, e.g. e-waste recycling sites and places for accidental fires the PBDD/F levels may be much higher than the PCDD/F levels.
- In indoor environments (house dust) the PBDD/F levels are often higher than the PCDD/F levels, which probably is because of the abundance of BFR containing material in such environments.
- According to estimations, there are several tons of PBDD/Fs hidden in the Swedish society, mainly in products such as EEE, vehicles and construction material, but also in waste and ashes. In addition, there is an even larger amount of not-yet-formed PBDD/Fs in all BFRs present in the same materials.
- To completely eliminate the risk for emissions from these materials, they would have to be removed from the society and subsequently destructed. However, in this context it should be noted that the risk for emission often will increase temporarily as a material is removed from its original placement and when it is being recycled and destructed.
- To minimize the emissions in these processes, as well as from waste material in general, a key factor would be the implementation of efficient and sensitive identification and separation technologies that are capable of separating BFR containing materials from non-BFR-containing materials, so that each fraction can be treated appropriately. The BFR containing fractions can then be destructed in authorized incineration facilities or metal smelters with highly developed flue gas cleaning systems and adequate treatments of ashes (including bottom ashes). Landfilling should only be used in exceptional cases as the very last alternative.

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