The presence of brominated flame retardants and organotin compounds in dusts collected from Parliament buildings from eight countries.

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Notes

This Technical Note represents an update of the previous Technical Note 03/2001, including the results of analyses of samples from the Austrian, German and UK Parliament buildings for brominated flame retardants which were in progress at the time of publication of the previous version.

In addition, part of the data set described here has recently been published as Leonards, P.E.G., Santillo, D., Brigden, K., van der Ween, I., Hesselingen, J.v., de Boer, J. & Johnston, P. (2001) Brominated flame retardants in office dust samples. *Abstracts of the Second International Workshop on Brominated Flame Retardants*, Stockholm, 14-16th May 2001: 299-302

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1. Summary

Samples of dust were collected from Parliament buildings in a total of 8 countries (Austria, Denmark, Finland, Germany, Italy, Netherlands, Sweden and UK) during the year 2000. In the case of the Netherlands, 3 samples were also collected from the offices of the popular computer/internet provider XS4all. Sub-samples were sent to the laboratories of the Netherlands Institute for Fisheries Research (RIVO) for analysis of the finely sieved fraction for brominated flame retardants and to GALAB (Geestacht, Germany) for analysis of organotins. Analyses for PCBs and (for selected dusts) chlorinated paraffins are still underway at RIVO.

Samples of dust from all countries contained significant levels of brominated flame retardants. Decabromodiphenyl ether (deca-BDE, or BDE-209) was the predominant diphenyl ether in each sample, although tetra-, penta- and hexa-BDE were also detected in all samples. Levels of deca-BDE varied from 0.26-6.9 mg/kg (ppm) dust, with the highest levels in the two samples from the Italian Parliament buildings (Senato, 6.9 ppm; Palazzo Marini, 4.6 ppm). Elevated levels of deca-BDE were also found in one of the two samples each from the UK (4.5 ppm) and German (1.5 ppm) Parliament buildings, as well as in the sample from the Finnish (1.1 ppm), Dutch (0.8 ppm) and Swedish Parliaments (0.7 ppm). Highest levels of BDE-99 (a penta-BDE) were found in dust from Italy's Palazzo Marini (0.17 ppm), though levels in dusts from the Dutch (0.13 ppm) and Finnish (0.16 ppm) Parliaments were also relatively high.

Several dust samples also contained residues of polybrominated biphenyls (PBBs), especially deca-BB (BB-209). Concentrations were much lower than those for BDEs, as expected. Among the highest levels of BB-209 were again recorded in dust samples from Parliament buildings in Netherlands (0.015 ppm) and Italy (0.013-0.014 ppm), although the concentration in dust from the OSPAR 2000 venue in Denmark (0.017 ppm) was also relatively high. The highest level of all samples (0.018 ppm) was determined for one of the samples from the Dutch internet provider, XS4all. An order of magnitude higher concentrations for PBB congener 169 may have resulted from interference from another, as yet unidentified, organobromine compound.

The brominated flame retardant hexabromocyclododecane (HBCD) was found in 13 of the 16 samples analysed to date, often at levels of a similar order as those recorded for deca-BDE (0.009-3.7 ppm). Of the Parliament dusts, highest levels were found in samples from the Austrian (1.8 ppm), German (0.82 and 0.94 ppm) and UK (0.98-3.7 ppm) Parliament buildings. Relatively high levels were also found in 2 of the 3 dust samples from the offices of XS4all (0.84-1.4 ppm). Tetrabromobisphenol-A was present above detection limits in 7 of the 16 samples analysed to date, with the highest values in dusts from the Austrian (0.015 and 0.033 ppm) and UK (0.012 and 0.047 ppm) Parliaments.

Substantial levels of organotins were found in all of the samples, including those from Austria, Germany and UK for which brominated flame retardant data are not yet available. Total organotin concentrations (butyl and octyltins combined) varied from 0.49 ppm (one sample from Italian Senato) to 3.48 ppm (one of two samples from the German Reichstag). High levels were also found in dusts from Parliament buildings in Austria (3.34 ppm) and the Netherlands (2.99 ppm), as well as in two of the three samples from internet provider XS4all (2.88-3.17 ppm). In all but two cases (the two least contaminated samples), total organotins were predominated by monobutyltin (MBT), with lower levels of DBT and even lower levels of TBT. Monooctyltin (MOT) was in all cases more abundant that DOT, though levels (0.015-0.83 ppm) were generally lower than for the MBT. Triphenyltin, as expected, was not found in any of the dust samples at levels above detection limits.

The results to date confirm the widespread contamination of dusts with a variety of brominated flame retardants and organotins, both groups of persistent organic pollutants which have been prioritised for substitution under the OSPAR strategy for hazardous substances. This study provides further evidence that our exposure to these compounds is continuous and ubiquitous, even in the general office environment. Although this study does not provide (and indeed was not intended to provide) data from which exposure could be estimated, the results clearly demonstrate the possibility for continuous exposure to these compounds especially via inhalation or contact with the skin.

For substances which are known to accumulate in the body, such as penta-BDE and some of the organotins, such exposure may contribute further to the overall body burden. Moreover, for substances thought to be less bioaccumulative, such as deca-BDE, their presence in dusts at ppm levels may well help to explain why they are nevertheless detectable in a significant proportion of the general population as background contaminants. Furthermore, irrespective of the potential for exposure to these hazardous substances through contact with dusts in the workplace, the ultimate disposal of dusts from vacuum cleaners and other sources may represent a significant input of these and other hazardous substances into waste repositories and, ultimately, the surrounding environment.

2. Introduction

Brominated flame retardants are a diverse group of bromine-containing organic compounds used in a variety of polymers, textiles and other materials to prevent or retard the spread of fire. They are present in a wide array of industrial and consumer products, including electrical and electronic appliances, vehicles, lighting and wiring, textiles (including carpets and other furnishings) and packaging materials, especially plastics (Lassen *et al.* 1999). Although the term brominated flame retardants covers a wide range of different chemicals (OECD 1994, Lassen *et al.* 1999), the substances used historically and/or currently in the greatest quantities are the polybrominated biphenyls (PBBs), polybrominated diphenylethers (PBDEs, or polybrominated diphenyloxides, PBDOs), hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBP-A) (de Boer *et al.* 1999, Lassen *et al.* 1999, Bergman 2000). Concerns regarding the persistence and toxicity of PBBs has now led to their virtual phase-out of production in Europe (KEMI 1999), while production of TBBP-A remains on the increase.

As a group, brominated flame retardants are highly stable compounds which are generally poorly degradable (highly persistent) in the environment. Most have high octanol:water partition coefficients (de Boer *et al.* 2000) indicative of high lipophilicity. Although the bioconcentration of some of the higher brominated PBDE congeners, which have some of the highest partition ratios, is thought to be limited to some degree by the high molecular weight of the compounds, these congeners are nevertheless clearly bioavailable (see below).

Brominated flame retardants may be present in products and materials either as simple additives or as reactive mixtures which bind more tightly to the product matrix. PBDEs and HBCD, like PBBs, are predominantly used as additive flame retardants and, as such, are relatively freely mobile and may readily migrate from products into the surrounding environment during manufacture, normal use and disposal. Additive flame retardants frequently make up 10-30% of the total mass of a range of polymers (OECD 1994, Lassen *et al.* 1999). TBBP-A is often incorporated as a reactive compound, though it is also used as an additive, especially in the internal components of computers and other electronic equipment (Lassen *et al.* 1999). Moreover, even when used in reactive form, the potential remains for loss to the environment through abrasion or polymers during use, as well as during manufacture and disposal. In short, brominated flame retardants are manufactured and used in large quantities through out the world, including in a wide array of consumer products and other open applications which allow for their wide market distribution. The potential therefore exists for both point and diffuse inputs of these compounds to the environment.

Environmental distribution

Most of the available data concerning the distribution of brominated flame retardants in the environment relate to the PBBs and, more recently, the PBDEs. Early concerns regarding the widespread presence of PBDEs in the environment were raised in the late 1980s and early 1990s (Loganathan *et al.* 1995). Nylund *et al.* (1992) identified two of the lower brominated groups of PBDEs, tetra- and penta-BDEs, in sediments from the Baltic Sea and described an increase in concentrations over time, in contrast with the gradually declining levels of PCBs. Around the same time, Andersson and Wartanian (1992) noted the presence of PBDEs in the tissues of Baltic seals, and both Sellstrom *et al.* (1993) and Jansson *et al.* (1993) stressed the ubiquitous nature of these compounds as contaminants in biota from the Swedish environment.

De Boer (1989) reported the presence of PBDEs in cod liver oil from the North Sea, recording the presence of these compounds already in archived samples from 1977, and describing a clear spatial trend for increasing levels of contamination from Northern to Central to Southern North Sea. Later reports have confirmed the presence of PBDEs, especially the lower brominated tetra-, penta- and hexa-BDE, in the tissues of carp from Buffalo River, New York (Loganathan *et al.* 1995), as well as in fish from the Great Lakes (Asplund *et al.* 1999a) and in Baltic salmon (Asplund *et al.* 1999b). Particularly high levels of PBDEs have been recorded in sediments and fish tissues downstream from a flame retardant manufacturing plant in UK (Allchin *et al.* 1999), as well as downstream from a number of textile companies using commercial formulations in Sweden (Sellstrom *et al.* 1998). The work of de Boer *et al.* (1998) on tissues from stranded sperm whales provided a strong indication that PBDEs, as well as PBBs, had reached the deep oceans where these animals feed. Analyses of stranded whitebeaked dolphins, minke whale and harbour seals by de Boer *et al.* (1998), and of pilot whales from the Faroe Islands by Lindstrom *et al.* (1999) confirmed the widespread occurrence of PBDEs in marine mammals. The presence of PBDEs in biota of the Canadian Arctic has also recently been confirmed (Alaee *et al.* 1999). Analysis of temporal trends in PBDE concentration in beluga from the SE Baffin region (Stern and Ikonomou 2000) indicates an approximate 6–fold increase in concentrations over the period 1982-1997. During this period, a decline in predominance of tri- and tetra-

BDEs and an increase in significance of penta- and hexa-BDEs has also occurred, possibly reflecting a market shift towards higher brominated congeners.

The lower brominated PBDEs, especially tetra- and penta-BDEs, are highly bioaccumulative in marine organisms. Gustaffson *et al.* (1999) reported that the bioaccumulation potentials for BDE-47 (tetra-) and BDE-99 (penta-) in blue mussels were even greater than those for PCBs of equivalent lipophilicity. More recently, Burreau *et al.* (2000) have suggested the partial metabolism of BDE-47 to yet more lipophilic metabolites as a contributory mechanism to its high propensity to bioconcentrate in fish tissues. De Boer and Dao (1993) estimated biomagnification factors for PBDEs from fish to marine mammals of 10-30.

Presence in human tissues

PBDEs, along with certain other brominated flame retardants, have also been detected in human tissues. Early reports of their presence in human adipose tissue in Sweden (Lindstrom *et al.* 1997) were later supported by reports of similar levels in adipose tissue of Spanish (Meneses *et al.* 1999), Finnish (Strandman *et al.* 1999) and North American (She *et al.* 2000) subjects. Meironyte *et al.* (1999) have recently demonstrated that PBDEs (tetra-, penta- and hex-BDEs) are not only present in human breast milk, but that their concentrations have increased rapidly in recent years, doubling every five years since the early 1970s, leading to renewed calls for large-scale breast milk monitoring programmes (Hooper and McDonald 2000), as well as for controls to prevent further contamination (Noren and Meironyte 2000).

Sources of human exposure remain poorly characterised and, although intake through food consumption is undoubtedly important, the potential for exposure to brominated flame retardants in the indoor environment, as a result of their loss from products in use, is also real. Bergman *et al.* (1997) identified a range of halogenated flame retardants in the particulate fraction of air in a number of computerised offices in Stockholm, including the BDE-47 and BDE-99, as well as TBBP-A. More recently, Sjodin *et al.* (2001) recorded the presence of eight PBDE congeners and TBBP-A as airborne contaminants in an electronics recycling plant. The higher molecular weight hepta- (BDE-183) and deca- (BDE-209) were present at the highest concentrations, and were also detected in air samples from offices in which computers were in use.

These results add weight to concerns regarding the loss of brominated flame retardants to the surrounding indoor environment during normal use of electronic equipment, and perhaps from furnishing textiles, and the potential, therefore, for continuous, low-level exposure to these compounds both at work and at home. Indeed, both Klasson-Wehler *et al.* (1997) and Sjodin *et al.* (1999) have reported the presence of brominated flame retardant residues, including BDE-209, in human blood. The presence of BDE-209 in human blood confirms its bioavailability, despite its high molecular weight and relatively low propensity to bioconcentrate. While highest blood concentrations of PBDEs have been reported so far for workers at an electronics recycling plant (Sjodin *et al.* 1999), elevated concentrations are also detectable in the blood of computer clerks compared to workers with no regular occupational use of electronic equipment. Hagmar *et al.* (2000a) provided further evidence for contamination of human blood with both PBDEs, including deca-BDE, and TBBP-A through occupational use of computer equipment. Although the half lives for residence in human blood of deca-BDE and TBBP-A are relatively short, 6.8 days and 2 days respectively (Hagmar *et al.* 2000b), during a normal working life exposure may be continuous, such that serum levels may be regularly “topped up”.

Brief description of toxicity

Although the most widely used brominated flame retardants are thought to have relatively low acute toxicities (Olsson et al 1998, de Boer *et al.* 1999), a number of PBDEs, as well as HBCD and TBBP-A, are known to exhibit mammalian toxicity following longer-term exposure. For example, prenatal exposure to penta-BDE has been demonstrated to have permanent effects on the developing brain and, therefore, on behaviour (Eriksson *et al.* 1999). Exposure of developing rat foetuses to high doses of deca-BDE resulted in delayed hardening of the skull bones (Olsson *et al.* 1998); octa-BDE and commercial mixtures of hexa-, hepta- and octa-BDE exhibited wider ranging developmental effects even at much lower doses. Darnerud and Sinjari (1996) and Meerts *et al.* (1998) have demonstrated the potential for hydroxylated metabolites of lower brominated PBDEs, as well as for TBBP-A, to compete with the thyroid hormone thyroxine for transthyretin binding sites and to reduce overall serum levels of thyroid hormones. More recently, Helleday *et al.* (1999) reported that both HBCD and lower brominated PBDEs are capable of inducing genetic recombination in mammalian cells lines, a possible indicator of carcinogenicity. De Boer *et al.* (2000) provide a more detailed, recent review of toxicity for the PBBs and PBDEs. In many ways, these substances may be seen to exhibit similar modes of toxicity to the PCBs and certain chlorinated pesticide residues.

Developing regulations

Because of the concerns relating to the toxicity of many of the brominated flame retardants, coupled with their widespread environmental distribution and use in a myriad of consumer products, a number of decisions and proposals exist at national and international levels to address these compounds. Following initial concerns raised within the context of the North Sea Ministerial Conferences, the OSPAR Commission[1] included brominated flame retardants as a group within its first list of substances requiring priority action which was drawn up in 1998 (OSPAR 1998). These, among other, substances were prioritised for action under the Commission's strategy to address hazardous substances, within which the target is set for the cessation of all releases of hazardous substances which could reach the marine environment by 2020 at the latest (OSPAR 1998). As such, OSPAR has targeted brominated flame retardants as a group for substitution with less hazardous alternatives as quickly as possible. To date, measures within OSPAR to achieve this target for these compounds have yet to be finalised.

At a national level, Sweden has proposed a phase-out of all uses of both PBBs and PBDEs (KEMI 1999). As lead country for OSPAR's work on brominated flame retardants, Sweden is currently proposing that European Member States that are also Contracting Parties to the OSPAR Convention should co-ordinate efforts to ensure that the risks assessments underway within the EU for brominated flame retardants will recognise the need to meet the OSPAR cessation target (OSPAR 2001). The EU risk assessment for penta-BDE has now been drafted and proposed risk reduction measures are expected to result in a complete phase out of production and use of commercial penta-BDE formulations (EC 2000). EU risk assessments for octa- and deca-BDE, as well as for HBCD and TBBP-A, are still underway.

Other proposed controls result from a recognition that combustion of wastes containing brominated flame retardants (both additive and reactive), for example by incineration, results in the generation of brominated dibenzo-p-dioxins and dibenzofurans (for reviews of sources and toxicity see Mennear and Lee 1994, WHO 1998). Indeed, it is in response to these concerns that the World Health Organisation recommended their substitution, wherever possible, with non-halogenated alternatives (WHO 1998). This aim is captured within the currently proposed EC Directive on waste electrical and electronic equipment (WEEE)(CEC 2000), requiring substitution by 2008 at the latest.

Much of the discussion and development of regulatory measures to address brominated flame retardants are therefore ongoing, and the outcomes remain to be determined. In the mean time, however, the use and release of PBDEs, HBCD and TBBP-A in industrial and consumer applications continue. Exposure to older formulations, including PBBs, is also likely to continue for some substantial time to come, despite cessation of production in Europe, because of their presence in older products, possibly in new products imported into Europe and because of their status as widespread environmental contaminants.

Context of the current study

Hardy (1999) and Tittlemier and Tomy (2001) have recently highlighted the low water solubilities and low vapour pressures of the PBDEs, especially the higher brominated congeners, and suggested that these properties may limit the long-range transport of these compounds. At the same time the evidence continues to build that PBDEs, along with the other brominated flame retardants in common use, are ubiquitous and widespread contaminants in biota and other environmental media as well as in the indoor environment and in human tissues. Mechanisms by which such a wide distribution occurs clearly exist, even if they are not yet fully understood. The detection of numerous PBDE congeners, including deca-BDE, in workplace air is a clear example of a potential human exposure pathway which, until relatively recently, had been overlooked. Transportation as particle bound contaminants on airborne dust may represent an important alternative pathway for the wide distribution for such low-volatility compounds and may explain the apparent widespread, low-level presence of brominated flame retardants in human blood serum. Despite recent research, however, relatively few data are available describing levels of these persistent organic contaminants in the indoor environment. Given the diversity of uses of brominated flame retardants, exposure to particle bound residues may be significant even in normal workplaces, not just in electronic recycling plants.

The current study was designed to contribute further data relating to concentrations of brominated flame retardants in the indoor workplace environment, using office dusts as a convenient integrative matrix of their distribution within and between offices and other buildings. Dust samples were drawn primarily from the offices or chambers of Parliament buildings in a total of eight countries in Europe or the European Economic Area, although three samples from the offices of a popular internet service provider in the Netherlands were also included for comparative purposes.

Other contaminants

In addition to the brominated flame retardants, the current study was designed also to quantify the presence in dusts of several other hazardous organic compounds historically or currently used as additives in consumer products, including organotins, PCBs and chlorinated paraffins. It was judged that, as for the brominated compounds, residues of these other groups of persistent synthetic chemicals may also partition significantly into dust.

Toxicity of organotins

Organotin compounds have been used for a variety of applications following their development and initial use as a moth repellent in the 1920's (Moore *et al.* 1991). Perhaps the best known application of organotins, especially tributyltin (TBT), has been the use for many years on a worldwide basis as an antifouling agent in paints for boats and ships. Because of the severe and widespread adverse effects on marine gastropod mollusc populations (Gibbs 1988, 1993, Bryan *et al.* 1986, 1987), use of TBT paints on small craft was prohibited in most countries by the early 1990's (Evans 2000). A general prohibition on the use of such paints (IMO Assembly Resolution A.895(21), November 1999) is due to be finalised under the auspices of the International Maritime Organisation later in 2001. Nevertheless, numerous other organic compounds of tin are synthesised and remain in widespread use both as biocides and as polymer stabilisers.

Several organotin compounds, primarily mono- and dibutyltin (MBT and DBT), though also including octyl tins (MOT and DOT) are used in large quantities as heat and light stabilisers in PVC and other plastics (Matthews 1996). According to Sadiki and Williams (1999), PVC represents about two-thirds of the global consumption of these organotin compounds. Octyltin stabilisers were initially developed as less toxic alternatives to the butyltins. Although more expansive than alternative, inorganic compounds, organotins are considered superior in performance and maintain the clarity of PVC products (Matthews 1996). Other organotin compounds, including TBT, are present as biocides to control bacterial or fungal growth in certain textile products, including carpets (see e.g. Allsopp *et al.* 2001).

It has been recognised for some time that butyltin stabilisers can migrate from PVC products during normal use, e.g. the leaching of MBT and DBT into drinking water from PVC pipes (Forsyth and Jay 1997, Sadiki and Williams 1999). Despite this propensity, organotins may still be found as high concentration additives in a variety of consumer products and children's toys. For example, Kawamura *et al.* (2000) reported levels up to the g/kg range for MOT in PVC containers. A recent study in Germany raised concern about the presence of comparatively high levels of TBT and other organotins in PVC flooring (Oeko-Test 2000). The data of Allsopp *et al.* (2000, 2001) for both PVC flooring and carpets available for retail in the UK confirm the ongoing use of these compounds in floor coverings, occasionally at very high concentrations (up to 0.57 g/kg DBT in PVC, 0.047 g/kg TBT in treated carpet fibre).

Organotins are known to exhibit toxicity at relatively low levels of exposure not only to marine invertebrates but also in mammalian systems. In marine invertebrates, toxicity appears to be primarily related to relative lipophilicity, such that TBT is often more toxic than DBT, which is in turn more toxic than MBT (Cima *et al.* 1996). However, this is by no means always the case, as DBT is more toxic than TBT to certain enzyme systems (Bouchard *et al.* 1999, Al-Ghais *et al.* 2000). In fish, DBT is frequently a more potent immunotoxin than TBT (O'Halloran *et al.* 1998).

Organotins have been demonstrated to have immunotoxic and teratogenic (developmental) properties also in mammalian systems (Kergosien and Rice 1998), with DBT again frequently appearing more toxic than TBT (Ema *et al.* 1995, De Santiago and Aguilar-Santelises 1999). DBT is neurotoxic to mammalian brain cells (Eskes *et al.* 1999). Ema *et al.* (1996, 1997) demonstrated the importance of the precise timing of exposure to DBT in induction of defects in developing rat embryos. Estimates of the significance of human exposure to organotins from consumption of contaminated seafood have taken the potential immunotoxicity of these compounds to humans as an effect parameter (Belfroid *et al.* 2000).

Developing regulations

As for the brominated flame retardants, organotins as a group are included on the OSPAR list of substances for priority action towards achieving the target of cessation of all releases by 2020. So far, work within OSPAR on this group of chemicals, co-ordinated by the Netherlands as lead country, has rightly focused on the achievement of the IMO Convention prohibiting the use of organotin compounds in antifouling paints (OSPAR 2000). However, progress in this field under the IMO may now allow the opportunity to develop measures to address other, more diffuse inputs of organotins arising from the manufacture, use and disposal of the many consumer products in which they are still incorporated (see above). In this context, it is significant that Germany has under development ordinance which will prohibit the use of organotin compounds in all such products.

In the mean time, however, and indefinitely in other countries, exposure to these highly bioactive substances will inevitably continue. Hence the interest in the current study to look also at distributions of these compounds in the office dusts.

3. Materials and methods

3.1 Sample collection

Samples of dust were collected from Parliament buildings in a total of 8 countries (Austria, Denmark, Finland, Germany, Italy, Netherlands, Sweden and UK) during the latter part of 2000. In the case of the Netherlands, 3 samples were also collected from the offices of the popular computer/internet provider XS4all. Details of the samples are given in Table 1 below.

In all cases, samples of dust were obtained from the bags of vacuum cleaners in regular use for the purpose of cleaning the buildings in question, with the full co-operation of the staff involved and full permission wherever necessary. Wherever possible, samples were collected from dusts arising from specific rooms or areas of the buildings in question, although this was not always possible.

Dust was emptied from the vacuum cleaner bags either directly into pre-cleaned (acid and solvent washed) 1 litre glass bottles (amber, wide-necked with paper-lined screw cap), or on to clean aluminium foil to allow discard of large pieces of debris. In the latter case, every effort was made to avoid contact with the dust and to minimise the time for which the dust was exposed to the air. Samples sorted in this way were then immediately transferred to pre-cleaned glass bottles for storage.

3.2 Sub-sampling

All samples were initially returned to the Greenpeace Research Laboratories, University of Exeter (UK) for sub-sampling. Separate sub-samples were taken from each sample for analysis of brominated flame retardants and organotin compounds (other than for one sample, for which

Sample number	**Country**	**Location**	**Date collected**	**Sample analysed for…**	
				BFRs	OTs
HD0003	Netherlands	Parliament, The Hague – offices and stairs with carpet	08-06-00	✓	✓
HD0004	Finland	Parliament, Helsinki – offices in East wing	05-00	✓	✓
HD0005	Sweden	Parliament, Stockholm – House of Representatives	28-05-00	✓	✓
HD0006	Italy	Senato (Senate)	07-00	✓	✓
HD0007	Italy	Palazzo Marini	07-00	✓	*
HD0008	Denmark	Eigtved Pakhus, Copenhagen - venue for OSPAR 2000	14-07-00	✓	✓
HD0009	Denmark	Christiansborg (Parliament), Copenhagen	31-07-00	✓	✓
HD0010	Netherlands	XS4all, internet provider, Diemen – sales	06-00	✓	✓
HD0011	Netherlands	XS4all, internet provider, Diemen – helpdesk	06-00	✓	✓
HD0012	Netherlands	XS4all, internet provider, Diemen – server room	06-00	✓	✓
HD0013	Austria	Parliament, Vienna – from offices and corridors	04-10-00	✓	✓
HD0014	Austria	Parliament, Vienna – from offices with carpets	04-10-00	✓	✓
HD0015	Germany	Reichstag (Parliament), Berlin	09-00	✓	✓
HD0016	Germany	Reichstag (Parliament), Berlin	19-10-00	✓	✓
HD0017	UK	Parliament, London – Commons Chamber	01-01	✓	✓
HD0018	UK	Parliament, London – Serjeant at Arms offices	01-01	✓	✓

Table 1: details of office dust samples collected, with an indication of the analyses conducted to date. *insufficient sample material for organotin analyses. Analyses for PCBs and chlorinated paraffins still underway.

insufficient material was available for organotin analysis – see below). Each sample was emptied onto a section of pre-cleaned (pentane washed) aluminium foil and transferred to separate pre-cleaned (acid and solvent washed) 100ml glass bottles using solvent washed forceps. Care was taken in each case to ensure that the samples, often heterogeneous mixtures of particle sizes and fibres, remained fully mixed during the sub-sampling, so as not to select for any particular particle size range at that stage. To ensure this, fine dust which settled from each sub-sample portion on to the foil during sub-sampling was transferred directly to the appropriate 100ml bottle by pouring from the foil.

3.3 Analysis for brominated flame retardants

Sub-samples for analysis of brominated flame retardants and PCBs were forwarded to the laboratories of the Netherlands Institute for Fisheries Research (RIVO, Ymuiden). On receipt, all samples were sieved to remove all particles > 1000um before Soxhlet extraction for 6 hours with a 3:1 v/v mixture of hexane and acetone. The extract was cleaned on an aluminium hydroxide column and through silica gel before being acidified with sulphuric acid. The organic fraction was separated, spiked with PCB-112 as an internal standard and evaporated to a final volume of 1ml. Extracts were analysed using gas chromatography/mass spectrometry (GC/MS), operated in negative chemical ionisation (NCI) mode using both a 15m DB-5 column (for quantification of deca-BB and deca-BDE only) and a 50m CP Sil 8 column (for quantification of all other congeners).

Concentrations of the following congeners were determined in each sample:-

- Polybrominated diphenylethers (PBDEs) – tri- (BDE-28), tetra- (BDE-47, 66, 71, 75, 77), penta- (BDE-85, 99, 100, 119), hexa- (BDE-138, 153, 154), hepta- (BDE-190) and deca- (BDE-209).
- Polybrominated biphenyls (PBBs) – di- (BB-15), tetra- (BB-49, 52), penta- (BB-101), hexa- (BB-153, 155) and deca- (BB-209).
- Hexabromocyclododecane (HBCD)
- Tetrabromobisphenol-A (TBBPA) – plus its methyl derivative.

Limits of detection varied from sample to sample and from congener to congener, depending on sample size and method/instrument sensitivity respectively. For PBDEs, detection limits ranged from 0.12 to 0.62 ug/kg (ppb) on a dry weight basis. For PBBs, detection limits ranged from 0.18 to 2.8 ppb, for HBCD from 2.5 to 12.8 ppb, for methyl-TBBPA from 0.1 to 0.5 ppb and for TBBPA itself from 0.5 to 3 ppb.

3.4 Analysis for organotin compounds

Sub-samples for organotin analyses were forwarded to the laboratories of GALAB (Geestacht, Germany). All samples were sieved to remove all particles with dimensions greater than 65 um prior to analysis. Organotin compounds were extracted using a mixture of methanol and hexane (with NaBEt4) and quantified by gas chromatography/atomic emission detection (GC/AED) according to accredited methods after DIN EN 17025. Concentrations of the following compounds were determined in each sample:-

- Butyltins - mono-, di-, tri- and tetrabutyltin (MBT, DBT, TBT and TeBT respectively)
- Octyltins - mono- and di-octyltin (MOT and DOT respectively)
- Tricyclohexyltin (TCHT)
- Triphenyltin (TPT)

Limits of detection for all organotin compounds were 1 ug tin cation/kg dry weight of sample in each case.

4. Results

4.1 Brominated flame retardants

Concentrations of brominated flame retardants in dust samples are shown in Tables 2 and 3 below.

Brominated diphenylethers were found in all of the 16 dust samples analysed (Table 2). Residues of BDE-47 (tetra-), 99 (penta-), 100 (penta-), 153 (hexa-) and 209 (deca-) were detected in all samples. BDE-71, 77, 119 and 190 were below limits of detection in all samples. Other BDE congeners were found in some samples but not others.

Predominant in each sample was decabromodiphenyl ether (deca-BDE, or BDE-209). Levels of deca-BDE varied from 0.26-6.9 mg/kg (ppm) dust, with the highest levels in the two samples from the Italian Parliament buildings (Senato, 6.9 ppm; Palazzo Marini, 4.6 ppm). Elevated levels of deca-BDE were also found in one of the two samples each from the UK (4.5 ppm) and German (1.5 ppm) Parliament buildings, as well as in the sample from the Finnish (1.1 ppm), Dutch (0.8 ppm) and Swedish Parliaments (0.7 ppm).

Highest levels of BDE-99 (penta-) were found in dust from Italy's Palazzo Marini (0.17 ppm), though levels in dusts from the Dutch (0.13 ppm) and Finnish (0.16 ppm) Parliaments were also relatively high. Lowest concentrations (0.010-0.015 ppm) were found in the three samples from the offices of XS4all and in one of the two samples from the German Parliament (0.012 ppm). Total concentrations for penta-BDE (sum of concentrations for congeners BDE-85, 99, 100 and 119) ranged from 0.012 to 0.204 ppm, with the same pattern of distribution as for BDE-99 alone.

Concentrations of brominated biphenyls (PBBs), HBCD and TBBPA are given in Table 3. BB-209 (deca-) was found in all but one sample (below limits of detection in the Swedish Parliament building dust sample). The most abundant congener, appearing in all samples, is listed in Table 3 as possibly BB-169, though the possibility cannot be ruled out that this peak results from the presence of another, unidentified brominated compound with the same retention time. None of the other congeners (including BB-15, 49, 52 and 101) were present in any of the samples at above limits of detection.

Concentrations were lower than those for BDEs, as expected. Among the highest levels of BB-209 were again recorded in dust samples from Parliament buildings in Netherlands (0.015 ppm) and Italy (0.013-0.014 ppm), although the concentration in dust from the OSPAR 2000 venue in Denmark (0.017 ppm) was also relatively high. The highest level of all samples (0.018 ppm) was determined for one of the samples from the Dutch internet provider, XS4all. As noted above, the order of magnitude higher concentrations for PBB congener 169 may have resulted from interference from another, as yet unidentified, organobromine compound.

The brominated flame retardant hexabromocyclododecane (HBCD) was found in 13 of the 16 samples analysed to date, often at levels of a similar order as those recorded for deca-BDE (0.009-3.7 ppm). Of the Parliament dusts, highest levels were found in samples from the Austrian (1.8 ppm), German (0.82 and 0.94 ppm) and UK (0.98-3.7 ppm) Parliament buildings. Relatively high levels were also found in 2 of the 3 dust samples from the offices of XS4all

Sample	**Country**	**Concentration of individual brominated diphenylether congeners (ug/kg dust, ppb)**														
		Tri-	**Tetra-**					**Penta-**				**Hexa-**			**Hepta-**	**Deca-**
		28	**47**	**66**	**71**	**75**	**77**	**85**	**99**	**100**	**119**	**138**	**153**	**154 ***	**190**	**209**
HD0003	Netherlands	<0.16	97	<0.16	<0.16	0.49	<0.17	7.4	130	30	<0.16	3.5	48	11	<0.16	800
HD0004	Finland	1.6	180	2.4	<0.60	<0.60	<0.62	7.5	160	36	<0.59	1.9	22	9.4	<0.60	1100
HD0005	Sweden	0.95	78	1.6	<0.36	<0.36	<0.38	3.1	68	19	<0.36	<0.36	9.8	5	<0.36	700
HD0006	Italy 1	2.8	89	2.3	<0.26	<0.26	<0.27	3.3	59	15	<0.26	2.3	21	5.4	<0.26	6900
HD0007	Italy 2	1.5	110	2.7	<0.20	<0.20	<0.21	11.2	170	23	<0.20	4.7	59	9.2	<0.20	4600
HD0008	Denmark 1	0.47	21	0.48	<0.29	<0.29	<0.30	1.6	27	5	<0.28	<0.28	6.1	5.2	<0.29	470
HD0009	Denmark 2	0.91	39	0.88	<0.26	<0.26	<0.27	2.2	40	8.3	<0.26	0.76	8.5	3	<0.26	330
HD0010	Netherlands	<0.16	15	0.58	<0.16	<0.16	<0.17	0.9	15	3.9	<0.16	0.89	17	2.3	<0.16	490
HD0011	Netherlands	<0.17	10	0.5	<0.17	<0.17	<0.18	<0.06	10	2.5	<0.17	<0.17	6.3	<0.43	<0.17	330
HD0012	Netherlands	<0.12	17	0.69	<0.12	<0.12	<0.12	0.99	14	3.4	<0.12	0.49	13	1	<0.12	260
HD0013	Austria 1	2.8	66	2.3	<0.03	<0.04	<0.04	5.5	68	26	<0.03	1.6	26	11	<0.08	340
HD0014	Austria 2	3.0	64	<0.04	<0.04	<0.04	<0.04	5.4	72	23	<0.04	<0.04	18	9.4	<0.09	510
HD0015	Germany 1	6.9	80	17	<0.04	<0.04	<0.04	2.9	50	14	<0.04	<0.04	17	6.3	<0.09	1500
HD0016	Germany 2	<0.03	8.6	<0.03	<0.03	<0.03	<0.03	0.87	12	3.4	<0.03	<0.03	4.8	<0.07	<0.06	290
HD0017	UK 1	16	320	36	<0.09	<0.09	<0.10	6.6	92	22	<0.09	<0.09	31	8.9	<0.2	4500
HD0018	UK 2	<0.08	19	<0.08	<0.08	<0.08	<0.08	2.2	29	8.2	<0.08	<0.08	11	<0.19	<0.17	550

Table 2: Concentrations of polybrominated diphenylethers (PBDEs, µg/kg dust, ppb) in sixteen samples of dust.

*value is for BDE-154 and BB-153 combined

Sample	Country	Concentration (ug/kg, ppb)								
		Brominated biphenyls						HBCD	TBBP-A	methyl-TBBP-A
		BB-15	BB-49	BB-52	BB-101	BB-169*	BB-209			
HD0003	Netherlands	<0.30	<0.29	5	<0.1	95	15	300	5	<0.1
HD0004	Finland	<1.1	<1.1	<3	<0.5	11	4.8	<12.8	<3	<0.5
HD0005	Sweden	<0.67	<0.64	<2	<0.3	9.8	<2.8	45	<2	<0.3
HD0006	Italy 1	<0.49	<0.47	<1	<0.2	48	14	8.6	<1	<0.2
HD0007	Italy 2	0.05	<0.35	<1	<0.1	75	13	<4.3	<1	<0.1
HD0008	Denmark 1	<0.53	<0.51	<1	<0.2	8	17	20	<1	<0.2
HD0009	Denmark 2	<0.49	<0.47	<1	<0.2	20	5.3	19	<1	<0.2
HD0010	Netherlands	<0.30	<0.28	<1	<0.1	73	2.8	840	<1	<0.1
HD0011	Netherlands	<0.32	<0.31	<1	<0.1	33	3	1400	<1	<0.1
HD0012	Netherlands	<0.22	<0.21	<0.5	<0.1	110	18	<2.5	<0.5	<0.1
HD0013	Austria 1	<0.07	<0.06	<0.09	<0.05	<18	7.2	1800	33	<0.06
HD0014	Austria 2	<0.08	<0.07	<0.10	<0.06	<12	5.3	1800	15	<0.07
HD0015	Germany 1	<0.08	<0.07	<0.10	<0.06	<23	50	940	20	<0.07
HD0016	Germany 2	<0.06	<0.05	<0.07	<0.05	<6.6	7.6	820	4.6	<0.05
HD0017	UK 1	<0.18	<0.17	<0.22	<0.14	<11	39	3700	47	<0.15
HD0018	UK 2	<0.15	<0.14	<0.19	<0.12	<24	10	980	12	<0.13

Table 3: Concentrations of polybrominated biphenyls (PBBs), hexabromocyclododecane (HBCD) and of tetrabromobisphenol-A and its methyl derivative (TBBP-A and methyl-TBBP-A) (µg/kg dust, ppb) in sixteen samples of dust.

*possibly interference from another, unidentified brominated compound

Sample	**Country**	**Concentration (ug/kg, ppb)**								
		MBT	DBT	TBT	TeBT	MOT	DOT	TCHT	TPT	Total organotins
HD0003	Netherlands	1720	891	19.6	<1	293	67.5	<1	<1	2991.1
HD0004	Finland	850	350	34.6	<1	256	34.3	<1	<1	1524.9
HD0005	Sweden	517	180	3.9	<1	81.4	10.4	<1	<1	792.7
HD0006	Italy 1	182	188	13.8	<1	62.3	44.2	<1	<1	490.3
HD0007	Italy 2	*	*	*	*	*	*	*	*	*
HD0008	Denmark 1	992	172	34.8	<1	234	24.2	<1	<1	1457
HD0009	Denmark 2	1050	292	33.5	<1	261	26.7	<1	<1	1663.2
HD0010	Netherlands	1540	814	187	<1	265	76.2	<1	<1	2882.2
HD0011	Netherlands	1670	480	46.6	<1	832	140	<1	<1	3168.6
HD0012	Netherlands	286	342	38.9	<1	15.1	4.3	<1	<1	686.3
HD0013	Austria 1	836	530	21.9	<1	318	74.4	<1	<1	1780.3
HD0014	Austria 2	2390	464	26.5	<1	390	76.4	<1	<1	3346.9
HD0015	Germany 1	1060	497	17.9	<1	337	57.1	<1	<1	1969
HD0016	Germany 2	2050	713	18.9	<1	581	116	<1	<1	3478.9
HD0017	UK 1	1150	543	8.5	<1	202	103	<1	<1	2006.5
HD0018	UK 2	708	278	9.1	<1	146	29.7	<1	<1	1170.8

Table 4: Concentrations of organotin compounds (ug/kg dust, ppb) in 16 dust samples.

* insufficient material available to include analysis for organotin compounds

(0.84-1.4 ppm). Tetrabromobisphenol-A was present above detection limits in 7 of the 16 samples analysed to date, with the highest values in dusts from the Austrian (0.015 and 0.033 ppm) and UK (0.012 and 0.047 ppm) Parliaments.

4.2 Organotins

Concentrations of organotins in dust samples from Parliament buildings in all eight countries are reported in Table 4 above. Data for the three samples of dust from the computer/internet provider XS4all are also included. Significant levels of organotins were found in all of the samples, including those from Austria, Germany and UK for which brominated flame retardant data are not yet available.

Total organotin concentrations (butyl and octyltins combined) varied from 0.49 ppm (one sample from the Italian Senato building) to 3.48 ppm (one of two samples from the German Reichstag building). High levels were also found in dusts from Parliament buildings in Austria (3.34 ppm) and the Netherlands (2.99 ppm), as well as in two of the three samples from the offices of XS4all (2.88-3.17 ppm).

In all but two cases (the two least contaminated samples), total organotins were dominated by monobutyltin (MBT), with lower levels of DBT and even lower levels of TBT. Monooctyltin (MOT) was in all cases more abundant that DOT, though levels (0.015-0.83 ppm) were generally lower than for the MBT. Triphenyltin, as expected, was not found in any of the dust samples at levels above detection limits (<0.001 ppm). This was also the case for tetrabutyltin (TeBT) and tricyclohexyltin (TCHT).

5. Discussion

Deca-BDE was consistently the most abundant PBDE congener identified in the dust samples. Its predominance over lower brominated congeners including tetra- and penta-BDE undoubtedly reflects the greater current market usage of deca-BDE. It is interesting to note that the BDE congener profile of the dusts from numerous locations in the current study show some parallels with the profiles for congeners in air samples collected in workplaces by Sjodin *et al.* (2001). These latter data are interesting in that the authors reported far higher air concentrations of the high molecular weight, low volatility deca-BDE than for the lighter, lower brominated congeners, perhaps indicative of the significance of the fine particle bound fraction in indoor air.

The report published by Allsopp *et al.* (2001) confirms the possible contribution to total deca-BDE in the dust samples from treated carpet fibres. Nevertheless, it is likely that a variety of sources, including furnishings, electronic equipment, cabling, etc. will have contributed to different degrees in different buildings. Clearly we cannot use the data from the current study to deduce anything about what the balance of sources may be.

What is clear, however, is that exposure to office dust may well be a significant route of exposure to deca-BDE. A number of studies have noted the presence of this congener in human blood, despite its relatively short residence time in the body. Continuous or repeated exposure to contaminated dusts in the indoor environment, by inhalation, skin contact or other routes, could represent a contributory mechanism to maintaining this level of background exposure. Clearly this aspect deserves further investigation.

Although similarities are apparent in BDE congener profiles, there are also some consistent differences between BDE congener profiles determined by Sjodin *et al.* (2001) and those from the current study, most notably the relative abundance of hexa-BDE in Sjodin *et al.*'s air samples, compared to tetra- and penta-BDE in the Parliament dusts. This may simply reflect different sources of BDEs in each case. Indeed, close comparison of congener profiles for individual dust samples reveals some substantial differences.

The lower levels of tetra- and penta-BDE (approximately 1-2 orders of magnitude below those of deca-BDE) do not detract from the significance of the presence of these compounds given their high propensity for bioconcentration in human tissues. The presence of high ppb concentrations in dusts from office buildings as opposed to recycling/shredding plants, is clearly cause for concern. Similar concerns arise from the presence of HBCD in several of the samples, also at high ppb concentrations.

The current study has also demonstrated the continued presence of some PBB congeners, albeit at lower concentrations than the PBDEs. Presumably the identification of PBBs in the dusts results from the presence of relatively old furnishings, paints, electrical equipment, etc. manufactured before the market shift away from these substances.

Somewhat surprisingly, TBBP-A was identified in fewer than half of the samples analysed, and then at concentrations at the lower end of levels recorded for diphenyl ether congeners. This is in contrast to the findings of Sjodin *et al.* (2001) regarding relative concentrations in air; those authors reported equivalent air concentrations of BDE-209 and TBBP-A in the electronics recycling plant, and comparable levels in air from other workplace environments. It is possible that discrepancies arise from differences in the types of electronic and other equipment present in the locations samples in the two studies, or perhaps differences in the balance of contributions between electronic equipment and furnishings. It is also possible, however, simply that TBBP-A partitions more readily into the gaseous or very fine particulate phase in the air, and has a lower tendency to settle into accumulated dust deposits.

In addition to the brominated flame retardants quantified, at least one unidentified brominated compound was consistently isolated from the dust samples (listed as BB-169 in Table 3). Several samples contained numerous unidentified organobromine compounds, some yielding peak areas suggestive of substantial concentrations (see, e.g. Leonards *et al.* 2001) Further investigations aimed at identifying not only this substance, but the potential presence of other brominated and chlorinated compounds in this sample type, could be extremely informative.

Organotin compounds were present in the dust samples analysed at levels of a similar order to those of the PBDEs, i.e. high ppb – low ppm concentrations. Again, previous studies published by Oekotest (2000) and Allsopp *et al.* (2000, 2001) have demonstrated the possible contribution from carpets or vinyl (PVC) floor coverings. Given the very widespread use of these substances as polymer additives, however, other sources are also likely to be significant. The apparent predominance of MBT over DBT and of DBT over TBT is suggestive of origins as stabiliser usage, rather than biocide treatment of textiles (which normally favours TBT).

For both brominated flame retardants and organotins, it is important to consider the potential for confounding factors to have influenced the results obtained. Some of the vacuum cleaners, or dust bags, used to collect the samples may well have contained brominated and/organotin compounds as additives and these may, therefore, have made some contribution to overall levels. The process of drawing air through the machines may have further enhanced the concentrations of non-particle-bound contaminants from the air onto the surface of the dust particles. In both cases, however, the potential contribution from these sources can probably be considered minimal, if at all significant. This judgement is supported by the observation that samples collected using the same make and model of vacuum cleaner but from different parts of a building (e.g. such as from the Austrian Parliament) yielded quite different levels and relative abundances of organotins. Moreover, as the samples were collected opportunistically using a range of models (and ages) of vacuum cleaners, and therefore of dust bags, it would have proven extremely difficult, if not impossible, to have controlled for these potential confounding factors.

6. Conclusions

The results to date confirm the widespread contamination of dusts with a variety of brominated flame retardants and organotins, both groups of persistent organic pollutants which have been prioritised for substitution under the OSPAR strategy for hazardous substances. This study provides further evidence that our exposure to these compounds is continuous and ubiquitous, even in the general office environment.

Although we cannot use these data to identify specific sources of these compounds, they undoubtedly enter the dusts as a result of leaching or abrasion from a wide variety of furnishings and/or electronic equipment in the vicinity from which the samples were collected, either via adsorption from residues in the air or directly attached to fine particles. In addition, although this study does not provide (and indeed was not intended to provide) data from which exposure could be estimated, the results clearly demonstrate the possibility for continuous exposure to these compounds especially via inhalation or contact with the skin.

For substances which are known to accumulate in the body, such as penta-BDE and some of the organotins, such exposure may contribute further to the overall body burden. Moreover, for substances thought to be less bioaccumulative, such as deca-BDE, their presence in dusts at ppm levels may well help to explain why they are nevertheless detectable in a significant proportion of the general population as background contaminants. It may also explain the somewhat wider environmental distribution of PBDEs in general than may be predicted on the basis of molecular mobility.

The effects which may result from such continuous exposure are not known, but the presence of deca-BDE in dusts may mean that everyone, not just workers in electronics manufacturing and/or recycling plants, will carry some levels of these highly persistent chemicals around in their bodies. Furthermore, irrespective of the potential for exposure to these hazardous substances through contact with dusts in the workplace, the ultimate disposal of dusts from vacuum cleaners and other sources may represent a significant input of these and other hazardous substances into waste repositories and, ultimately, the surrounding environment.

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