

Exposure to Flame Retardants in Electronics Recycling Sites

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Waste electrical and electronic equipment (WEEE) contains various hazardous substances such as flame retardants (FRs). Inhalation exposures to many FRs simultaneously among WEEE recycling site workers have been little studied previously. The breathing zone airborne concentrations of five brominated FR compounds tetrabromobisphenol-A (TBBP-A), decabromodiphenylethane (DBDPE), hexabromocyclododecane, 1,2-bis(2,4,6-tribromophenoxy)-ethane, hexabromobenzene, and one chlorinated FR (Dechlorane Plus®) were measured at four electronics recycling sites in two consecutive years. In addition, concentrations of polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls were measured. The three most abundant FRs in personal air samples were PBDEs (comprising mostly of decabromodiphenylethane, TBBP-A, and DBDPE, with mean concentrations ranging from 21 to 2320 ng m⁻³, from 8.7 to 430 ng m⁻³, and from 3.5 to 360 ng m⁻³, respectively. At two of the sites, the emission control actions (such as improvements in ventilation and its maintenance and changes in cleaning habits) proved successful, the mean levels of FRs in personal samples being 10–68 and 14–79% of those from the previous year or alternatively below the limit of quantification. At the two remaining sites, the reductions in FR exposures were less consistent. The concentrations reported may pose a health hazard to the workers, although evaluation of the association between FR exposure and adverse health effects is hampered by lacking occupational exposure limits. Therefore, the exposures should be minimized by adequate control measures and maintaining good occupational hygiene practice.

Keywords: decabromodiphenylethane; electrical waste; electronic waste; polybrominated diphenyl ethers; tetrabromobisphenol-A

INTRODUCTION

Production of electrical and electronic equipment (EEE) is one of the fastest growing areas of industry. This has also resulted in proliferation of waste electrical and electronic equipment (WEEE). In the European Union (EU), the treatment, recovery, and disposal of WEEE are regulated by the directive on WEEE issued

in 2002 (Directive 2002/96/EC, 2003). The directive is aimed at reducing the production of WEEE and promoting the reuse, recycling, and recovery of waste from a variety of consumer products. The impact of waste batteries and accumulators on the environment is addressed by the EU directive on batteries and accumulators, issued in 2006 (Directive 2006/66/EC, 2006). The first certification program for electronics recycling was announced in early 2010 in North America [Environment News Service (ENS), 2010]. The new e-Stewards Certification is intended to ensure safe and ethical disposal of unwanted discarded

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electronics. The annual generation of WEEE is estimated at 40 million metric tons worldwide (Sepúlveda *et al.*, 2010). In Finland, the amount was ~53 metric tons in 2008, corresponding to 9.6 kg per person (Statistics, Finland, 2009). More than 95% of the WEEE in Western Europe consists of large and small household appliances and information technology (IT), telecommunications, and consumer equipments (Widmer *et al.*, 2005).

One of the challenges in the WEEE industry is the presence of hazardous substances in waste that may pose significant risks to human and environmental health. Such materials include heavy metals (e.g. lead, cadmium, mercury) and flame retardants (FRs) and other additives in plastics [e.g. polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol-A (TBBP-A), phthalates]. Toxic materials in WEEE can cause cancer, reproductive disorders, endocrine disruption, and many other health problems if the WEEE stream is not properly managed (Tsydenova and Bengtsson, 2011). The WEEE Directive in the EU is complemented by a directive from 2003 on the restriction of the use of certain hazardous substances in new production of EEE (Directive 2002/95/EC, 2003). Of the brominated flame retardants (BFRs), PBDEs [with the exception of decabromodiphenyl ether (deca-BDE)] and polybrominated biphenyls (PBBs) were banned as of 1 July 2006.

PBDEs, PBBs, and TBBP-A have been widely produced and used as FRs since the 1970s. At present, the main BFRs in commercial use are TBBP-A, hexabromocyclododecane (HBCD), and deca-BDE (Kemmlein *et al.*, 2009). TBBP-A is the largest volume BFR used in printed circuit boards and plastics in EEE [European Brominated Flame Retardant Industry Panel (EBFRIP), 2009]. HBCD's main use is in expanded and extruded polystyrene foams for thermal insulation in buildings and in upholstery textiles. A minor application is in high impact polystyrene for EEE and appliances (Alaee *et al.*, 2003; Covaci *et al.*, 2006). Deca-BDE is used in many plastics such as thermoplastics for home or office furnishing, appliance casings, polyurethane (PUR) foam, and synthetic fabrics (WHO/ICPS, 1994). A comprehensive overview of BFRs in the environment has been given by de Wit (2002).

Occurrence of BFRs at WEEE recycling sites as well as the occupational exposures among electronics recycling personnel have been reported in Sweden (Sjodin *et al.*, 1999, 2001; Pettersson-Julander *et al.*, 2004; Julander *et al.*, 2005a,b; Thuresson *et al.*, 2006), Switzerland (Morf *et al.*, 2005), USA (Cahill *et al.*, 2007), China (Bi *et al.*, 2007; Yuan *et al.*, 2008; Zhao *et al.*, 2009; Zhang *et al.*, 2010), and Japan (Takigami *et al.*, 2006). There are little published data on Finland.

The work of Mäkinen *et al.* (2009) describes respiratory and dermal exposures to organophosphorus-based FRs and TBBP-A among WEEE recyclers in Finland.

The current study was aimed at determining the occurrence of and occupational exposures to brominated and chlorinated FRs in WEEE recycling sites in Finland. The effectiveness of control measures implemented to reduce airborne FR concentrations was examined by occupational hygiene surveys on two consecutive years, 2008 and 2009. The sites chosen for the study consisted of two commercial workplaces and one social enterprise where workers dismantled and sorted WEEE and operated crushing processes. In a third commercial workplace, the workers dealt exclusively with discarded batteries and accumulators. This paper reports measurements of respiratory exposure to brominated and chlorinated FRs.

METHODS

Work processes at recycling sites

Two commercial recycling sites (A and B) and the social enterprise site (C) carried out manual disassembly and sorting of WEEE and selective removal of hazardous and valuable components. The waste was mainly from small household appliances, IT, and consumer equipment and electrical tools and toys. Those sites also performed mechanical size reduction, for example, by separating television (TV) cathode ray tubes from the plastic covers and collecting the fractions and sending them on for further processing. Commercial Site A did additional crude crushing of TV set glass and plastic fractions. Commercial Site B carried out a supplementary separation of the tube, based on laser technique, removing the lead-containing back pane from the rest of the tube. This semiautomatic operation took place in fume cupboards. The glass fractions were then mechanically ground and sent for further processing. Site B also performed mechanical separation of metals based on their magnetic properties. Site D processed discarded batteries and dry accumulators which were recycled using an enclosed dry process for crushing and grinding the products. The recovered metal fractions were sent for further processing. The material volume handled was the same in both years within each site but differed among the four sites.

Measures to reduce exposures

Measures to reduce exposures to FRs were suggested after the first year's survey. The recyclers were asked to improve the maintenance of the ventilation at the sites. Particular attention was to be paid

to the air pressure ratio between the factory shed and the adjacent restrooms, lunchrooms, or offices. Sorting and dismantling areas should be equipped with local exhaust ventilation or if possible with fume cupboards. Furthermore, cleaning of working areas should be stepped up by vacuum cleaning or wet brushing of floors and other surfaces instead of dry brushing. The workers at Sites A and B used 3M 9322 Protective Respirators (Berkshire, UK) during particularly dusty operations. At Site C, none of the workers used respirators, whereas four of the six workers at Site D used Clean-air Basic 2000 respirators (dual flow with HEPA P3 filter and full face mask; Birmingham, UK). The importance of the adequate use, maintenance, and storage of personal protective equipment was emphasized. The measurements were, however, all collected outside the respirator and therefore, the airborne concentrations represent the highest possible inhalation exposure.

Identification of FRs

Surface dust samples were collected from floors of the recycling sites directly into pre-cleaned sample vials except at Site D where samples were taken from the dust bag of an industrial vacuum cleaner. These qualitative dust samples, one representative sample per recycling site, were collected for preliminary screening of FRs occurring in the workplace atmospheres originating from the EEE waste. A subsample of ~50 mg of each dust sample was extracted without pre-cleaning according to the method described for the personal air samples. The final extract was reconstituted in 200 µl of nonane. The subsequent analyses were performed using a 1:100 dilution of the extract by gas chromatography–mass spectrometry (GC–MS) as described in the supplementary material (available at *Annals of Occupational Hygiene* online).

Recruits and sample collection for quantitative analyses of airborne FRs

Thirty-four exposed workers were recruited from the four recycling sites. Eleven workers participated in both years. The workers were either sorters or dismantlers, or both, or process controllers. As the work processes were done in open factory sheds, it was not possible to distinguish separate areas for the different tasks. Air was monitored during one work shift. Measurements were started on the second day of the working week after a production stop during the weekend. Altogether 45 personal (breathing zone) air samples were collected. The sampling periods ranged from 191 to 408 min. FRs were collected

by pumping air through an Occupational Health and Safety Administration (OSHA) versatile sampler (OVS; 226-30-16, SKC Ltd, Eighty Four, PA, USA) at a flow rate of 2.5 l min⁻¹. The OVS contained a glass fibre filter to collect FRs in the particulate phase and two XAD-2 resin layers, 270 and 140 mg (backup), to collect compounds in the vapour phase. The layers were separated by PUR foam. After sampling, the samplers were sealed and stored in glass jars at +4°C until extraction, which was done within 1 week. The vapour and particulate phases were not separated in the analysis.

Chemicals

Methyl-*tert*-butyl ether (MTBE) and hexane were purchased from Rathburn Chemicals (Walkerburn, Scotland, UK), acetone from Merck (Darmstadt, Germany), and methanol from Lab-Scan (Gliwice, Poland). These solvents were either of HPLC or of *pro analysi* grade. Purum grade (>99.0%) nonane was obtained from Sigma-Aldrich Chemie (Steinheim, Germany). The reference standards and carbon-13-labelled standards used as internal standards are listed in supplementary Table S1 (available at *Annals of Occupational Hygiene* online).

Extraction procedure

Extraction of the FRs from the OVSs was carried out in an accelerated solvent extractor ASE 100® System (Dionex, Sunnyvale, CA, USA). The extraction conditions were a modification of the program for polychlorinated biphenyl analysis suggested by the instrument's manufacturer (Dionex, 1966) and the solvent was MTBE:hexane (1:1, v v⁻¹). The samples were spiked with carbon-13-labelled internal standards prior to extraction. The extract was then evaporated to near dryness using a TurboVap® LV (Zymark, Hopkinton, MA, USA) evaporator and reconstituted to 100 µl with nonane containing 50 ng PBB 30 and 20 ng PBB 101 as injection standards and was analysed without further cleanup. The extraction procedure is described in more detail in the supplementary material (available at *Annals of Occupational Hygiene* online).

Identification and quantitative analysis of FRs

The structures of the FRs in the qualitative dust samples were characterized by GC–MS. Full-scan spectra were obtained using a triple quadrupole mass spectrometer Quattro Micro GC (Waters Corp., Milford, MA, USA) connected to an Agilent 6890N gas chromatograph (Agilent Technologies, Santa Clara, CA, USA). The modes used were electron impact,

positive chemical ionization, and negative chemical ionization (NCI). Some of the sample extracts were additionally analysed with a high-resolution mass spectrometer (VG AutoSpec Q, Fisons Instruments, Essex, UK) for clarification of the elemental composition.

Analyte quantification by the isotope dilution technique using the internal standard method was conducted by gas chromatography–NCI mass spectrometry in the selected ion recording mode. In cases where no carbon-13-labelled compounds were available, the responses were normalized against the responses of the injection standards PBB 30 and PBB 101 and quantified using the external standard method and the results were calculated as the arithmetic means of these responses. Calibration curves with at least six data points were used for quantification. All compounds showed linearity within the concentration range for the calibration curves. Compounds in the exposure assessment samples were quantified using the calibration curve from analyte-spiked OVSs. Supplementary Tables S2, S3, S4a, and S4b (available at *Annals of Occupational Hygiene* online) contain details of chromatographic, mass spectrometric, identification, and quantification procedures.

Quality control

For each sampling series, two samplers were mounted on sample holders, caps were removed, then straight away closed, and then removed for field blanks. Two extraction reagent blanks, one with the extraction cell only and one including the OVS, were prepared with every set of actual samples extracted. The levels of the analysed FRs were all below the limit of quantification (LOQ) in the reagent, OVS as well as field blanks. Recovery was determined by spiking the OVS with the analytes. The overall analytical recovery ranged from 54 to 125%. The instrumental limit of detection was defined as a concentration with a GC/MS response distinguishable from the background with a signal-to-noise ratio of 3:1. The LOQ was derived from the extraction standard calibration curves and was generally three times or more the instrumental limit of detection. The LOQ values calculated for a 6-h air sample ranged from <0.005 to 2.5 ng m^{-3} . Details of the recovery and LOQ parameters are presented in supplementary Tables S4a and S4b (available at *Annals of Occupational Hygiene* online).

For breakthrough studies, six stationary samples were collected simultaneously at one recycling site (A) and the sampling was stopped for parallel samples after 2, 4, and 6 hours. The layers for collection of particulates and vapour phase as well as the

backup section were separated and analysed in a similar fashion as the exposure assessment samples. The vapour phase layer consisted of the first XAD-2 resin and PUR plug and the backup section of the second XAD-2 resin and PUR plug.

RESULTS AND DISCUSSION

Identification of FRs

Seven brominated compounds or groups of compounds and one chlorinated compound were identified in all surface dust samples by combining data from full-scan mass spectra and elemental composition data. Comparison with the mass spectra and retention times of the pure standards of the compounds was used to corroborate the identification. The brominated FRs were PBDEs, TBBP-A, decabromodiphenylethane (DBDPE), HBCD, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), hexabromobenzene (HBBE), and PBBs. The chlorinated compound was the 12-chlorine FR Dechlorane Plus® (DP). To the best of our knowledge, this is the first report on WEEE recycler inhalation exposures to eight different FRs derived from a single sampling and extraction procedure with subsequent analysis by GC–MS.

Analytical aspects

FRs have been previously collected by devices consisting of a glass fibre filter combined with a PUR foam plug (Sjödén *et al.*, 2001; Björklund *et al.*, 2004; Remberger *et al.*, 2004; Moeckel *et al.*, 2010), XAD resin (Hoh *et al.*, 2005), or an Empore SDB-XD disk (Inoue *et al.*, 2006). Glass fibre filters and PUR foam plugs have also been used in a passive air sampler configuration (Abdallah and Harrad, 2010). The OVS, used in our study, as used in the study of Mäkinen *et al.*, 2009 retained satisfactorily all but one of the compounds determined. Results for the 6-h sample revealed that PBDEs, PBBs, γ -isomer of HBCD (γ -HBCD), *syn*-isomer of DP, DBDPE, and BTBPE were fully retained in the particulate-phase (filter) section of the sampler. TBBP-A and HBBE were retained in equal amounts on the filter and in the first XAD-2 layer. Eighteen and 4% of the respective total contents were found in the backup section. The *anti*-isomer of DP was not quantitatively retained in the sampler as 35% of the total content was detected in the backup section. The DP concentrations, calculated as the sum of the *syn*- and *anti*-isomers, are therefore to be regarded as ‘minimum amount present’ (Melcher *et al.*, 1978). The concentrations in these stationary samples were comparable to those in the personal air samples. Therefore, we concluded that saturation of the personal samplers did not occur.

FRs have been extracted from different samplers by various methods as reviewed by Kemmlein *et al.* (2009). These comprise vigorous shaking, ultrasonication, Soxhlet extraction, and microwave-assisted or accelerated solvent extraction. Solvents such as toluene, tetrahydrofuran, acetonitrile, propanol (Kemmlein *et al.*, 2009), dichloromethane (Sjödén *et al.*, 2001), hexane (Björklund *et al.*, 2001), acetone:hexane (1:1, v v⁻¹), dichloromethane:acetone (1:1, v v⁻¹) (Björklund and Nilsson, 2000; Lacorte and Guillamon, 2008; Wang *et al.*, 2010), methanol (Inoue *et al.*, 2006), and MTBE (Chu *et al.*, 2005) have yielded high extraction efficiencies. In our study, we chose the accelerated solvent extraction procedure to isolate the compounds of interest. The extraction capacities of toluene, a 10% solution of methanol in toluene and MTBE:hexane (1:1, v v⁻¹), for the analytes were evaluated. The last-mentioned solvent mixture provided optimum recoveries as shown in supplementary Tables S4a and S4b in the supplementary material (available at *Annals of Occupational Hygiene* online). The accelerated solvent extraction method was chosen because it was fast to use and provided a cleanup of the extract. The satisfactory recoveries confirmed the justification of the choice.

The FRs addressed by this study were quantified with sufficient specificity, with one exception by the GC/MS method. The method lacks stereoisomer specificity for HBCD and hence, the results are expressed as total HBCD. The γ -isomer of HBCD was used as

quantification standard. Technical HBCD consist primarily of γ -HBCD (75–89%) but it also contains α - and β -HBCD (Covaci *et al.*, 2006). The γ -isomer also predominates in air samples (de Wit *et al.*, 2009), whereas α -HBCD is the main form in biological samples (Covaci *et al.*, 2006). PBB congeners were quantified using the average response factors of hexa and deca reference standards (details of the quantification procedure are presented in the Supplementary material available at *Annals of Occupational Hygiene* online) and hence, these results should be treated as semiquantitative.

Exposure measurements

The arithmetic mean concentrations (ng m⁻³) of the FRs in personal air samples are presented in Fig. 1. The details of the results of airborne concentrations, arithmetic means, medians, and ranges are presented in supplementary Tables S5 and S6 in the supplementary material (available at *Annals of Occupational Hygiene* online).

The range of mean levels at recycling Sites A and B was 1.3–305 ng m⁻³ and <LOQ to 2320 ng m⁻³, respectively (Supplementary Table S5 is available at *Annals of Occupational Hygiene* online). The concentrations were of the same order of magnitude in the samples from Sites C and D (Supplementary Table S6 is available at *Annals of Occupational Hygiene* online), <LOQ to 44 ng m⁻³ and <LOQ to 36 ng m⁻³, respectively. The three most abundant

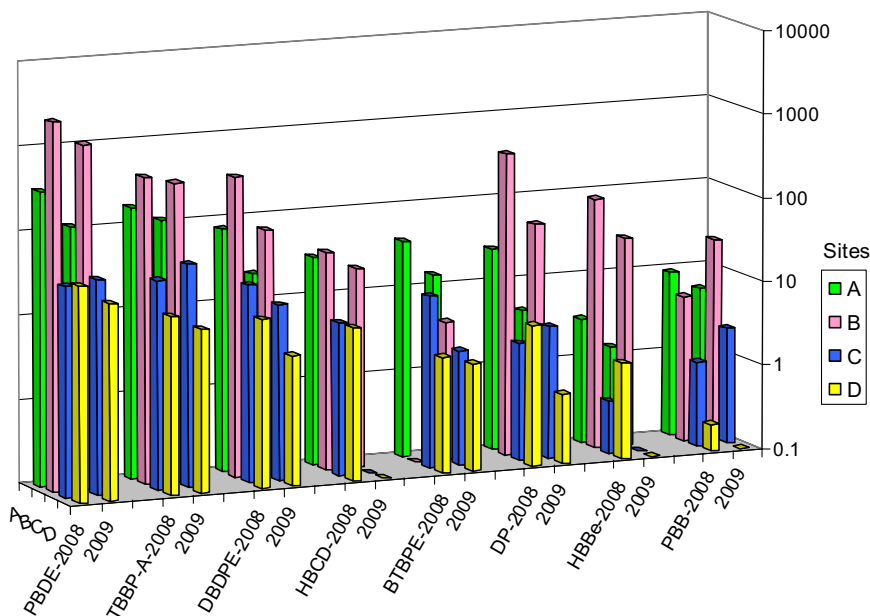


Fig. 1. Concentrations (ng m⁻³), expressed as arithmetic means, in personal air samples of seven brominated FRs and one chlorinated FR.

FRs at each site were PBDEs (comprising mostly of deca-BDE), TBBP-A, and DBDPE. The difference in concentrations at Sites A, B, C, and D was explained partly by working conditions at the sites and partly by the material volumes and type of materials processed. Recyclers A, B, and C processed the same type of material but the volumes at Sites A and B were 5–10 times higher compared with that processed at Site C. The material processed at Site D contained less plastics and therefore less FRs.

Control measures to diminish exposure levels were undertaken to various degrees at all four recycling sites. None of Recyclers A, C, and D were able to install local exhaust ventilation or fume cupboards in the dismantling lines. At Site A, a full-time cleaner was employed and a new floor covering was laid facilitating cleaning. At site D, four of the six workers used Clean-air Basic respirators. Filters were installed for the exhaust air and care was taken not to recirculate the air from the work premises. A new, less dust creating feeder line to the crushing and grinding machine for sorted batteries and accumulators was installed. Effectiveness of the remedial actions was evident at Sites A and D in the results of the follow-up study in 2009. The mean levels of FRs in personal samples were 10–68% of those in 2008 at Site A. At Site D, the corresponding figures were 14–79% with the exception of the concentrations for HBCD, HBBe, and PBB. The concentrations of these compounds were below the LOQ in 2009. At Sites B and C, the reductions in FR exposures were less consistent.

The total concentrations of the PBDE congeners analysed in 2008 and 2009 ranged from 4.6 to 5200 ng m⁻³ in personal samples (Supplementary Tables S5 and S6 are available at *Annals of Occupational Hygiene* online). The concentrations at Sites C and D were of the same order of magnitude, 18–66 and 6.8–51 ng m⁻³, respectively, in 2009, whereas higher, ~5-fold to 50-fold, concentrations were measured at Sites A and B. Eleven congeners were identified and quantified: the tetra (BDE 47), penta (BDE 99, 100), hexa (BDE 153), hepta (BDE 183), octa (BDE 196, 197, 203), nona (BDE 206, 207, 208), and deca (BDE 209). The congener pattern was similar at Sites A, B, and D, with BDE 209 accounting for an average of 81% in 2008 and 91% in 2009 of the sum of PBDEs. The pattern differed at Site C where BDE 209 constituted 66% (2008) and 62% (2009) of the total concentration. The concentration profiles of the remaining congeners are presented in Table S7 in the supplementary material (available at *Annals of Occupational Hygiene* online). Concentrations of PBDEs comparable to those at Site C (Sjödin *et al.*, 2001; Pettersson-Julander *et al.*, 2004), on the one hand,

and Sites A and D (Julander *et al.*, 2005b; Takigami *et al.*, 2006; Cahill *et al.*, 2007), on the other, have been reported in studies conducted in Sweden, Japan, and the USA. Concentrations as high as those observed at Site B have not been reported elsewhere.

The TBBP-A concentrations in personal samples in 2008 and 2009 varied between <LOQ and 1100 ng m⁻³. In 2009, the lowest mean exposure to TBBP-A, 8.7 ng m⁻³, was observed at Site D where no plastics and circuit boards were handled. Corresponding levels at Sites C, A, and B were 44, 110, and 345 ng m⁻³, respectively. Sjödin *et al.* (2001) and Takigami *et al.* (2006) reported concentrations similar to those detected at Sites C and D, whereas Mäkinen *et al.* (2009) reported a concentration of 11900 ng m⁻³ which is 10 times the highest reading at Site B.

The DBDPE concentrations in personal samples in 2008 and 2009 ranged from <LOQ to 1700 ng m⁻³. DBDPE exposures followed the same pattern as the exposures to TBBP-A. The lowest mean concentrations were measured at Site D in 2009, 3.5 ng m⁻³, and the highest at Site B, 79 ng m⁻³. The figure was 12 ng m⁻³ for Site C and 21 ng m⁻³ for Site A. Lower levels have been reported from Sweden, ~1 ng m⁻³ and below (Pettersson-Julander *et al.*, 2004; Julander *et al.*, 2005b).

The ranges of mean concentrations of HBCD, BTBPE, DP, and HBBe in personal samples were <LOQ to 23, 1.9–14, 0.67–53, and <LOQ to 30 ng m⁻³, respectively, in 2009. The highly chlorinated DP occurs in two stereoisomers of which the anti-form constitutes ~80% of the total (Hoh *et al.*, 2006). This was clearly reflected in the measurements in the present study, with the anti-form comprising ~78% of the sum of anti- and syn-stereoisomers. Taking into account the breakthrough results, the percentage is probably higher. There are only a few previous reports on the occurrence of these FRs in WEEE recycling environments. Comparable levels have been reported by Takigami *et al.* (2006) for HBCD and Sjödin *et al.* (2001) and Julander *et al.* (2005b) for BTBPE.

The workers' mean exposures to PBBs ranged from <LOQ to 24 ng m⁻³ in 2009. No PBB was observed at recycling Site D. The highest concentration was detected at Site B. The deca congener and the sum of the nona congeners accounted for ~50 and 35%, respectively, of the total concentrations, with remaining 15% being made up of the sum of hexa and octa congeners. The congeners were characterized as hexa-, octa-, and nona-brominated isomers but were not further identified. No previous data are available on recycler exposures to PBBs. Li *et al.* (2009) developed a method for the determination of PBBs in electronics samples but did not find detectable levels.

Exposures and health concerns

In this study, the highest exposure levels at all recycling sites were recorded for PBDEs, TBBP-A, and DBDPE. In addition, concentrations of DP comparable to those of DBDPE were detected at Site B. The evaluation of potential associations between FR exposures and adverse health effects is hampered by the scarcity of occupational exposure limits (OELs). There are currently no OELs for the compounds in focus in Finland. A way to get around the lack of OELs might be to describe inhalation exposures in relation to toxicological data postulated by Cahill *et al.* (2007). Thus, exposures could be compared with a reference dose (RfD) based on entries in the Integrated Risk Information System [Integrated Risk Information System (IRIS), 2010]. An RfD is an estimate of the level of exposure over a lifetime that is not expected to result in adverse health effects. Examples of RfDs for PBDEs are 7×10^{-3} mg kg⁻¹ day⁻¹ (BDE 209), 2×10^{-4} mg kg⁻¹ day⁻¹ (BDE 153), and 1×10^{-4} mg kg⁻¹ day⁻¹ (BDE 99 and BDE 47). Applying Cahill's concept and the RfD to BDE 209, concentrations observed in this study in 2009 yield a mean hazard quotient of $0.2\text{--}10 \times 10^{-3}$ or 1/100–1/5300 of the level of any health concern (Supplementary Table S8 is available at *Annals of Occupational Hygiene* online).

CONCLUSIONS

Seven brominated FRs and one chlorinated FR were detected in personal air samples at all recycling sites. The concentrations spanned 4 orders of magnitude. The three most abundant FRs were PBDEs (comprising mostly of deca-BDE), TBBP-A, and DBDPE. Given the lack of OELs for the FRs and considering the multiple exposure scenarios, it is important to minimize the exposure. The results showed that adequate control measures and good occupational hygiene practice at recycling sites diminish the workers' exposure to the FRs.

SUPPLEMENTARY DATA

Supplementary data can be found at the online version of this paper at <http://annhyg.oxfordjournals.org/>.

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REFERENCES

- Abdallah MA, Harrad S. (2010) Modification and calibration of a passive air sampler for monitoring vapor and particulate phase brominated flame retardants in indoor air: application to car interiors. *Environ Sci Technol*; 44: 3059–65.
- Alaee M, Arias P, Sjödin A *et al.* (2003) An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ Int*; 29: 683–9.
- Bi X, Thomas GO, Jones KC *et al.* (2007) Exposure of electronics dismantling workers to polybrominated diphenyl ethers, polychlorinated biphenyls, and organochlorine pesticides in South China. *Environ Sci Technol*; 41: 5647–53.
- Björklund E, Müller A, von Holst C. (2001) Comparison of fat retainers in accelerated solvent extraction for the selective extraction of PCBs from fat-containing samples. *Anal Chem*; 73: 4050–3.
- Björklund E, Nilsson T. (2000) Pressurised liquid extraction of persistent organic pollutants in environmental analysis. *Trends Anal Chem*; 19: 434–45.
- Björklund J, Tollbäck P, Hiärne C *et al.* (2004) Influence of the injection technique and the column system on gas chromatographic determination of polybrominated diphenyl ethers. *J Chromatogr A*; 1041: 201–10.
- Cahill TM, Groskova D, Charles MJ *et al.* (2007) Atmospheric concentrations of polybrominated diphenyl ethers at near-source sites. *Environ Sci Technol*; 41: 6370–7.
- Chu S, Haffner GD, Letcher RJ. (2005) Simultaneous determination of tetrabromobisphenol A, tetrachlorobisphenol A, bisphenol A and other halogenated analogues in sediment and sludge by high performance liquid chromatography-electrospray tandem mass spectrometry. *J Chromatogr A*; 1097: 25–32.
- Covaci A, Gerecke AC, Law RJ *et al.* (2006) Hexabromocyclododecanes (HBCDs) in the environment and humans: a review. *Environ Sci Technol*; 40: 3679–88.
- de Wit CA. (2002) An overview of brominated flame retardants in the environment. *Chemosphere*; 46: 583–624.
- de Wit CA, Herzke D, Vorkamp K. (2009) Brominated flame retardants in the Arctic environment—trends and new candidates. *Sci Total Environ*; 408: 2885–918.
- Dionex. (1966) Application note ASE 322. Sunnyvale, CA: Dionex Corporation.
- Directive 2002/95/EC. (2003) Directive of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment. Official Journal of the European Union L 37/19 EN 13.2.2003. Luxembourg: Publication Office of the European Union.
- Directive 2002/96/EC. (2003) Directive of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE). Official Journal of the European Union L 37/24 EN 13.2.2003. Luxembourg: Publication Office of the European Union.
- Directive 2006/66/EC. (2006) Directive of the European Parliament and of the Council of 6 September 2006 on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC. Official Journal of the European Union L 266/1 EN 26.9.2006. Luxembourg: Publication Office of the European Union.

- Environment News Service (ENS). (2010) Certification for electronic waste recycling gathers support. News release dated February 10, 2010. Available at <http://www.ens-newswire.com/ens/feb2010/2010-02-10-093.html>. Accessed 17 February 2010.
- European Brominated Flame Retardant Industry Panel (EBFRIP). (2008) Most used flame retardant TBBPA approved by EU. Available at www.ebfrip.org/. Accessed 4 April 2009.
- Hoh E, Zhu L, Hites RA. (2005) Novel flame retardants, 1,2-bis(2,4,6-tribromophenoxy)ethane and 2,3,4,5,6-pentabromoethylbenzene, in United States' environmental samples. *Environ Sci Technol*; 39: 2472–7.
- Hoh E, Zhu L, Hites RA. (2006) Dechlorane plus, a chlorinated flame retardant, in the Great Lakes. *Environ Sci Technol*; 40: 1184–9.
- Inoue K, Yoshida S, Nakayama S *et al.* (2006) H. Development of stable isotope dilution quantification liquid chromatography-mass spectrometry method for estimation of exposure levels of bisphenol A, 4-tert-octylphenol, 4-nonylphenol, tetrabromobisphenol A, and pentachlorophenol in indoor air. *Arch Environ Contam Toxicol*; 51: 503–8.
- Integrated Risk Information System (IRIS). (2010) Toxicological Review. Available at <http://www.epa.gov/IRIS/>. Accessed 23 August 2010.
- Julander A, Karlsson M, Hagström K *et al.* (2005a) Polybrominated diphenyl ethers-plasma levels and thyroid status of workers at an electronic recycling facility. *Int Arch Occup Environ Health*; 78: 584–92.
- Julander A, Westberg H, Engwall M *et al.* (2005b) Distribution of brominated flame retardants in different dust fractions in air from an electronics recycling facility. *Sci Total Environ*; 350: 151–60.
- Kemmlein S, Herzke D, Law RJ. (2009) Brominated flame retardants in the European chemicals policy of REACH—regulation and determination in materials. *J Chromatogr A*; 1216: 320–33.
- Lacorte S, Guillamon M. (2008) Validation of a pressurized solvent extraction and GC-NCI-MS method for the low level determination of 40 polybrominated diphenyl ethers in mothers' milk. *Chemosphere*; 73: 70–5.
- Li Y, Wang T, Hashi Y *et al.* (2009) Determination of brominated flame retardants in electrical and electronic equipments with microwave-assisted extraction and gas chromatography-mass spectrometry. *Talanta*; 78: 1429–35.
- Mäkinen MS, Mäkinen MR, Koistinen JT *et al.* (2009) Respiratory and dermal exposure to organophosphorus flame retardants and tetrabromobisphenol A at five work environments. *Environ Sci Technol*; 43: 941–7.
- Melcher RG, Langner RR, Kagel RO. (1978) Criteria for the evaluation of methods for the collection of organic pollutants in air using solid sorbents. *Am Ind Hyg Assoc J*; 39: 349–61.
- Moeckel C, Gasic B, Macleod M *et al.* (2010) Estimation of the source strength of polybrominated diphenyl ethers based on their diel variability in air in Zurich, Switzerland. *Environ Sci Technol*; 44: 4225–31.
- Morf LS, Tremp J, Gloor R *et al.* (2005) Brominated flame retardants in waste electrical and electronic equipment: substance flows in a recycling plant. *Environ Sci Technol*; 39: 8691–9.
- Pettersson-Julander A, van Bavel B, Engwall M *et al.* (2004) Personal air sampling and analysis of polybrominated diphenyl ethers and other bromine containing compounds at an electronic recycling facility in Sweden. *J Environ Monit*; 6: 874–80.
- Remberger M, Sternbeck J, Palm A *et al.* (2004) The environmental occurrence of hexabromocyclododecane in Sweden. *Chemosphere*; 54: 9–21.
- Sepúlveda A, Schluep M, Fabrice GR *et al.* (2010) A review of the environmental fate and effects of hazardous substances released from electrical and electronic equipments during recycling: examples from China and India. *Environ Impact Assess Rev*; 30: 28–41.
- Sjödin A, Carlsson H, Thuresson K *et al.* (2001) Flame retardants in indoor air at an electronics recycling plant and at other work environments. *Environ Sci Technol*; 35: 448–54.
- Sjödin A, Hagmar L, Klasson-Wehler E *et al.* (1999) Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. *Environ Health Perspect*; 107: 643–8.
- Statistics, Finland. (2009) Municipal waste statistics. Available at http://www.stat.fi/til/jate/2008/jate_2008_2009-12-16_tau_001_fi.html. Accessed 19 August 2010.
- Takigami H, Hirai Y, Matsuzawa Y *et al.* (2006) Brominated flame retardants and brominated dioxins in the working environment and environmental emission—a case study at an electronic recycling plant. *Organohalogen Compd*; 68: 2190–3.
- Thuresson K, Bergman K, Rothenbacher K *et al.* (2006) Polybrominated diphenyl ether exposure to electronics recycling workers—a follow up study. *Chemosphere*; 64: 1855–61.
- Tsydenova O, Bengtsson M. (2011) Chemical hazards associated with treatment of waste electrical and electronic equipment. *Waste Manag*; 31: 45–58.
- Wang P, Zhang Q, Wang Y *et al.* (2010) Evaluation of Soxhlet extraction, accelerated solvent extraction and microwave-assisted extraction for the determination of polychlorinated biphenyls and polybrominated diphenyl ethers in soil and fish samples. *Anal Chim Acta*; 663: 43–8.
- WHO/ICPS. (1994) Environmental health criteria 162: brominated diphenyl ethers. Geneva, Switzerland: World Health Organization.
- Widmer R, Oswald-Krapf H, Sinha-Khetriwal D *et al.* (2005) Global perspectives on e-waste. *Environ Impact Assess Rev*; 25: 436–58.
- Yuan J, Chen L, Chen D *et al.* (2008) Elevated serum polybrominated diphenyl ethers and thyroid-stimulating hormone associated with lymphocytic micronuclei in Chinese workers from an e-waste dismantling site. *Environ Sci Technol*; 42: 2195–200.
- Zhang J, Jiang Y, Zhou J *et al.* (2010) Elevated body burdens of PBDEs, dioxins, and PCBs on thyroid hormone homeostasis at an electronic waste recycling site in China. *Environ Sci Technol*; 44: 3956–62.
- Zhao YX, Qin XF, Li Y *et al.* (2009) Diffusion of polybrominated diphenyl ether (PBDE) from an e-waste recycling area to the surrounding regions in Southeast China. *Chemosphere*; 76: 1470–6.