Near-Source Ambient Air Monitoring of Polybrominated Diphenyl Ethers

Report Prepared for the California Air Resources Board
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Abstract

Concentrations of polybrominated diphenyl ethers (PBDEs) were determined in air samples from near suspected sources, namely indoors in a computer training laboratory, indoors and outdoors at an electronics recycling facility, and outdoors at an automotive shredding/metal recycling facility. Air samples were collected using quartz filters followed by XAD-2 resin adsorbent to trap particulate and gas phase PBDEs. The samples were extracted by Soxhlet extraction and the extracts were analyzed by gas chromatography – electron capture negative ionization mass spectrometry. The results from the computer laboratory sampling showed that computers emitted decabromodiphenyl ether, while the emissions of lower brominated PBDEs was less significant when compared to concentrations in the indoor office environment when the computers were turned off. Air samples collected at the electronics recycling facility showed higher concentrations of PBDEs in the dismantling hall compared with published concentrations from other facilities. These concentrations appeared to originate from the electronics shredding activity that generated airborne particulate matter consisting of plastics. The concentrations of PBDEs outside and downwind of the building were higher than a control site, at University of California, Davis. Lastly, PBDE concentrations at the downwind fenceline of an automotive shredding/metal recycling facility were higher than an upwind perimeter site, thus demonstrating the contribution of a source to near-source downwind PBDE concentrations.

Executive Summary

Background

Polybrominated diphenyl ethers (PBDEs) are common fire retardants that have been used in various foams and electronics applications. Recently, there have been increasing concerns about the safety of exposure to these chemicals. PBDEs have been detected in human blood serum and breast milk as well as in remote geographical regions. People are being exposed to these chemicals, which are now becoming ubiquitous worldwide. Another cause for concern is that PBDEs are very hydrophobic due to the presence of a large number of bromines attached to the molecule. This high degree of hydrophobicity contributes to their ability to bioaccumulate and bioconcentrate in both humans and wildlife. Lastly, there are significant structural similarities between PBDEs and polychlorinated biphenyls (PCBs), which are known to exert adverse health impacts.

The objectives of this research were to: 1) refine sampling and analysis methods for PBDEs and 2) determine the air concentration of PBDEs in areas near point sources of PBDEs to better determine potential exposure of people to these chemicals as well as the impact of these operations on the local PBDE air concentrations. The test sites included: 1) a computer training laboratory in a public office building, 2) an electronics recycling facility, and 3) an automotive shredding/metal recycling facility.

Methods

Outdoor air samples were collected with Andersen High-Volume air samplers at a flow rate of approximately 30 m^3/hour. The samplers were equipped with a quartz microfiber filter followed by XAD-2 adsorbent to trap gas phase and blow-off. The filter + XAD-2 combination was chosen in preference to filter + polyurethane foam (PUF) configuration since the large PUF adsorbents created interferences that prevented the determination of decabromodiphenyl ether. Indoor air samples were collected in a similar fashion except a "low volume" air sampler was used that could collect approximately 0.9 m^3 of air per hour and the filter size and amount of XAD-2 resin were correspondingly smaller. The samples were extracted by Soxhlet extraction and then polar interferences were removed by passing the extract through a silica gel column.

The PBDEs in the sample extracts were determined by gas chromatography- electron capture negative chemical ionization (ECNCI) mass spectrometry. The ECNCI mass spectrometry was able to achieve lower detection limits compared to simple electron ionization (EI) that is commonly used in mass spectrometry. Using GC-ECNCI mass spectrometry with selected ion monitoring, we were able to achieve instrumental detection limits in the range of 0.08 to 2.81 picograms per microliter (pg/µl) of sample extract.

Three field sites near suspected point sources of PBDEs were sampled in addition to a control site at the University of California, Davis. The first site was a computer laboratory in a public office building where air samples of 24 hours in duration were collected on 8 days. Two conditions, namely "computers on" and "computers off," were sampled to estimate the contribution of computers to the PBDE loading in the office environment. The "computers off" condition provided an estimate of PBDE background in an office building. The second site sampled was an electronics recycling facility, where both indoor and outdoor air samples were collected. In this case, the indoor air samplers were located within 2 m of the shredding equipment, thus the observed concentrations would represent a "worse case exposure scenario."

Air samples of 8 hours in duration were collected on three days during business hours with varying degrees of activity. Lastly, ambient air samples were collected upwind and downwind of an automotive shredding/metal recycling facility. These 24-hour air samples were collected on one day with the shredder shut down and two days with shredding operations being conducted. Local meteorological data were collected at both the electronics recycling facility and the automotive shredding/metal recycling facility to discern the contribution of the site to near-source PBDE concentrations by comparing upwind and downwind conditions.

Results

The results from the three sampling campaigns clearly showed that PBDE concentrations in the air at the three test sites exceeded the PBDE concentrations at the outdoor control site at the University of California, Davis, where the average sum of PBDE congeners was 58 picograms of PBDE per cubic meter of sampled air (pg/m^3).

The indoor air sampling in the computer laboratory showed elevated PBDE concentrations when the computers were turned on compared to when the computers were turned off. Concentrations were as high as 1550 pg/m^3 for PBDE 47. For most PBDE congeners, the increase was relatively minor (<2-fold increase) with the exception of decabromodiphenyl ether (PBDE 209), which increased about 5-fold. These data suggest that computers may be a significant source of PBDE 209 in the office environment. These data also compare with other published studies which have shown indoor concentrations of PBDEs up to 1,800 pg/m^3.

The indoor and outdoor air sampling at an electronics recycling facility showed that air concentrations of PBDEs were greatly elevated within the electronics dismantling hall compared to outside the facility. Concentrations of PBDE 209 were as high as 833,000 pg/m^3 inside the dismantling hall and as high as 11,400 pg/m^3 outside the facility. These data suggest that the recycling activity, and shredding of circuit boards in particular, generated airborne particulate matter consisting of plastics that contain large amounts of PBDEs. Despite the highly elevated concentrations within the facility, the impact of the facility on air concentrations outside the facility appeared to be rather localized.

Lastly, air samples collected downwind of an automotive shredding facility showed elevated concentrations of PBDEs, up to 1940 pg/m^3 for PBDE 209, that were about 3- to 5- fold higher than the upwind concentrations.

Conclusions

The results of this research demonstrated methods for collecting and analyzing air samples with a great degree of sensitivity for PBDEs in indoor and near-source ambient air. This research also suggested that the impacts of the electronics recycling and automotive shredding operations on near-source downwind concentrations could be measured and compared with upwind concentrations. These near-source results and the results from the indoor monitoring at the electronics recycling facility also point to the need to further evaluate the health effects from exposure to PBDEs. The observation that PBDE concentrations were higher in an office environment than outdoors at a control site suggests that people are probably more likely to be exposed to higher PBDE concentrations in the indoor environment. Therefore, future exposure assessments should focus on the indoor environment.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been used extensively over the past three to four decades as fire retardants in most types of polymers used in electronic circuit boards, computers, TVs, housing, furniture, building materials, textiles, carpets and vehicles (automobile padding).[1-3] The increased use of PBDEs in consumer products has resulted in the ubiquitous presence of these compounds in private housing, offices, public buildings,[4-7] other work environments[8-11] and the outdoor environment.

The most frequently used PBDE mixture (54,800 tons in 1999)[1] is currently the "deca" formulation which consists of primarily decabrominated diphenyl ether along with some octa- and nona-PBDE congeners. The two other common PBDE mixtures are the pentabrominated diphenyl ethers (penta-mix; e.g. Bromkal 70-5DE) and octabrominated diphenyl ethers (octa-mix). Penta-mix technical products are used in epoxy resins, phenol resins, polyesters, polyurethane foam and textiles.[12] Octa-mix technical products are used in acrylonitrile butadiene styrene, polycarbonate and thermosets. Deca-PBDE products are used in most types of synthetic materials including textiles and polyester used for printed circuit boards and in high-impact plastics used in consumer electronics.

Flame retarded polyurethane foam (PUF) used for car seating, home furnishing and insulation etc. is the principal use of the commercial pentabromodiphenyl ether (penta-PBDE) mix which contains mainly tetra- and penta-PBDEs, particularly PBDE 47, PBDE 99 and PBDE 100 with a smaller contribution of PBDE 153, PBDE 154 and PBDE 85.[13] PBDEs comprise 5-30% by mass of the plastics and so PUF represents a significant reservoir of PBDEs.[12] This usage pattern results in PBDEs distribution throughout the indoor environment and PBDEs released by volatilization from products in service may represent an important pathway of human exposure.[14] Penta-mix was used in circuit boards until the mid-1990s.[13,15] Many of these electronics remain in service and their future disposal may be an avenue for the release of penta-mix to the environment.

The PBDE fire retardants are used as additives in polymers, but they are not chemically bonded to the plastic structure. Therefore, the PBDEs can simply volatilize from the plastic or foam and escape into the environment. The use of PBDEs as fire retardants secures an overall higher fire safety, however the presence of these compounds during waste incineration or accidental fires may result in the formation of undesirable by-products such as brominated dibenzo-p-dioxins (PBDDs) and brominated dibenzofurans (PBDFs).[16]

Ambient air concentrations of PBDEs have been reported as ranging from 5 to 300 pg/m^3 with the highest concentrations observed in urban areas.[17] Indoor workplace concentrations have been measured as high as 200,000 pg/m^3 in the air inside an electronics recycling facility.[9]

Concern regarding PBDE usage

PBDEs are highly hydrophobic (log K_{ow} values 4-10)[18] with the more brominated congeners being more hydrophobic. The high hydrophobicity of the PBDEs makes them prone to bioaccumulation in humans and wildlife.[17] PBDEs have been reported in various environmental matrices, such as an indoor[5,6] and outdoor air,[19-26] dust,[4] sediment,[27] freshwater[28-30] and marine[31-34] organisms, and in human serum[35,36] and adipose tissue.[32,37-39] The fact that PBDEs are widely distributed in the environment has raised concerns about their safety and persistence.[40]

We understand that PBDEs fall under the definition of a class of compounds called polycyclic organic matter (POM). POM is listed as a federal hazardous air pollutant and a toxic air contaminant in California.

One specific concern about the health effects of PBDEs arises from the structural similarity between both PBDEs and PCBs and thyroid hormones, namely 3,3',5-triiodothyronine (T3) and 3,3',5,5'-tetraiodothyronine (thyroxine, T4).[40] The prolonged exposure to high concentrations of PBDEs can cause serious health effects such as thyroidogenic, estrogenic, hepatic and neurodevelopmental effects.[40]

Due to the increasing concerns about the ubiquitous exposure and the toxicity of PBDEs, the European Union has phased out the penta- and octa-formulations of PBDEs.[41] In 2003, legislation was enacted in California (Assembly Bill 302, Chan) that banned the sale of products that contain either the penta- or octa-formulations as of January 1, 2008.[41] Great Lakes Chemical, one of the major producers of PBDEs will voluntarily phase out production of the penta- and octa-formulations starting in 2005.[17]

Selection of study locations

Several possible source locations were considered for air monitoring. For indoor air monitoring of PBDEs, computer training laboratories were evaluated at the University of California, Davis (UCD). However, in recent years several manufactures of personal computers have switched to alternative fire retardants and the UCD computer laboratories were found to contain these newer computers. A computer training laboratory in a public office building was found to contain computers thought to be old enough to still have been manufactured with PBDEs, although some of the PBDEs would likely have out-gassed from these computers over time. This computer laboratory was selected for indoor air monitoring.

For near-source ambient air monitoring, several possible source sites were contacted by staff of the California Air Resources Board (ARB) and evaluated for: potential (current and future) PBDE emissions, logistics of conducting near-source monitoring, and proximity of source to potential public exposure. These sources included: plastics recyclers, carpet pad recyclers, polyurethane foam manufacturers, electronics manufacturers, municipal landfills, electronics recyclers and automotive shredding/metal recycling facilities.

Electronics recycling facilities were chosen as one of the near-source industries for monitoring because of the potential for current and on-going PBDE emissions. Several electronics recyclers were contacted. A facility which lacked any air pollution control equipment was selected for near-source monitoring. This facility represented a potential worst-case scenario for PBDEs. While no air pollution controls were currently required at this facility, electronics recycling facilities exist that have installed bag houses and high efficiency filtration systems for control of particulate matter in their emissions.

The California legislation that banned the sale of products containing the penta- and the octa-formulations also directed the California Senate Office of Research (SOR) to submit a report with recommendations regarding PBDEs. The SOR report[41] notes that facilities that shred old automobiles for metal recycling may be sources of PBDEs in the environment. PBDEs may be present in the plastics, upholstery and/or foam in the automobiles. After old cars are shredded at an automotive shredding facility, the shredded metal is separated from the non-metallic materials. The non-metallic material is referred to as auto shredder fluff and it may contain PBDEs. The fluff is usually treated to make it less dusty, after which it is referred to as treated auto shredder waste. This waste is used at some landfills as a daily cover spread over municipal waste for vector control. Because of the potential for PBDE emissions from auto shredder facilities, one of these facilities was selected for air monitoring of near-source PBDE concentrations.

PBDEs in air samples

The determination of PBDEs in air samples can be conducted by either passive or active sampling techniques. The passive sampling approaches include: collecting particles with an ionizer using an aluminum collector cup; using personal sampling equipment with anodized aluminum[42]; passively collect vapors using PUF discs[22] or semipermeable membrane devices (SPMDs).[21,24,43] The active sampling approaches use a pump to pass air through the sampling matrices, typically quartz microfiber filter combined with PUF[5,7-9,19,23,25,26,44] or XAD (styrene divinylbenzene) resin,[6,11,20] to collect both the particle and gas-phase compounds. In most cases, the PUF substrate was preferred for usage, probably from an ease of operation point of view. However, the presented research discusses the limitations of PUF for sampling of the ambient air and the determination of decabrominated diphenyl ether (PBDE 209).

Project objectives

This research project was designed to determine the atmospheric concentrations of PBDEs in near-source sites with potential for human exposure.

The project consisted of the following phases:

1) Refinement of sampling and analytical procedures for the determination of PBDEs in ambient air samples. Analytical experiments were conducted on the University of California, Davis, campus to refine sampling protocols, select the best sample collection substrate, and to conduct spike-recovery trials.
2) Determination of PBDEs in a computer training laboratory in a public office building. Since computers in the laboratory were thought to contain PBDEs, this potentially represented a highly concentrated indoor air sample.
3) Determination of PBDEs in and around an electronics recycling facility. This site encompassed both indoor air sampling near the electronics shredding equipment as well as outdoor air sampling around the facility.
4) Determination of PBDEs at an automotive shredding/metal recycling facility. This site was chosen due to the potential for PBDEs in the foams and plastics of cars. Only outdoor air samples were collected at this site since all of the activity was conducted outdoors.

2. Materials and Methods

2.1 Chemicals and supplies

PBDEs are named in a similar fashion as polychlorinated biphenyls (PCBs). The abbreviation PBDE is followed by the congener number, where the International Union of Pure and Applied Chemistry (IUPAC) numbering system is used. These abbreviations will be used throughout this report.

PBDE analytical standard solution EO-5113 was purchased from Cambridge Isotope Laboratories (Andover, MA.). The mixture contained 39 PBDE congeners: three mono-PBDEs (PBDE 1, 2 and 3), seven di-PBDEs (PBDE 7, 8, 10, 11, 12, 13 and 15), eight tri-PBDEs (PBDE 17, 25, 28, 30, 32, 33, 35 and 37), six tetra-PBDEs (PBDE 47, 49, 66, 71, 75 and 77), seven penta-PBDEs (PBDE 85, 99, 100, 116, 118, 119 and 126), five hexa-PBDEs (PBDE 138, 153, 154, 155 and 166) and three hepta-PBDEs (PBDE 181, 183 and 190). The concentration of compounds in the mixture ranged from 100 pg/µl for the mono congeners to 250 pg/µl for the hepta congeners.

Authentic standards of 2,3,5,6-tetrachlorbiphenyl (PCB 65), decachlorobiphenyl (PCB 209), some individual standards of PBDEs as PBDE 1, 30, 47, 99, 100, 153, 154, 190, 203, 206, 207, 208 and ^{13}C-labeled decabromodiphenyl ether ($^{13}C_{12}$-PBDE 209) were obtained also from Cambridge Isotope Laboratories. Octabrominated diphenyl ethers PBDE 196 and 197 were purchased from Terra Chem, Inc. (Shawnee Mission, KS). PBDE 15 and unlabeled PBDE 209 were supplied by Aldrich (Milwaukee, WI.). Table 2.1 summarizes the standards used in this project.

Instrumental calibration solutions, which ranged from ~0.5 to 500 pg/µl (see Appendix A for exact concentrations), were prepared by diluting the PBDE mixtures into nanograde isooctane (Mallinckrodt Baker Inc., Paris, KY). The calibration curves consisted of 5 standards each. Octa- Nona- and Deca-PBDEs were determined in a separate analysis run (described later) and these analyses had a different calibration curves that had higher concentrations up to ~500 pg/µl. Further details about the calibration procedures are provided under Section 2.8.

Table 2.1. PBDE standards used in this study along with their source information.

Compound	Substitution Pattern	Compound	Substitution Pattern
Mono-		**Penta-**	
PBDE 1[a]	2-	PBDE 85[a]	2,2’,3,4,4’-
PBDE 2[a]	3-	PBDE 99[a]	2,2’,4,4’,5-
PBDE 3[a]	4-	PBDE 100[a]	2,2’,4,4’,6-
Di-		PBDE 116[a]	2,3,4,5,6-
PBDE 7[a]	2,4-	PBDE 118[a]	2,3’,4,4’,5-
PBDE 8[a]	2,4’-	PBDE 119[a]	2,3’,4,4’,6-
PBDE 11[a]	3,3’-	PBDE 126[a]	3,3’,4,4’,5-
PBDE 10[a]	2,6-	**Hexa-**	
PBDE 12[a]	3,4-	PBDE 138[a]	2,2’,3,4,4’,5’-
PBDE 13[a]	3,4’-	PBDE 153[a]	2,2’,4,4’,5,5’-
PBDE 15[c]	4,4’-	PBDE 154[a]	2,2’,4,4’,5,6’-
Tri-		PBDE 155[a]	2,2’,4,4’,6,6’-
PBDE 17[a]	2,2’,4-	PBDE 166[a]	2,3,4,4’,5,6-
PBDE 25[a]	2,3’,4-	**Hepta-**	
PBDE 28[a]	2,4,4’-	PBDE 181[a]	2,2’,3,4,4’,5,6-
PBDE 30[a]	2,4,6-	PBDE 183[a]	2,2’,3,4,4’,5’,6-
PBDE 32[a]	2,4’,6-	PBDE 190[a]	2,3,3’,4,4’,5,6-
PBDE 33[a]	2’,3,4-	**Octa-**	
PBDE 35[a]	3,3’,4-	PBDE 196[b]	2,2’,3,3’,4,4’,5,6’-
PBDE 37[a]	3, 4, 4’-	PBDE 197[b]	2,2’,3,3’,4,4’,6,6’-
Tetra-		PBDE 203[a]	2,2’,3,4,4’,5,5’,6-
PBDE 47[a]	2,2’,4,4’-	**Nona-**	
PBDE 49[a]	2,2’,4,5-	PBDE 206[a]	2,2’,3,3’,4,4’,5,5’,6-
PBDE 66[a]	2,3’,4, 4’-	PBDE 207[a]	2,2’,3,3’,4,4’,5,6,6’-
PBDE 71[a]	2,3’,4’,6-	PBDE 208[a]	2,2’,3,3’,4,5,5’,6,6’-
PBDE 75[a]	2,4,4’,6-	**Deca-**	
PBDE 77[a]	3,3’,4,4’-	PBDE 209[c]	2,2’,3,3’,4,4’,5,5’,6,6’-
Internal Standards			
PCB 65[a]	2,3,5,6-		
PCB 209[a]	2,2’,3,3’,4,4’,5,5’,6,6’-		
$^{13}C_{12}$ PBDE 209[a]	2,2’,3,3’,4,4’,5,5’,6,6’-		

[a] Standard from Cambridge Isotope Laboratories.
[b] Standard from Terra Chem Inc.
[c] Standard from Aldrich.

High-grade (B&J CG^2 grade) acetone and dichloromethane were obtained from Burdick & Jackson (Honeywell International, Inc., Muskegon, MI.). The dichloromethane was used for sample extraction and elution of the clean-up column. Silica gel (70-230 mesh) was obtained from Aldrich and was used for a clean-up column for the sample extracts to remove unwanted polar constituents. Sodium sulfate (10-60 mesh), which was used to dry the sample extract in the clean-up column, was obtained from Fisher Scientific (Pittsburgh, PA).

2.2 Air sampling equipment

This project employed two different types of samplers. The first was a high-volume air sampler for the collection of particulate and gas phase PBDEs in outdoor situations while the second was a “low volume” sampler which was used for indoor experiments to limit noise and disturbance of the indoor air flows.

Ambient air samples were collected using total suspended particulate (TSP) high-volume air samplers (model GBM2000H, Andersen Instruments Inc., Georgia, USA) as shown in Figure 2.1. The air intake was about 4 feet above ground. The samplers collected particulate matter onto Whatman QM-A quartz microfiber filters (20.3 × 25.4 cm, VWR Scientific, Brisbane, CA.). A fire-retardant free polyurethane foam plug (PUF, diameter 10 cm x height 10 cm, about 16.6-19.5 g, Shawnee Instruments, Inc., Village of Cleves, Ohio) or Amberlite XAD-2 resin (90 g, Supelco Inc., Bellefone, PA.) was mounted in a 9 cm wide by 6 cm high aluminum holder downstream of the filter to collect gas-phase PBDEs as well as any PBDEs that blow-off of the particulate matter trapped on the quartz filter. Since the adsorbent collects both ambient gas-phase PBDEs and blow-off PBDEs, it cannot be accurately used to discriminate between the gas-particulate distribution of the PBDEs in the ambient samples. The exhaust of the sampler was transported by aluminum ducting to approximately 16 feet from the sampler to avoid any contamination (particularly of carbon dust) from the sampler motor brushes.

Prior to sampling, the accuracy of the flows of the high-volume samplers was verified by UC Davis personnel. During sampling, the air flow through the sampler was monitored continuously by a paper disc type flow recorder. To verify the precision of the flow meters in the four samplers, each sampler’s flow meter was compared to the flow measured by the other three sampler flow meters, which included a new flow meter. No significant differences were observed between the flows measured by the different flow meters.

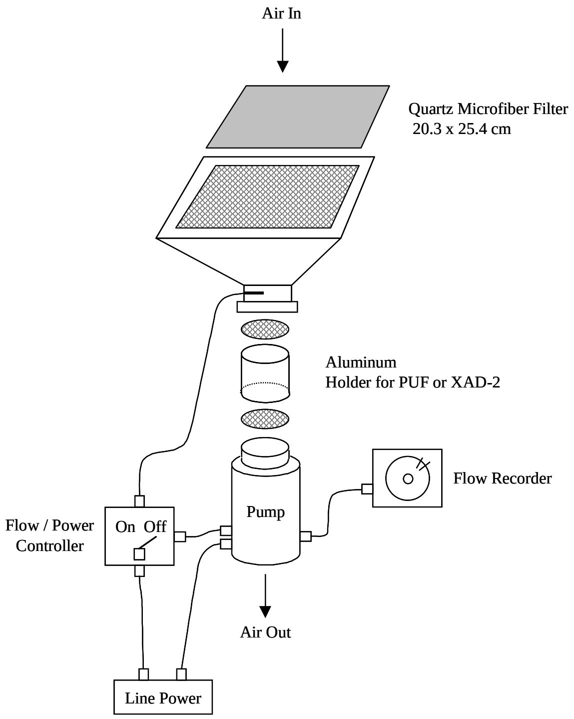

Figure 2.1. Diagram of Andersen High-Volume TSP sampler.

"Low-volume" air samplers (shown in Figure 2.2) were used for indoor air sampling to avoid disturbing the air flow patterns of the room as well as to reduce the noise of the sampler. The sampler followed the same basic design as the high-volume air sampler by collecting particulate matter onto a quartz filter (diameter 47 mm, PALL Life Sciences, Ann Arbor, MI.) and then collecting gas-phase PBDEs and blow-off on XAD-2 resin (6 g, Supelco Inc.). Each of these sample substrates were placed in stainless steel holders and connected together. The dimensions of the filter holder were 7.62 cm in diameter and 2.54 cm in height. The internal dimensions of the holder for XAD-2 adsorbent (or PUF, which was initially evaluated) were 1.6 cm in diameter and 10 cm in height. The entire sample collection apparatus was made from stainless steel to avoid any contamination from plastics and to reduce and PBDE adsorption.

Sampled air was drawn through the samplers by using a Medo VP0660 V1003-D3-0511 pump (Nitto Kohki Co. LTD, Tokyo, Japan) and the flow rate was controlled and verified during the course of sampling by using a Hastings Instruments mass flow controllers (Model No. 400, Teledyne Electronic Technologies- Hastings Instruments, Hampton, VA). The accuracy of the mass flow controllers was verified by the calibration against a DryCal DC-Lite primary flow meter (Bios International Corporation, Butler, NJ) that measured the time required to displace a given volume of air. The calibration verification was conducted using a sampling train identical to those used to collect the samples. The vacuum pumps were equipped with an activated charcoal trap, approximately 20 cm long, on the exhaust line to prevent the pumps from contributing any organic material to the air of the room that was being sampled.

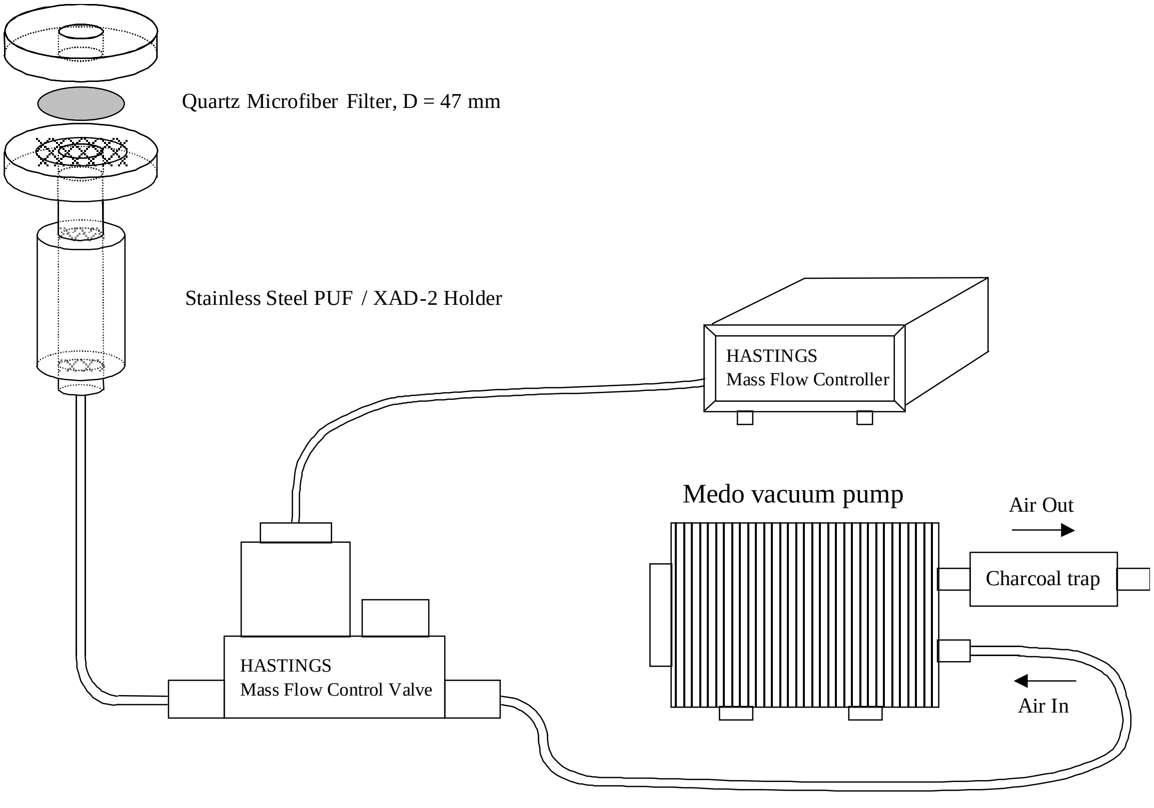

Figure 2.2. Diagram of "low volume" indoor air sampler.

2.3 Meteorological equipment

During outdoor air sampling, meteorological data were collected for wind speed, wind direction, temperature, and relative humidity. These data were collected using a portable meteorological station (Automet 466A, manufactured by Met One Instruments, Grants Pass, Oregon). Sensors were located about 12 feet above ground. The meteorological equipment was calibrated by ARB staff prior to each monitoring study and rechecked following each monitoring study to verify the accuracy of the equipment. The rechecks showed consistent accuracy.

2.4 Sample collection procedures

To reduce possible contamination, all sample collecting materials were pre-cleaned in the laboratory. Quartz filters were baked at 800°C for 8 h and stored wrapped in baked aluminum foil (baked at 550°C for 8 h) to reduce filter contact with air. PUF adsorbents were cleaned by Soxhlet-extraction with dichloromethane for 24 h. XAD-2 adsorbents were cleaned by Soxhlet extraction with acetone for 4 h followed 24 h of Soxhlet-extraction by dichloromethane. Both adsorbents, PUF and XAD-2, were dried in a vacuum desiccator and stored in baked (550^{o}C for 8 hours) amber glass containers.

The air samplers themselves were also cleaned prior to sample collection events. All parts of the outdoor air sampling units were rinsed by distilled water and methanol and air dried. Plastic parts in the sampling head were wrapped with the aluminum foil to avoid a contact of the plastics and the quartz filter. In the case of indoor air samplers, the sampling units were rinsed by dichloromethane and air dried.

The air samples were collected for different time lengths, typically 8 or 24 hours, from the four sampling sites depending on the sampling objectives. All details regarding the sampling, such as the sampling site description, the flow rate, total volume of taken air, etc, are described in each sampling case.

After sampling, the PUF and XAD-2 adsorbents were individually sealed in amber glass jars to avoid the photochemical reaction and contact with air during transport and storage. Filters were folded individually in aluminum foil and also sealed in glass jars. The samples were transported to the laboratory in the ice chest (+4°C) and stored in the freezer at -20°C until extraction.

2.5 Sample extraction procedures

All samples, regardless of the physical size of the substrate, were extracted and concentrated in a similar fashion. The sample extraction procedure consisted of Soxhlet extraction of the substrate (filter, PUF or XAD-2) for 24 h with dichloromethane followed by concentration by rotoevaporation, clean-up on a silica gel column, and nitrogen evaporation to the final sample volume.

To reduce possible contamination, all extraction glassware was washed (in hot water and Alconox soap), solvent-rinsed (three times with deionized water, acetone and hexane), and baked (8 h at 550^{o}C) and wrapped in aluminum foil before use. Further, the glassware was rinsed twice with high-quality dichloromethane immediately before use.

The Soxhlet extractions of all samples were conducted in a darkened fume hood to reduce sample exposure to light since some PBDEs, such as deca PBDE, may degrade in light. A few studies have demonstrated that PBDE 209 can be debrominated to lower brominated PBDE congeners photolytically by both UV light, and under certain conditions, by natural sunlight with half-lives ranging from 15 minutes up to 81 hours.[2] The Soxhlet extractors were additionally wrapped in aluminum foil to further shield the samples from laboratory light. The filters, PUF and XAD from the large, high-volume outdoor air samples were extracted in large Soxhlet extractors with 600 ml of dichloromethane for 24 hours. The Soxhlet extractors were run at a reflux rate of about 2 to 3 refluxes an hour. The smaller filters and XAD from indoor samples were extracted in smaller (125 ml capacity) Soxhlet extractors with 200 ml of dichloromethane for 24 h at a reflux rate of about 3 to 4 refluxes per hour. In both cases, three PTFE boiling chips were added to the round bottom flask of the Soxhlet extractor to ensure constant and even boiling of the solvent.

After the samples were extracted, the sample extract was reduced to ~3 ml by rotoevaporation. Once again, the flasks containing the samples were wrapped in aluminum foil to shield the sample extracts from laboratory light.

The sample extracts were then passed through a clean-up column to remove polar impurities, trapped particles and moisture. These clean-up columns consisted of a glass column (1 cm I.D., 30 cm length) containing 5 g of silica gel (baked at 550^{o}C for 8 hours), 1 cm of dried sodium sulfate (baked at 150°C for 8 h) and a glass wool plug (baked at 450°C for 8 h). Prior to sample introduction, the clean-up column was conditioned by 50 ml of dichloromethane. The column was then eluted with 50 ml of dichloromethane. The clean-up column was also wrapped in aluminum foil to shield the samples from light.

The sample extract was then evaporated under a gentle stream of nitrogen (99.997% purity) to a volume of 300-500 μl. At this point, 1.5 ml of isooctane was added to the sample and the sample volume was reduced to 300-500 μl. This solvent exchange step was designed to improve sample stability by reducing potential solvent evaporation during sample analysis, particularly if multiple injections of the sample were required.

2.6 Instrumental analysis conditions

2.6.1 Gas chromatographic conditions

PBDEs determinations were accomplished using an Agilent 6890 gas chromatograph coupled to an Agilent 5973 quadrupole mass spectrometer being run in electron capture negative chemical ionization mode (GC-ECNCI-MS). The samples were injected onto the instrument by a 7683 series autosampler injector. The sample injection used a pulsed splitless mode with an injection port temperature of 270°C and a pulsed pressure 20 psi, which was held for 1.5 min. The purge valve was activated 1.5 min after sample injection.

The analysis of mono- through hepta- PBDEs used a DB-5ms capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness, 5% phenyl substituted polysiloxane). Helium was used as the carrier gas at the constant column flow 1 ml/min, which corresponds to a linear velocity of about 37 cm/sec. The temperature of the GC oven was programmed as follows: isothermal at 110°C for 1 min, 12°C/min to 155°C, 2°C/min to 215°C, 3°C/min to 320°C and held at 320°C for 5 min. The total run time was 75 min.

Octa- through deca- PBDEs were analyzed on a shorter 15 meter DB-5 column (15 m × 0.25 mm i.d., 0.25 μm film thickness) to get the heavier analytes off the column more rapidly. The chromatographic conditions were: isothermal at 110°C for 1 min, 15°C/min to 320°C and held at 320°C for 10 min. The total run time was 25 minutes. In this case a pulsed pressure of only 10 psi was used.

2.6.2 Mass spectrometer conditions and optimization

Several mass spectrometer parameters were evaluated and optimized during the course of this project, but the final conditions for the electron capture negative chemical ionization (ECNCI) were: a quadrupole temperature of 150°C, an ion source temperature of 150°C, the interface temperature 280°C, methane (99.99%) as a chemical ionization moderating gas at an ion source pressure 2.5×10^{-4} torr (0.0333 Pa), an electron energy 130 eV and an emission current 300 μA. The mechanisms of ECNCI mass spectrometry and the influence of different instrumental conditions are detailed in Stemmler and Hites ([45,46]).

To obtain the maximum sensitivity in the analysis for PBDEs, ECNCI-MS instrumental parameters needed to be optimized. Experiments were conducted in a similar fashion as Eljarrat et al.[47] using the same GC-ECNCI-MS instrumentation. However, the application of the optimal instrumental parameters presented by Eljarrat et al.[47] differed from the optimal conditions determined in our laboratory. The parameters investigated and optimized were:

1) the ion source pressure (1.0×10^{-4} - 2.5×10^{-4} torr or 0.0133 to 0.0333 Pa);
2) the ion source temperature (150°-250°C);
3) the ionization electron energy (70-220 eV) and
4) the emission current (25-300 μA).

The endpoint for the optimization experiments was the intensity of ions in ECNCI-MS spectra of mono- through hepta- PBDEs.

The effect of ion source pressure was investigated by varying the source pressure from 1.0×10^{-4} to 2.5×10^{-4} torr (0.0133 to 0.0333 Pa). The ion source temperature (150°C), electron energy (130 eV) and the emission current (300 μA) were held constant during these experiments. The effect of varying the ion source temperature from 150 to 250°C was monitored while the ion source pressure (2.0×10^{-4} torr; 0.0267 Pa), electron energy (130 eV) and emission current (300 μA) were held constant. The emission current, ranging from 25 to 300 μA was investigated at the ion source temperature 150°C, ion source pressure 2.0×10^{-4} torr (0.0267 Pa) and electron energy 130 eV. Lastly, the electron energy was varied from 70 to 220 eV while the ion source temperature (150°C), ion source pressure (2.0×10^{-4} torr; 0.0267 Pa) and emission current (300 μA) where held constant.

The experiments were repeated twice and the mean values are reported herein. The obtained data have been processed by two different ways. In the first approach, the ratio of fragment ions in the spectra of the selected congeners was compared to the sum of the ions from all the fragment clusters for a given PBDE congener. Only ions with the 100% abundance in clusters were used, but the final observation should be the same. The second approach compares the absolute abundance of the ion with the 100% abundance in the ion cluster to the maximal absolute abundance of the same ion obtained in the given set of experiments.

The effect of the ion source pressure, ion source temperature, electron energy and emission current on the ECNCI-MS spectra of hexa-PBDE 153 is shown on Figure 2.3. It was observed that the ratio of fragmentation ions $[Br]^-$, $[HBr_2]^-$ and $[M\text{-}H\text{-}3Br]^-$ in the ECNCI spectra of PBDE 153 is not, or very slightly, affected by studied instrumental parameters. The same trend was confirmed in the spectra of other studied mono- through hepta-PBDEs. The major ion in spectra of all investigated PBDEs was $[Br]^-$ (*m/z* 79) with the fragmentation ratio in the range of about 0.7 - 0.9.

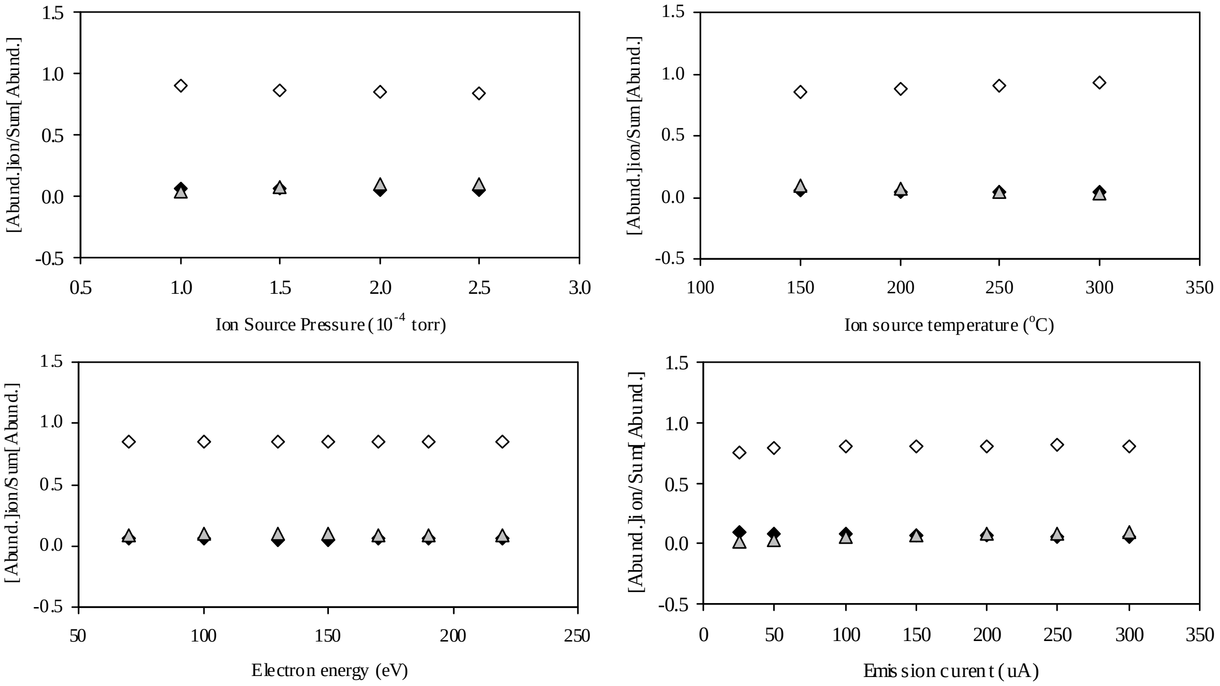

Figure 2.3. Effect of the studied instrumental parameters on the fragmentation of PBDE 153 in ECNCI-MS spectra. These graphs present the abundance of the 100% ion in the isotope cluster divided by the sum of the ion abundances from all isotope clusters (fragments) of PBDE 153. Open diamonds (◊) = $[Br]^-$, filled diamonds (♦) = $[HBr2]^-$, and triangles (Δ) = $[M-H-3Br]^-$

The effect of the studied instrumental parameters on the total abundance of ions in the ECNCI-MS spectra of PBDE 153 is presented on Figure 2.4. The total ion abundances showed very strong dependency on the mass spectrometer parameters for all studied compounds without exceptions. While the significant influence of the electron energy in the range 130-220 eV was not observed, the strong effect of the ion source pressure, ion source temperature and emission current was confirmed. The abundances of fragmentation ions increased with increasing ion source pressure and emission current. However, increasing of ion source temperature resulted in the loss of sensitivity for investigated ions.

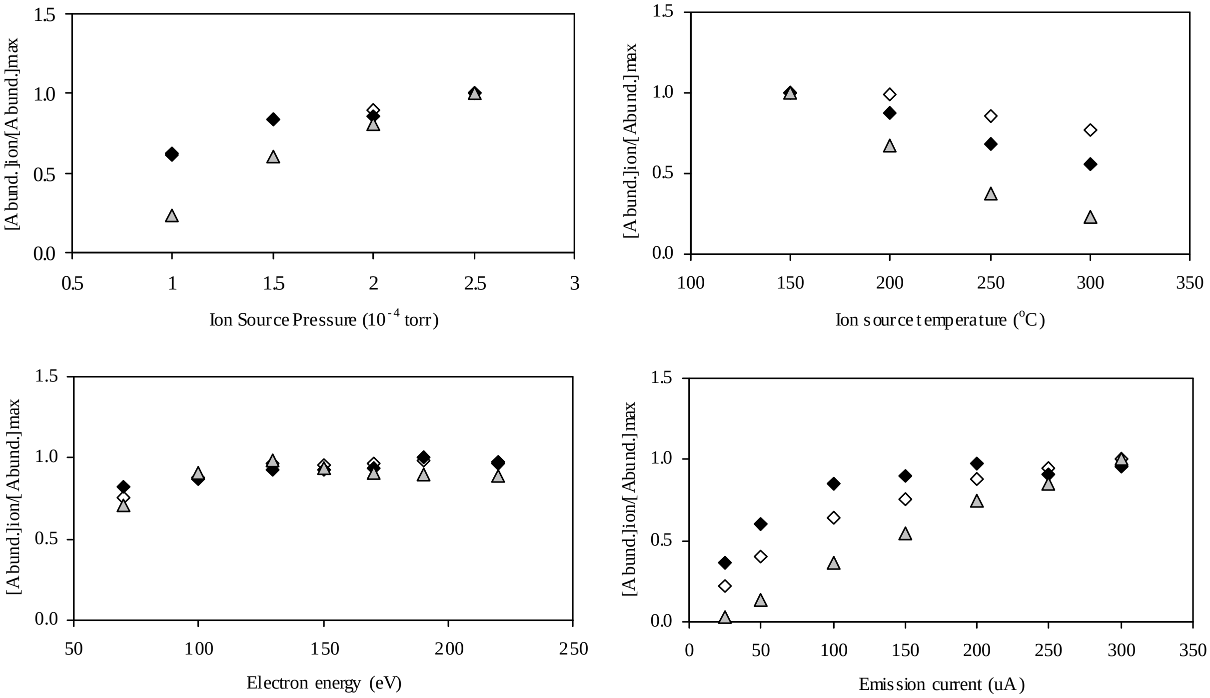

Figure 2.4. Effect of the studied instrumental parameters on the absolute ion abundances of PBDE 153 in ECNCI-MS spectra. These graphs present the abundance of the investigated ion divided by the intensity of the maximum ion (base ion) in the spectra of PBDE 153. Open diamonds (◊) = $[Br]^-$, filled diamonds (♦) = $[HBr2]^-$, and triangles (Δ) = $[M\text{-}H\text{-}3Br]^-$

Ultimately, the highest sensitivity for PBDEs homologues in ECNCI-MS mode was accomplished at the ion source pressure 2.5×10^{-4} torr (0.0333 Pa), the ion source temperature 150°C, the electron energy 130 eV and the emission current 300 μA. This observation differs from the results of Eljarrat et al.[47] where the maximum ion abundances of PBDEs congeners in NCI mode had obtained also at the highest ion source pressure 2.7×10^{-4} torr (0.0360 Pa), however, at the ion source temperature 250°C. The electron energy and emission current used by Eljarrat et al.[47] had not been described.

2.7 Mass spectra characterization of the PBDEs

Both electron-capture negative chemical ionization (ECNCI) and electron ionization (EI) were investigated for the analysis of PBDEs in this project. Figure 2.5 shows a typical EI spectrum for a PBDE while Figure 2.6 shows the ECNCI spectra for the same compound. Ultimately, ECNCI was chosen as the preferred ionization system since it provided greater sensitivity for the PBDEs. The details of EI optimization and mass spectra characterization are presented in Appendix B because EI was not used for sample quantification in this project.

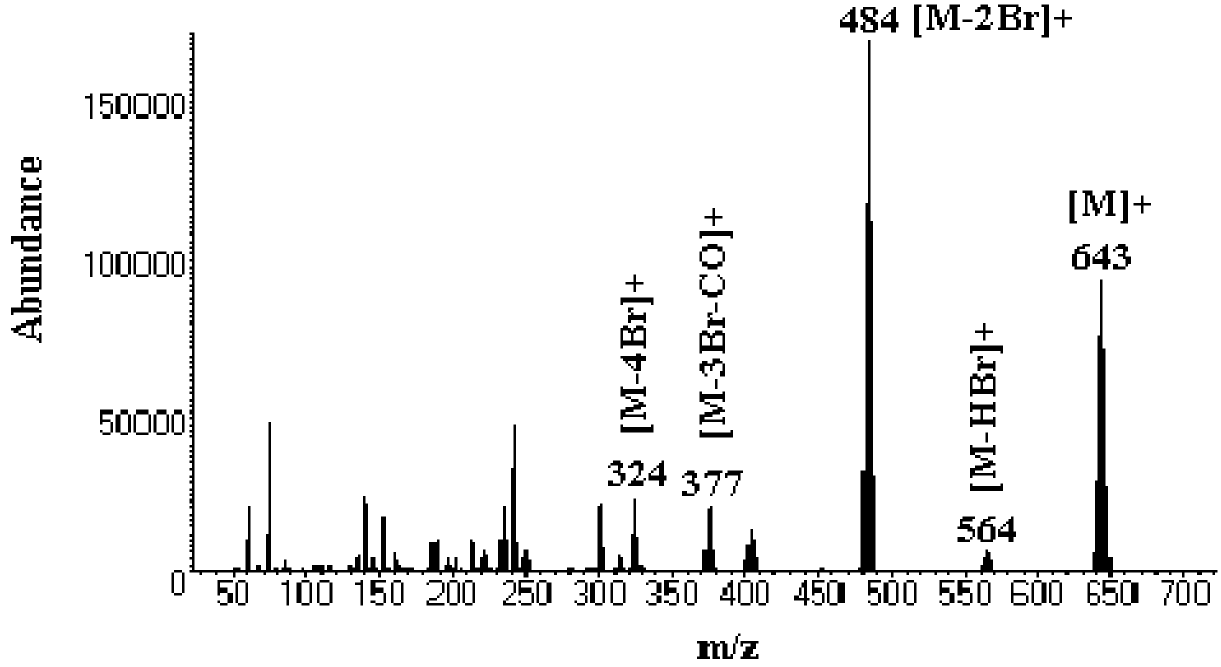

Figure 2.5. Typical electron ionization (EI) mass spectrum of PBDE 153.

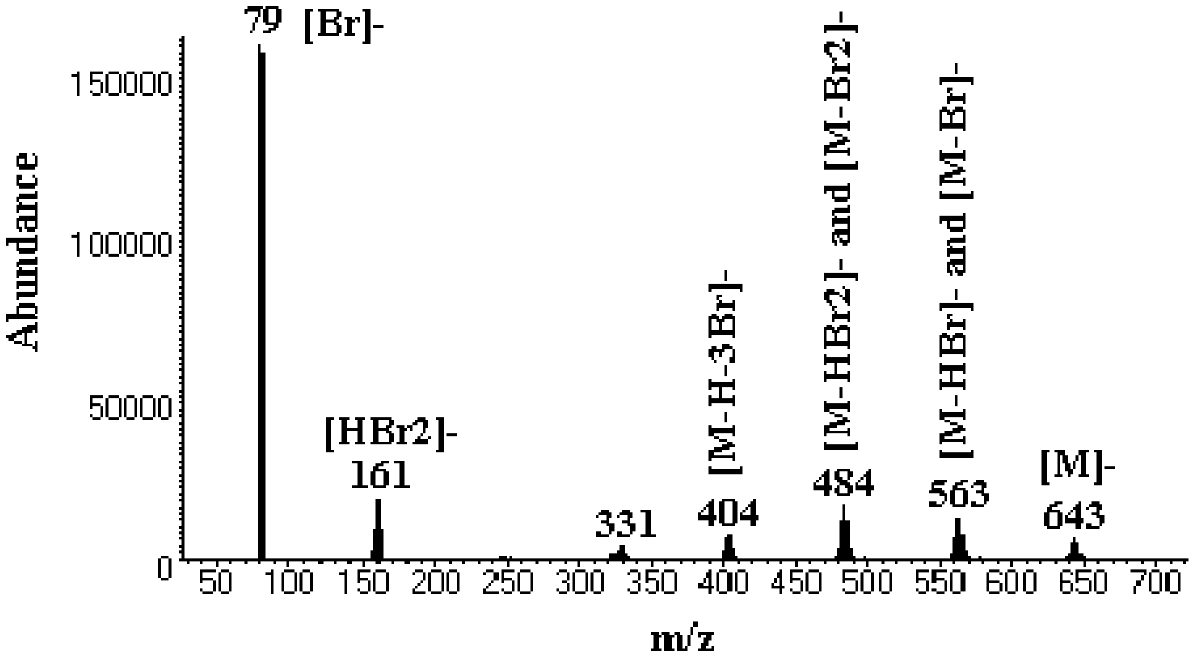

Figure 2.6. Typical electron-capture negative chemical ionization (ECNCI) mass spectrum of PBDE 153 under optimal instrumental conditions.

The ECNCI mass spectra characterization of the PBDEs studied is summarized in Table 2.2. The mass fragment $[Br]^-$ (m/z 79, 81) was dominant in ECNCI-MS spectrum of studied

PBDEs while the molecular cluster [M]$^-$ is not observed or constitutes only a minor peak (relative intensity < 3%). In the case of octa- through deca-PBDEs, the molecular ion is not observed because of the mass spectrometer's upper *m/z* limit of 800.

Other intensive ions observed in ECNCI-MS spectra, except mono- and di-PBDEs, were fragments [HBr$_2$]$^-$ with the relative intensity in the range of 6.8% up to 43.3%, [M-HBr$_2$]$^-$ with the relative intensity in the range 4.2% up to 37.2% and in the case of hexa- and hepta- PBDEs an ion [M-H-3Br]$^-$ with the relative intensity 13.1% and 22.6%. In ECNCI-MS spectra of hexa- and hepta-PBDEs congeners, the contribution of the ions [M-Br]$^-$, [M-Br$_2$]$^-$ and [M-3Br]$^-$ to the absolute intensities of ions [M-HBr]$^-$, [M-HBr$_2$]$^-$ and [M-H-3Br]$^-$ was observed. The relative intensities of mentioned ions are under 10%.

Octa-PBDE 203 spectrum contained an [M-Br$_2$]$^-$ ion with the relative intensity 15.6% and an ion of [HBr$_2$]$^-$ (12.9%). In the spectra of nona- and deca-PBDEs intense fragments of [C$_6$Br$_5$O]$^-$ (relative intensities 63.6% and 76.9%) and [C$_6$Br$_4$O]$^-$ (relative intensities about 22%) were observed.

Table 2.2. The major ions of selected mono- through deca-PBDEs (relative intensity >3%) in ECNCI-MS spectra.

# of bromines	Congener	% Relative Intensity of Fragmentation Ions							
		[M-Br]$^-$	[M-Br$_2$]$^-$	[M-HBr$_2$]$^-$	[M-H-3Br]$^-$	[C$_6$Br$_5$O]$^-$	[C$_6$Br$_4$O]$^-$	[HBr$_2$]$^-$	[Br]$^-$
Mono-	PBDE 1								100
Di-	PBDE 15								100
Tri-	PBDE 30	5.8		4.8				43.3	100
Tetra-	PBDE 47	3.4		10.0				29.2	100
Penta-	PBDE 100		5.3	37.2				16.0	100
Hexa-	PBDE 153 [a]	6.7	4.6	4.3	13.1			6.8	100
Hepta-	PBDE 190 [b]		8.5	4.2	22.6			8.4	100
Octa-	PBDE 203		15.6					12.9	100
Nona-	PBDE 208		4.9			63.6	22.9		100
Deca-	PBDE 209					76.9	22.6		100

[a] PBDE 153 also has a [M-HBr]$^-$ ion at 3.9% relative intensity and a [M-3Br]$^-$ ion at 5.5% relative intensity.

[b] PBDE 190 also had a [M-HBr]$^-$ ion at 6.9% relative intensity; a [M-3Br]$^-$ ion at 4.6% relative intensity and a [M-4Br]$^-$ ion at 8.0% relative intensity.

2.8 Identification and quantification of PBDEs in samples

The presence of PBDEs in field samples were confirmed by:

1) the comparison of relative retention times, which is the ratio of the retention time of the analyte to the retention time of an internal standard. The relative retention times for the different PBDEs were obtained by the analysis of the PBDEs standard solution.
2) the comparison of the measured isotope ratio of monitored ions (Appendix C) to the expected isotope ratio. Since bromine has a very strong natural +2 isotope peak (mass = 81 amu), at 98% of the intensity of the primary bromine isotope (mass = 79 amu), the number of bromines on a molecule results in a characteristic isotope cluster. Therefore, the presence of an isotope cluster in the proper proportion can prove the number of bromines present on a molecule. Chlorine also has a natural +2 isotope (mass = 37 amu) at about 35% on the primary isotope, so the isotope cluster can also be used to confirm the presence of the internal standard PCBs used in the analysis.

The compound was positively confirmed as a PBDE if the relative retention time was within ± 0.002 of the standard and the isotope ratio was within ± 20% of the theoretical isotope ratio.

The mass spectrometer was operated in selected ion monitoring (SIM) mode. The ions (*m/z*) used to detect mono- through hepta-PBDEs on 30 m DB-5ms column are in Table D.1 in Appendix D, the ions (*m/z*) for octa- through deca-PBDEs on 15 m DB-5 column are shown in Table D.2 in Appendix D. Both of these tables also include the monitoring ions for selected polybrominated dibenzofurans and dibenzo-p-dioxins.

For the mono- through hepta-PBDEs ions at *m/z* 79 and 81 were monitored, *m/z* 35 and 37 was monitored for detection of PCB 65, and m/z 498 $[M+4]^-$ and 500 $[M+6]^-$ for the analysis of decachlorobiphenyl (PCB 209). For the analysis of decabrominated diphenyl ether and $^{13}C_{12}$ decabrominated diphenyl ether, ions were monitored at m/z 485 and 487, and 495 and 497, respectively. These ions arise from the loss of C_6Br_5 from the molecule. The ions at m/z 485 and 487 are the $[M+4]^-$ and $[M+6]^-$ ions in the isotope cluster and correspond to $[C_6{}^{79}Br_4{}^{81}BrO]^-$, and $[C_6{}^{79}Br_3{}^{81}Br_2O]^-$. The ions at m/z 495 and 497 are the $[M+6]^-$ and $[M+8]^-$ ions in the isotope cluster and correspond to $[{}^{13}C_6{}^{79}Br_2{}^{81}Br_3O]^-$ and $[{}^{13}C_6{}^{79}Br{}^{81}B_4O]^-$. These ions were chosen due to interference from the $[M+8]^-$ and $[M+10]^-$ ions that arise at m/z 491 and 493 in the $[M\text{-}C_6Br_5]^-$ isotope cluster of decabrominated diphenyl ether and the $[M+2]^-$ and $[M+4]^-$ ions that arise at the same m/z in the $[M\text{-}{}^{13}C_6Br_5]^-$ isotope cluster of the isotopically labeled standard of decabrominated biphenyl ether.

Different ions were used to quantify various PBDE congeners (see Appendix C). Bromide ion, namely *m/z* 78.90, was used for mono- through hepta-PBDEs. In the case of octa-PBDEs, ions *m/z* 559.6 for PBDE 196 and PBDE 203 and *m/z* 408.7 for PBDE 197 were used. For the quantification of nona- and deca- PBDEs an ion *m/z* 486.60 was employed. The quantification ions for the internal standards of PCB 65, PCB 209 and $^{13}C_{12}$-deca-PBDE were *m/z* 35, 497.7 and 494.6, respectively.

The concentration of PBDEs in the sample extracts was calculated from the corresponding calibration curve constructed by plotting the relative response factor (Peak area $_{\text{analyte}}$ / Peak area $_{\text{internal standard}}$) of the quantifying ion versus the PBDE concentration obtained by the analysis of five points calibration standard (see Figure 2.7 for an example of the calibration curve). The concentration of PBDEs in the calibration solutions and the concentration of internal standards are in Tables A.1 and A.2 in Appendix A.

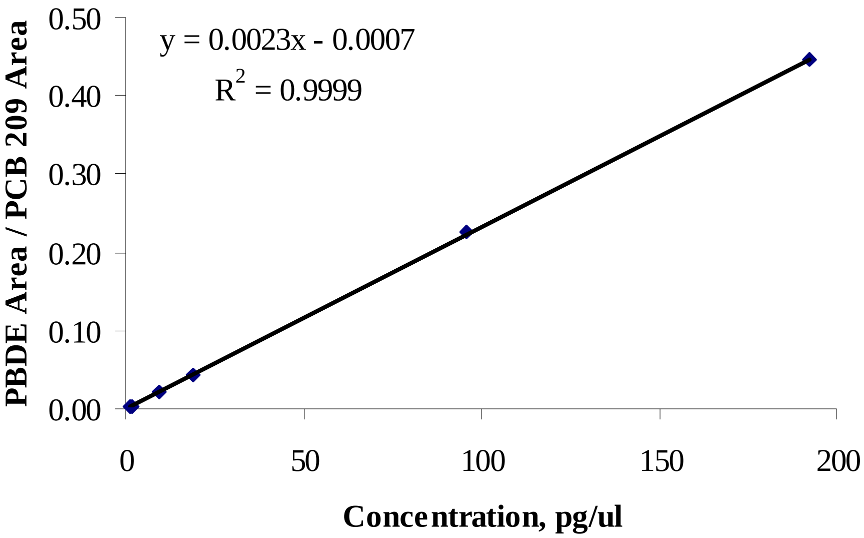

Figure 2.7 Example of a calibration curve for PBDEs. PBDE 153 was used for this example.

PCB-65, at the concentration of 2.376 ng/µl, was used as an internal standard for the quantification of mono- through tri-PBDEs. PCB-209, at the concentration of 112.47 pg/µl, was used as the internal standard for the quantification of tetra- through hepta-PBDEs. Octa- through deca-PBDEs were quantified using $^{13}C_{12}$-deca-PBDE at the concentration of 490.19 pg/µl.

The analysis of sample extracts was accompanied by the analysis of “blank” samples to determine the background concentration of PBDEs in the sample matrices, namely filters, PUFs and XAD resin. The concentrations of PBDEs in air samples were calculated as the difference between the concentrations quantified in the sample extracts and PBDEs concentrations in the blank sample matrices.

All field results were rounded to three significant figures of accuracy. Additional digits of accuracy were carried through the calculations, but the final results were rounded to three digits of accuracy.

2.9 Limit of detection

The Limit of Detection (LOD) was calculated for both the ECNCI and EI analyses in order to compare the sensitivity of the two different ionization approaches. The limit of detection was defined as the concentration that would result in a signal-to-noise ratio (S/N) of 3:1. The S/N was calculated for the lowest observable standard and then this value was extrapolated to estimate the concentration that would yield a S/N ratio of 3:1. Optimal instrumental conditions were used in conjunction with selected ion monitoring (SIM) to achieve the maximum sensitivity possible for each ionization method. In ECNCI-MS-SIM mode, only the $[Br]^-$ ion was monitored (*m/z* 79 and 81). The concentration of the standards used to estimate the LOD ranged from 0.1 pg/µl to 2.0 pg/µl. In EI-MS-SIM mode, two of the most intense ions in $[M]^+$ cluster were monitored along with the confirmation ions. The concentration of the standards used to estimate the LOD for the EI-MS-SIM analyses ranged from 1 to 25 pg/µl.

The results, summarized in Table 2.3, showed that ECNCI-MS was a more sensitive technique for all PBDEs except for mono-PBDEs. In ECNCI-MS, the limit of detection for di- through hepta-PBDEs was in the range of 0.08-0.62 pg/µl. In contrast, the EI-MS-SIM technique gave LOD values for the di- through hepta-PBDEs of 0.91-42.1 pg/µl. The mono-PBDEs were the exception in that the LOD for ECNCI-MS-SIM mode was 0.62-2.18 pg/µl, while the LOD for the EI-MS-SIM model were 0.34 to 0.41 pg/µl.

In comparison with published data,[47] EI-MS-SIM under our optimal conditions showed better sensitivity for the mono-PBDEs, while LODs of most PBDEs congeners reached the published values. The LOD for our optimal ECNCI-MS-SIM analysis gave higher LOD than the published literature.

Table 2.3. Comparison of the Limit of Detection (LOD, pg/µl) for ECNCI-MS-SIM and EI-MS-SIM.

	ECNCI-MS-SIM LOD for $[Br]^-$		EI-MS-SIM LOD for $[M]^+$	
Congener	Published [a]	Measured	Published [a]	Measured
Mono-				
PBDE 1	0.53	0.62	0.86	0.41
PBDE 2	1.06	1.18	0.61	0.34
PBDE 3	1.37	2.18	0.56	0.40
Di-				
PBDE 7	0.06	0.13	1.19	1.35
PBDE 8	0.10	0.18	1.31	1.34
PBDE 10	0.06	0.08	1.02	0.91
PBDE 11	0.11	0.25	0.95	1.22
PBDE 12+13[b]	0.11	0.15	0.53	0.96
PBDE 15	0.16	0.32	0.86	1.37
Tri-				
PBDE 17	0.09	0.16	1.72	3.09
PBDE 25	0.07	0.16	2.29	3.44
PBDE 28+33[b]	0.09	0.12	0.69	1.81
PBDE 30	0.09	0.09	1.62	1.46
PBDE 32	0.08	0.15	2.11	2.10
PBDE 35	0.07	0.23	2.11	3.14
PBDE 37	0.09	0.22	1.83	3.85
Tetra-				
PBDE 47	0.09	0.14	1.96	2.75
PBDE 49	0.06	0.17	2.29	3.20
PBDE 66	0.09	0.23	3.43	4.85
PBDE 71	0.06	0.15	2.75	2.75
PBDE 75	0.06	0.15	1.53	2.41
PBDE 77	0.07	0.25	1.83	4.07

Table 2.3 (cont.)

Penta-				
PBDE 85	0.11	0.36	12.29	13.13
PBDE 99	0.10	0.28	6.62	6.75
PBDE 100	0.08	0.18	4.30	3.70
PBDE 116	0.08	0.26	8.60	16.87
PBDE 118	---	0.38	---	14.46
PBDE 119	0.07	0.22	3.91	5.09
PBDE 126	---	---	17.20	15.75
Hexa-				
PBDE 138	0.09	0.30	6.37	6.67
PBDE 153	0.08	0.24	4.78	5.96
PBDE 154	0.10	0.21	2.55	5.38
PBDE 155	---	---	5.21	6.88
PBDE 166	0.16	0.32	8.19	5.75
Hepta-				
PBDE 181	0.18	0.49	29.42	32.89
PBDE 183	0.12	0.30	13.58	13.78
PBDE 190	0.16	0.62	32.09	42.13

[a] Eljarrat et al.[47]

[b] These two congeners coelute and cannot be separated.

3. Quality Assurance Programs

3.1 "Travel" blanks

A series of "travel" blanks were created and analyzed to determine any possible contamination arising from sample transport to and from the sampling site as well as from sample storage. Three blanks for each sampling substrate (filter, PUF and XAD-2) were taken from the same batch of sampling material as was used in the sampling episode. The travel blanks were sealed in amber glass jars (in the same way as the sampling media), transported to the sampling site and returned to the laboratory in the ice chest (+4°C). The travel blanks were stored in a freezer at -20^{o}C along with the samples. The travel blanks were extracted and analyzed in the same fashion as the field samples.

The concentrations in the air samples were blank-subtracted, which means that the amount of PBDEs in the travel blanks was subtracted from the amount of PBDE detected in the air samples.

3.2. PBDE extraction efficiency from filter, PUF and XAD-2

The efficacy of the extraction procedure for PBDEs was tested for each of the sample substrate types. This was done to determine the accuracy and precision of the analytical procedure for a range of PBDE. Known amounts of PBDE 47, 99, 100, 153, 154 and 209 were added to three replicates of the quartz filters (20.3×25.4 cm size), PUF (10 cm diameter × 10 cm high) or XAD-2 substrates (90 g). These enriched substrates were extracted and analyzed in an identical fashion as the field samples. The accuracy of the analytical procedure was then calculated as the ratio between the measured amount of PBDEs and the amount of PBDEs used to enrich the sample substrate, namely,

Recovery (%) = [(measured analyte)/(enrichment amount)]×100

A recovery of 100% would indicate perfect recovery of the analyte. Values less than 100% indicate that some of the analyte was lost in the analytical procedures while values greater than 100% suggest that contamination has occurred during the analytical procedure. The precision of the analytical procedure was determined by calculating the relative standard deviation (%RSD, %) for the replicates. The RSD is also sometime called the coefficient of variation. Regardless of which nomenclature is used, the precision is calculated as:

Precision (%) = [(standard deviation of replicates)/(mean value of replicates)] ×100

A low value for %RSD indicates consistent values are obtained between the replicate analyses.

The results, shown in Table 3.1, clearly demonstrate that the extraction procedure was effective from removing PBDEs from quartz filters and XAD-2 resin. The recovery of PBDEs from the quartz filters ranged from 72.9 to 90% while the recovery from XAD-2 resin ranged from 77.0 to 107.5%. The PUF substrate, however, had more erratic results the recoveries ranging from 67.4 to 121.2 %. Furthermore, PBDE 209 could not be determined from the PUF substrate due to an interference (see Section 3.5 for details). This is surprising since PUF is frequently used by other research groups to conduct sampling for PBDEs in the environment. These recovery results suggest that large PUF substrates are not the preferred sample substrates for collecting PBDEs from ambient air.

The precision of the analytical procedures also varied between the substrates. The quartz substrates gave reasonably consistent results with relative standard deviations ranging from 13.9 to 20.6%. The XAD-2 also gave consistent results with %RSD ranging from 2.5 to 10.1%. Once again, the PUF substrate proved the worst sample substrate with precision ranging from 11.5 to 32.7%.

Table 3.1. Extraction efficiencies of PBDEs from triplicate filters, XAD-2 and PUF substrates.

Substrate	Congener	Enriched Amount (ng)	Measured amount (ng) Mean ± SD	Mean % recovery	Precision (%RSD)
Filter	PBDE 47	49.02	44.4 ± 7.8	90.0	17.6
	PBDE 99	49.02	40.0 ± 8.0	81.5	20.0
	PBDE 100	49.02	39.9 ± 6.9	81.4	17.3
	PBDE 153	49.02	37.9 ± 7.8	77.3	20.6
	PBDE 154	49.02	38.2 ± 7.5	77.8	19.6
	PBDE 209	44.37	32.4 ± 4.5	72.9	13.9
XAD-2	PBDE 47	50.00	46.7 ± 1.2	93.5	2.6
	PBDE 99	50.00	49.0 ± 1.4	97.9	2.9
	PBDE 100	50.00	44.4 ± 1.1	88.7	2.5
	PBDE 153	50.00	38.8 ± 3.9	77.6	10.1
	PBDE 154	50.00	46.5 ± 1.6	93.0	3.4
	PBDE 209	49.82	53.6 ± 3.6	107.5	6.7
PUF	PBDE 47	49.02	59.4 ± 7.7	121.2	13.0
	PBDE 99	49.02	49.4 ± 7.7	100.7	15.6
	PBDE 100	49.02	50.5 ± 5.8	103.0	11.5
	PBDE 153	49.02	33.0 ± 10.8	67.4	32.7
	PBDE 154	49.02	41.4 ± 8.9	84.4	21.5
	PBDE 209	44.37	[a]	[a]	[a]

[a] Quantification not possible due to analytical problems.

Based on these results, the quartz filter followed by XAD-2 was selected as the air sampling substrates for this project. Both of these substrates were shown to be acceptable for the analysis of PBDEs with recoveries between 72 to 108%. The PUF substrate, in contrast, had lower precision and it had an interference that prevented the determination of PBDE 209.

3.3. Sample stability of PBDEs on filters, XAD-2 and PUF substrates

To evaluate a possible degradation of PBDEs during the storage, replicate samples (n = 3) of a quartz filters, PUF, and XAD-2 were enriched with a known amount of PBDE 47, PBDE 99, PBDE 100, PBDE 153, PBDE 154 and PBDE 209. The amount of enrichment varied slightly from 44.7 to 50.0 ng for different congeners due to slightly different concentrations in the standard solution. These enriched substrates were then sealed in amber glass jars and stored in a freezer at -20°C. PBDEs were measured in the three substrates immediately (t_o), after 2 weeks (t_2) and after 4 weeks (t_4). The results are presented in Table 3.2.

Table 3.2. Recovery of PBDEs on filter, PUF and XAD-2 substrates over one month.

			% Recovery ± SD			% Relative Difference [a]	
Substrate	Congener	Enriched Amount (ng)	Immediate analysis	2-week storage	4-week storage	Between t_0 and t_2	Between t_0 and t_4
Filter	PBDE 47	49.02	90.0±15.9	83.6±11.2	102.2±3.8	7.1	-13.6
	PBDE 99	49.02	81.5±16.4	74.6±12.8	94.0±4.5	8.5	-15.3
	PBDE 100	49.02	81.4±14.1	73.1±12.0	91.6±3.5	10.2	-12.5
	PBDE 153	49.02	77.3±16.0	69.7±10.5	91.2±3.8	9.8	-18.0
	PBDE 154	49.02	77.8±15.2	71.0±11.5	90.5±2.8	8.7	-16.3
	PBDE 209	44.37	72.9±10.2	80.8±6.9	87.3±17.3	-10.8	-19.8
XAD-2	PBDE 47	50.00	93.5±2.5	89.8±1.8	72.5±13.7	4.0	22.5
	PBDE 99	50.00	97.9±2.7	91.8±1.4	74.0±14.6	6.2	24.4
	PBDE 100	50.00	88.7±2.1	84.8±2.1	67.9±13.0	4.4	23.4
	PBDE 153	50.00	77.6±7.8	73.9±2.0	60.9±11.9	4.9	21.5
	PBDE 154	50.00	93.0±3.2	89.1±1.0	72.0±14.9	4.3	22.6
	PBDE 209	49.82	107.5±7.3	98.3±5.6	90.3±14.0	8.6	16.1
PUF	PBDE 47	49.02	121.2±15.6	185.3±82.8	148.5±51.9	-52.9	-22.5
	PBDE 99	49.02	100.7±15.8	128.2±55.2	104.8±56.2	-27.4	-4.1
	PBDE 100	49.02	103.0±11.7	100.8±9.9	89.3±21.8	2.1	13.3
	PBDE 153	49.02	67.4±22.1	32.6±16.0	42.7±31.8	51.6	36.7
	PBDE 154	49.02	84.4±18.1	62.0±14.7	64.9±35.1	26.6	23.1
	PBDE 209	44.37	[b]	[b]	[b]		

[a] Relative difference was calculated as $[(t_o - t_i)/t_o]\times100$, where t_o is the initial value and t_i is the amount measured after 2 or 4 weeks.

[b] Quantification of this analyte was not possible due to a detection problem.

Since the precision among the measurements of PBDEs enriched on quartz filters and in XAD-2 was generally less than 20%, a % relative difference between the two time periods of greater than 20% was used to indicate change in concentrations between the two times. The percent relative difference after two and four weeks of storage for the filter extracts did not exceed 20%, indicating stability of the compounds during this period. The higher amount of PBDEs on the filter measured after 4 weeks may indicate a contamination during the storage. However, the trend was not as obvious for the other matrices indicating that the contamination was not the cause for the higher values. In the analysis of the XAD-2 extracts, the percent relative difference between t_o and t_2 did not exceed 10% relative difference, indicating the stability of the PBDEs on XAD-2 resin over this period, although the longer time period of 4 weeks may have shown some degradation, but it is borderline based on the precision of the method.

The amount of PBDE 47 and PBDE 99 found on the PUFs after 2 (the % relative difference -52.9% and -27.4%) and 4 weeks (the % relative difference -22.5% and -4.1%) was higher than the amount found at t_0, indicating a contamination during the storage. On the other hand, the high % difference between t_o and t_2 for PBDE 153 and PBDE 154 (51.6% and 26.6%) and between t_o and t_4 (36.7% and 23.1%) has showed a possible degradation of the congeners during the storage. For PBDE 100, the % difference between t_o and t_2; and t_o and t_4 respectively, was 2.1% and 13.3% indicating the stability of this congener on the PUF. The PUF substrates were also enriched with PBDE 209, however, because of the analytical problems with this congener in PUF extracts (see Section 3.5 below) the data are not available.

Overall, the data indicate that PBDEs sorbed / trapped on quartz filters or XAD-2 resin can be stored at -20°C for a period of 4 weeks without a loss of the sample integrity. This is also likely true for PUF, but the greater variability between measurements makes it difficult to evaluate the data.

3.4 Field test of analytical protocols

To verify the PBDEs air sampling method efficiency, the ambient air was sampled on the UC Davis campus on 3/17/2004 and 3/18/2004. Ambient air samples were collected simultaneously by four high-volume air samplers. Two of the samplers were equipped with a quartz filter followed by a polyurethane foam plug while the other two samplers were equipped with a quartz filter followed by XAD-2 resin. Therefore, this sampling was not only designed to test the efficacy of the analytical procedure, but also to test for differences in PBDE collection efficiency between PUF and XAD resin. The samplers were operated for 24 h at a flow rate about 34.2 m^3/h, thus giving total of 778 – 903 m^3 of air. For these tests, the particulate and gas-phase PBDEs were summed to give a total PBDE concentration in the atmosphere. The sampling conditions are summarized in Table 3.3.

Table 3.3. Sampling conditions for Ambient PBDE Measurements in Davis, California.

Date	**Sampler No.**	**Sampling Substrate**	**Matrix Amount (g)**	**Air Flow (m^3/h)**	**Air Sampled (m^3)**	**Temperature (°C)**		**Relative Humidity (%)**	
						Day	**Night**	**Day**	**Night**
3/17/04	1	XAD-2	90.05	37.6	902.9	25	11	48	63
	2	XAD-2	90.15	37.6	902.9				
	3	PUF	19.27	34.2	820.8				
	4	PUF	18.74	25.7	778.1				
3/18/04	1	XAD-2	90.24	35.9	861.8	26	9	44	67
	2	XAD-2	90.07	37.6	902.9				
	3	PUF	19.14	35.9	861.8				
	4	PUF	18.99	35.9	861.8				

The results, with atmospheric PBDE concentrations presented in Table 3.4 and the blanks, LOD and recovery data are presented in Appendix E, demonstrate that the analytical methods were successful in determining PBDEs in ambient air samples. PBDEs 47, 99 and 209 were the congeners that were present in the highest concentrations in these samples while most other congeners detected were present at concentrations ranging from about 0.20 to 6.0 pg/m^3. In total, 23 different PBDE congeners were detected in these test samples. For the most part, more of the lighter PBDE congeners (tri- to penta-PBDEs) were detected than the heavier congeners. Differences between the two types of adsorbents were generally insignificant (see next section) with the exception of PBDE 209, which could not be detected in the PUF adsorbent extracts. Mono- and di-BDEs were not determined because of interferences from sample’s impurities (bromo-chloro- organic compounds) coeluting with studied PBDEs.

Table 3.4. PBDE Concentrations in outdoor air samples (pg/m^3) as determined by filter/PUF sampling and by filter/XAD-2 sampling at the University of California, Davis central campus location. The particulate and gas-phase PBDEs were summed to give a total concentration of PBDEs in the atmosphere. “ND” indicates that the compound was monitored but not detected. “---“ indicates that the compound was not monitored in this set of samples.

	Filter-PUF samplers					Filter-XAD-2 samplers				
Congener	#1 03/17	#2 03/17	#1 03/18	#2 03/18	Mean ± SD	#1 03/17	#2 03/17	#1 03/18	#2 03/18	Mean ± SD
Tri-										
PBDE 17	2.73	1.44	1.53	0.63	1.58 ± 0.87	1.01	0.26	20.88	0.19	5.59 ± 10.2
PBDE 25	6.94	2.16	2.35	1.12	3.14 ± 2.59	2.41	0.78	1.30	1.61	1.53 ± 0.68
PBDE 28/33	1.43	2.86	1.79	2.00	2.02 ± 0.61	4.37	1.56	7.11	3.19	4.06 ± 2.34
PBDE 30	0.37	0.20	0.40	0.37	0.34 ± 0.09	ND	ND	0.15	0.19	0.09 ± 0.10
PBDE 32	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PBDE 35	0.39	ND	0.93	0.31	0.41 ± 0.39	0.41	0.37	0.32	0.33	0.36 ± 0.04
PBDE 37	0.36	0.88	1.43	0.63	0.83 ± 0.46	0.39	0.37	14.00	0.32	3.77 ± 6.82
Tetra-										
PBDE 47	42.0	44.5	30.5	22.4	34.9 ± 10.3	46.3	42.4	26.6	21.9	34.3 ± 11.9
PBDE 49	1.17	2.95	0.82	0.35	1.32 ± 1.14	0.21	2.69	ND	1.52	1.11 ± 1.25
PBDE 66	3.03	1.61	1.87	0.61	1.78 ± 0.99	2.00	1.84	1.06	0.99	1.47 ± 0.52
PBDE 71	4.27	ND	2.77	1.13	2.04 ± 1.87	3.38	ND	2.15	ND	1.38 ± 1.67
PBDE 75	0.60	0.60	0.40	0.15	0.44 ± 0.21	0.60	0.60	0.16	0.16	0.38 ± 0.25
PBDE 77	0.77	0.65	0.59	ND	0.50 ± 0.34	0.23	0.50	0.21	ND	0.24 ± 0.21
Penta-										
PBDE 85	1.25	0.93	0.61	0.52	0.83 ± 0.33	1.60	1.49	1.23	1.15	1.37 ± 0.21
PBDE 99	18.9	15.9	9.42	8.02	13.1 ± 5.2	16.8	13.6	9.03	7.68	11.8 ± 4.2
PBDE 100	6.63	6.33	3.63	3.32	4.98 ± 1.74	6.44	5.74	3.46	3.16	4.70 ± 1.63
PBDE 116	0.43	ND	ND	ND	0.11 ± 0.22	0.87	ND	0.36	ND	0.31 ± 0.41
PBDE 118	0.70	0.55	0.20	ND	0.36 ± 0.32	0.65	0.50	0.17	ND	0.33 ± 0.30
PBDE 119	0.94	2.96	0.82	ND	1.18 ± 1.26	1.19	3.80	0.68	0.36	1.51 ± 1.57
PBDE 126	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexa-										
PBDE 138	0.91	1.00	0.86	0.85	0.91 ± 0.07	0.86	0.84	0.86	0.80	0.84 ± 0.03
PBDE 153	3.04	2.76	1.46	1.39	2.16 ± 0.86	2.99	3.99	2.31	2.27	2.89 ± 0.80
PBDE 154	3.33	3.30	1.53	1.59	2.44 ± 1.01	4.25	3.67	2.39	2.31	3.16 ± 0.96
PBDE 155	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PBDE 166	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hepta-										
PBDE 181	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PBDE 183	1.60	1.67	1.43	1.13	1.46 ± 0.24	1.48	1.33	1.15	1.07	1.26 ± 0.18
PBDE 190	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Octa-										
PBDE 196	---	---	---	---	---	---	---	---	---	---
PBDE 197	---	---	---	---	---	---	---	---	---	---
PBDE 203	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nona-										
PBDE 206	---	---	---	---	---	---	---	---	---	---

PBDE 207	---	---	---	---	---	---	---	---	---	---
PBDE 208	---	---	---	---	---	---	---	---	---	---
Deca-										
PBDE 209	[a]	[a]	[a]	[a]	[a]	17.8	14.4	5.58	4.44	10.6 ± 6.6
Sum	50.1	49.3	30.3	21.9	37.9 ± 14.0	116.2	100.8	101.3	53.8	93.0 ± 27.1

[a] compound was not determined due to analytical difficulties.

The concentrations observed in these samples were generally higher than those reported in rural and remote areas in Europe and the United States. PBDE 47, 99, 100, 153 and 154 were the most commonly reported PBDE congeners in these studies. To compare the total PBDEs reported in these areas, the sum of these congeners was calculated. The total concentration of these congeners was 3.7 pg/m^3 in Gotska, Sweden, [19] from 2.24 to 9.15 pg/m^3 in remote and semi-rural sites in the United Kingdom (UK),[26] from 1 to 2.1 pg/m^3 in a transect from the UK to Norway,[43] and from 4.87 to 20.89 pg/m^3 in remote and rural areas surrounding Lake Michigan, United States.[20] In urban areas, the total concentration of these congeners was 5.36 pg/m^3 in Toronto[48] and from 22.21-33.97 pg/m^3 in Chicago.[20] In this study, the average of the sum of PBDE congeners 47, 99, 100, 153, and 154 was 58.1 pg/m^3. Therefore, the outdoor concentrations observed in Davis were higher than values reported in the literature, although the concentrations from Chicago are reasonably similar.

Decabrominated diphenyl ether has not been extensively analyzed in ambient air. One study reports non-detectable levels,[20] and another of 6.9 pg/m^3 in Gotska, Sweden, a rural/remote environment.[19] The levels of PBDE 209 measured in Davis air are slightly higher than in rural Sweden, and was the third most abundant congener in air, following PBDE 47 and 99.

A few studies have demonstrated that PBDE 209 can be de-brominated to lower brominated PBDE congeners by both UV light, and under certain conditions, by natural sunlight with half-lives ranging from 15 minutes up to 81 hours.[2]

3.5 Ambient air sampling: filter/XAD-2 vs. filter/PUF

The % relative difference between the concentrations of PBDEs between paired PUF-XAD samples was evaluated to determine whether differences exist between the concentration of PBDEs obtained by sampling using a quartz filter followed by XAD-2 or a quartz filter followed by PUF. Statistical analyses of the data were performed using the paired student t-test to determine if significant differences exist between the differences of the mean values. These analyses were conducted by comparing the concentration (pg/m^3) of PBDE 47, PBDE 99, PBDE 100, PBDE 153, PBDE 154 and PBDE 209 measured as the total (sum of the concentrations measured in the filter + adsorbent extracts). The data and the % relative difference between the methods are presented in Table 3.5.

Table 3.5. Comparison of filter/XAD-2 vs. filter/PUF high-volume sampler for the determination of polybrominated diphenyl ethers in ambient air samples.

		Total atmospheric concentration (pg/m^3)		
Congener	Date	Filter + XAD-2	Filter + PUF	|% Rel. Diff.|
PBDE 47	3/17/04	46.27	42.01	9.21
	3/17/04	42.43	44.49	4.86
	3/18/04	26.62	30.54	14.73
	3/18/04	21.90	22.40	2.28
	Average	34.31	34.86	7.77
	SD	11.86	10.29	
PBDE 99	3/17/04	16.75	18.85	12.54
	3/17/04	13.63	15.94	16.95
	3/18/04	9.02	9.42	4.43
	3/18/04	7.68	8.02	4.43
	Average	11.77	13.06	9.59
	SD	5.18	0.38	
PBDE 100	3/17/04	6.44	6.62	2.80
	3/17/04	5.74	6.33	10.28
	3/18/04	3.46	3.62	4.62
	3/18/04	3.16	3.32	5.06
	Average	4.70	4.97	5.69
	SD	1.63	1.74	
PBDE 153	3/17/04	2.99	4.82	61.20
	3/17/04	3.99	4.96	24.31
	3/18/04	2.31	2.39	3.46
	3/18/04	2.28	2.33	2.19
	Average	2.89	3.63	22.79
	SD	0.80	1.46	
PBDE 154	3/17/04	4.25	4.45	4.71
	3/17/04	3.67	4.29	16.89
	3/18/04	2.39	2.40	0.42
	3/18/04	2.32	2.42	4.31
	Average	3.16	3.39	6.58
	SD	0.96	1.13	
PBDE 209	3/17/04	17.84	[a]	---
	3/17/04	14.43	[a]	---
	3/18/04	5.59	[a]	---
	3/18/04	4.44	[a]	---
	Average	10.58	[a]	
	SD	6.59		

[a] problem with detection so this PBDE cannot be quantified.

To evaluate whether the measured concentrations of PBDEs were affected by the type of sampler (e.g. filter+XAD-2 vs. filter + PUF), statistical analysis of the data was conducted by using a paired student t-test. The analyses were conducted on the total (filter + adsorbent) atmospheric PBDE concentration. No significant differences were observed between the filter+XAD-2 and the filter + PUF sampling systems, which indicates that both sampling procedures work well of PBDE sampling.

The exception, however, was PBDE 209, which could not be quantified in the PUF extracts due to analytical difficulties. This difficulty was exemplified by the analysis of a standard comprised of native and isotopically-labeled PBDE 209 before and after the analysis of a PUF extract (see Figure 3.1). A peak area of 615 units was obtained for the *m/z* 487 anion $[^{12}C_6{}^{79}Br_3{}^{81}Br_2{}^{16}O]^-$ at 9 pg/µL prior to the analysis of the PUF extract. After analysis of the extract, the response was sufficiently altered to so that the *m/z* 487 anion was not observed. The ability to measure PBDE 209 did not return after injection of isooctane. Similar analyses were conducted with respect to the *m/z* 495 $(^{13}C_6{}^{79}Br_2{}^{81}Br_3{}^{16}O)^-$ ion in the $(M\text{-}C_6Br_5)^-$ bromine cluster of isotopically-labeled PBDE 209. A peak area of 37,240 was obtained on the *m/z* 495 ion prior to analysis of a PUF extract. After the analysis of a PUF extract, the *m/z* 495 ion was not detectable in the analysis of a standard. However, since the concentration of the isotopically-labeled species was present at an order of magnitude greater than the native species, the *m/z* 495 ion was observed after injection of solvent indicating the presence of interferences in the PUF extract which can be eliminated after continual injection of solvent. We observed this phenomenon many times in the analysis of PBDE 209 in extracts of samples of ambient air as well as blank PUFs which were not used in air sampling. This effect was not observed during the analysis of the mono- to hepta-brominated diphenyl ethers in PUF extracts.

The reason for the analytical difficulties was not clear. One hypothesis was that the PUF substrate could contaminate the gas chromatograph injector, column and/or ion source with heavy polymers. These heavy polymers then caused interferences late in the chromatogram that affected the detection of PBDE 209. Since the analyses used negative chemical ionization-selected ion monitoring, the analysis procedure was blind to a myriad of other chemicals that might affect chromatography or ionization. When one of the PUF extracts was analyzed in electron ionization mass spectrometry, huge peaks appeared late in the chromatogram that could easily obscure the presence of trace amounts of an analyte. Some of these heavy interfering PUF polymers may be retained on the column between analysis runs, hence why analysis of standards immediately after a PUF extract showed no detectable amounts of PBDE 209 since the column and/or the injector were still contaminated. Furthermore, the heavy interfering chemicals would slowly bleed off the column, hence why sensitivity slowly returned after the injection of pure solvent.

Due to the problems arising with the analysis of PBDE 209 in PUF extracts, we selected the “filter + XAD-2” configuration for all future sampling episodes. The nature and elimination of the interference needs to be further addressed if PBDE 209 is to be determined in PUF extracts.

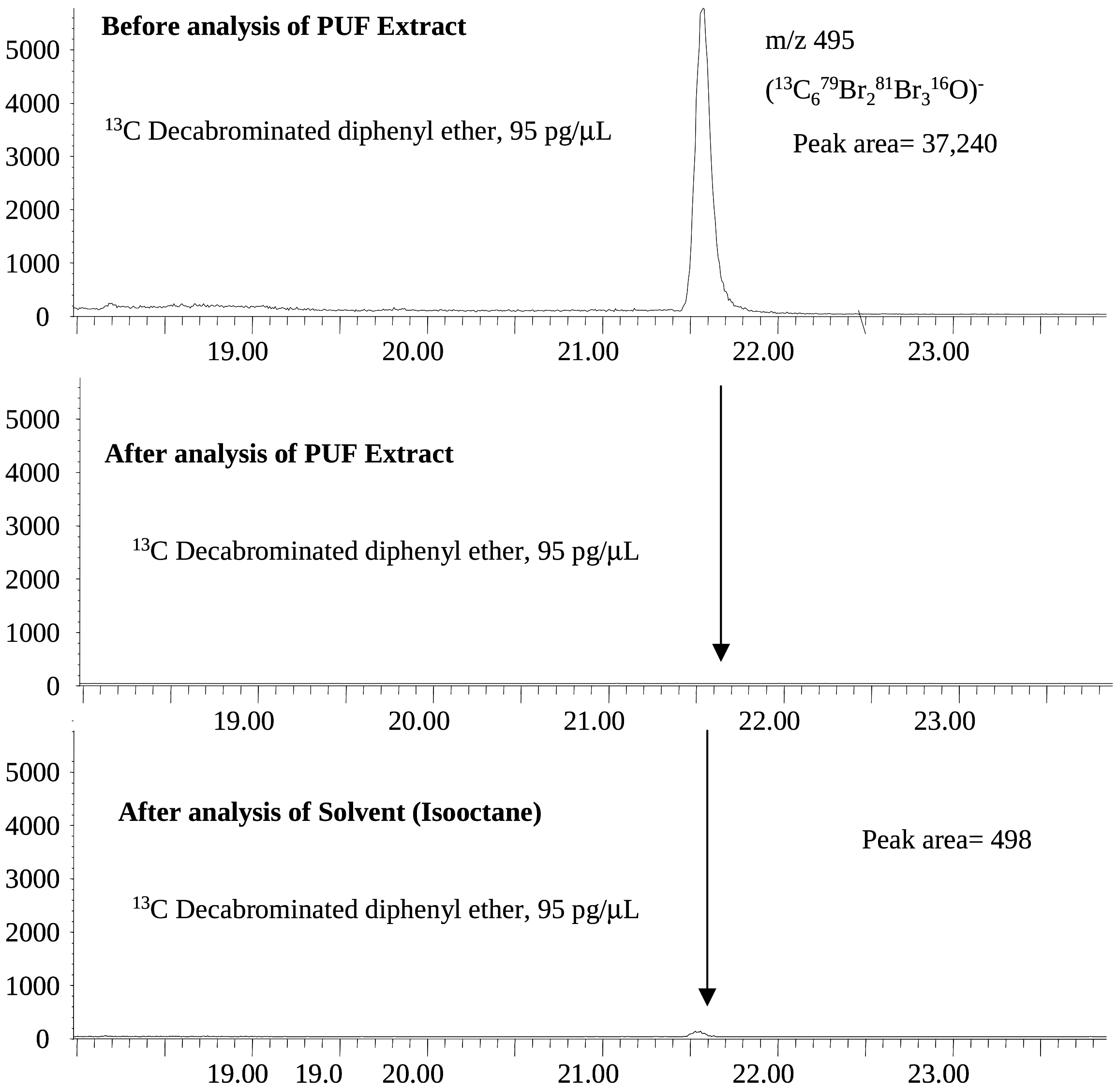

Figure 3.1. Chromatograms showing the degradation of instrument detection of PBDE 209 from PUF sample substrates. The three chromatograms represent the same concentration of $^{13}C_{12}$-PBDE 209 in a standard before a PUF extract analysis, immediately after a PUF extract analysis run, and after a PUF analysis run and a pure solvent analysis run, which was designed to clean out the chromatographic column.

4. Indoor Air Monitoring in a Computer Laboratory

PBDEs were extensively used in some types of electronics, such as computer equipment, so some electronics are expected to be sources of PBDEs. Therefore, PBDE concentrations may be higher in confined locations with older computers. It should be noted that in recent years many computer manufacturers have switched to alternative fire retardants. To test this hypothesis, PBDE concentrations were determined in indoor air and dust samples in a computer training laboratory in a public office building.

4.1 Computer laboratory description

The computer laboratory (Figure 4.1) was a closed room with dimensions of 9.4 × 4.5 × 2.7 m (length×width×height) giving a total room volume 114.2 m^3. The room contained the following computer-related equipment:

13 DF1 personal computers (with updated hardware),
11 View sonic MultiMedia Series M70 monitors,
1 ViewSonic Graphic Series G70M monitor,
1 ViewSonic EA771 monitor,
13 Gateway keyboards,
12 Microsoft mice,
1 HP LaserJet 2100 TN printer and
16 chairs with polyurethane foam pads.

For this PBDE sampling, the ventilation was turned off so the room was essentially sealed.

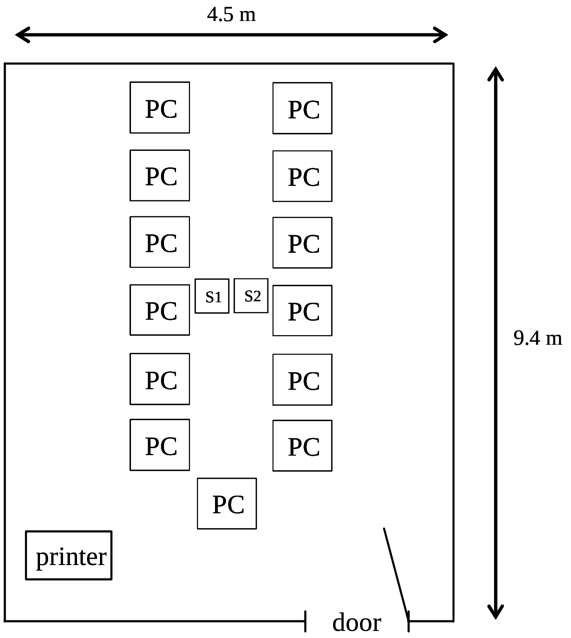

Figure 4.1 Schematic of the sampled computer laboratory. “S1” and “S2” were the locations of the air samplers while “PC” marks the locations of the 13 personal computers in the room.

4.2 Air sample collection

Two different sampling conditions were tested, namely with the computers turned on and with the computers turned off. The hypothesis was that the computers should emit more PBDEs when turned on since they are warm, which promotes volatilization, and the computer cooling fans will blow more air through the computers. The 1/24/04 and 2/1/04 sampling days tested the "computers off" conditions while all other days (1/25/04, 1/26/04, 1/27/04, 2/2/04, 2/3/04 and 2/4/04) tested the "computers on" condition. PBDEs were collected using the "low volume" air sampler described in section 2.2. The air was collected for 24 h (except for 1/27/04 where it was 15 h) at a rate 13.2 – 18.0 L/min giving totally 11.9 – 25.9 m^3. The samplers were centrally located and the air intake was placed at the height of the computers. The pumps were placed in the corner of the room.

For sampling, two indoor air samplers were used. One sampler was equipped by quartz filter followed by a polyurethane foam adsorbent; the other sampler consisted of the same quartz filter followed by XAD-2 resin. However, only the results from the XAD-2 samplers are reported herein given the problems associated with PUF adsorbents. The sampling time, the flow rate, the total volume of the taken air, the amount of the used matrices, the average temperature and relative humidity measured during the sampling are presented in Table 4.1. Filter and adsorbent extraction was conducted as described in section 2.4. Sample extract quantification was conducted by GC-ECNCI-MS as described in Sections 2.5.1 and 2.5.2.

Table 4.1. Sampling details for indoor air sampling.

Date	Computer State	XAD-2 (g)	Sampling Time (h)	Air Flow (L/min)	Air Sampled (m^3)	Temperature (°C)	Relative Humidity
1/24/04	Off	6.08	24	18.0	25.9	24.0 ± 0.3	37.0 ± 1.5
1/25/04	On	6.07	24	17.5	25.2	26.2 ± 0.7	30.8 ± 3.8
1/26/04	On	6.04	24	17.6	25.3	27.1 ± 0.3	27.9 ± 1.4
1/27/04	On	6.02	15	13.2	11.9	27.2 ± 0.2	31.5 ± 0.7
2/01/04	Off	6.04	24	17.1	24.7	23.7 ± 0.2	32.6 ± 1.4
2/02/04	On	6.02	24	17.1	24.7	25.8 ± 0.7	32.9 ± 1.4
2/03/04	On	6.04	24	15.4	22.2	26.8 ± 0.1	32.3 ± 1.2
2/04/04	On	6.07	24	14.4	20.7	27.2 ± 0.3	31.6 ± 3.8

4.3 Dust collection in the computer laboratory

The carpet of the computer laboratory was vacuumed on 2/03/2004 with a high volume small surface sampler HVS3 (CS_3, Inc.) that was specially designed to collect surface dust. Particles greater than 5 μm in diameter are collected in a cyclone catch bottle (Teflon, Nalge Nunc International, Rochester, NY). The cyclone collected 99% of the house dust picked by the nozzle. Any dust that was not collected moves through the fan and is collected by the vacuum cleaner bag.

The carpet in the computer laboratory was vacuumed on both sides of the room (Figure 4.1) to get two duplicate samples. The total vacuumed area for each side was 3.48 m^2. To determine the PBDEs contribution from the vacuum cleaner, a new teflon bottle was installed and the vacuum cleaner was running for 15 minutes just taking the air. After sample collection, the sampling bottles were sealed, wrapped in an aluminum foil, transported to the laboratory in an ice chest and stored in a freezer at -20°C.

The total amount of the collected dust for the left and right sides of the room were 3.79 g and 3.92 g, respectively. To remove the larger particles, the dust was sieved through the 100 mesh screen and only the particles that were less than 150 μm were weighed and analyzed. The total amount of the fine dust taken from the left side of the room was 1.86 g and from the right side 1.93 g.

The dust samples were extracted by Soxhlet in a similar fashion as the filter and XAD-2 substrates. After the Soxhlet extraction of the fine dust by dichloromethane for 24 h, the extract was treated the same fashion as air samples. However to get a homogeneous solution after the solvent exchange, toluene was used as a solvent instead of isooctane. To determine the concentration of PBDEs in the dust extracts, the PBDEs calibration curve was likewise created in toluene. The samples were then quantified by GC-ECNCI-MS as described in Sections 2.5.1 and 2.5.2.

4.4 Carpet sample extraction and cleaning procedure

A new piece of the carpet (2.5 x 2.5 cm) of the same type used in the computer room was extracted and analyzed for PBDEs to determine a contribution of PBDEs from the carpet to the concentration of PBDEs observed in dust samples. The carpet samples included a thin foam backing as part of the sample. The sample of carpet was Soxhlet-extracted with 200 ml of dichloromethane for 24 h and the extract was reduced to ~ 50 ml by the rotary evaporation. To decrease the interference of polar compounds, the extract was cleaned-up by a liquid-liquid extraction with 50 ml of pure water, which was discarded after extraction. A total of three water washes of the dichloromethane extract were conducted to remove the polar constituents of the carpet extract. To improve a separation of polar compounds, possibly acidic compounds, a small amount of sodium carbonate was added (pH ~ 7) to the second water rinse of the carpet extract. After the separation of polar fraction, 10 ml of isooctane was added to the non-polar fraction and stirred intensively. The extract was reduced to ~ 3 ml by the rotary evaporation and cleaned on the glass column (internal diameter 1 cm, length 30 cm) containing 5 g of 3.5% w/w water-deactivated silica gel, 1 cm of dried sodium sulfate (baked at 150°C for 8 h) and a glass wool plug (baked at 450°C for 8 h) using 50 ml of dichloromethane. Prior to the cleaning procedure, the silica gel in the glass column was conditioned by 50 ml of dichloromethane. The final extract was concentrated under a gentle stream of nitrogen (99.997% purity) to a volume of 1 ml for the GC-ECNCI-MS analysis. Nine carpet samples were extracted. However, due to massive interferences from other organic chemicals (probably small polymer units) extracted from the carpet, only one carpet sample was analyzed. A blank sample was also processed through the whole procedure to test for contamination during sample processing. Once again, the sample extracts were quantified by GC-ECNCI-MS as described in Sections 2.5.1 and 2.5.2.

4.5 PBDE concentrations in computer laboratory air samples

The concentration (pg/m^3) of PBDEs are presented in two tables (Table 4.2 and 4.3) corresponding to the two sampling campaigns in the computer laboratory. The dominant PBDE congener was PBDE 47 followed by PBDE 99, PBDE 100, and PBDE 28. Decabrominated diphenyl ether (PBDE 209) was also determined in indoor air. The octabrominated diphenyl ether was not detected in air. The quality assurance samples (blanks, limit of detection calculations and extraction efficiencies) for this sampling campaign are presented in Appendix F.

Table 4.2 Total PBDE concentrations (pg/m^3) in indoor air samples for a computer laboratory in a public office building during the January 24 – 27, 2004 sampling campaign. “ND” indicates that the compound was not detected.

	Sampling Day / Computer State					
	1	2	3	4	Mean ± SD	Difference
Compound	Off	On	On	On	On	On - Off
Tri-						
PBDE 17	48.9	44.0	39.0	74.9	52.6 ± 19.5	3.71
PBDE 25	39.7	25.8	19.0	104.2	49.7 ± 47.4	9.93
PBDE 28	101.9	97.2	99.0	139.6	111.9 ± 24.0	10.0
PBDE 30	ND	ND	ND	ND	ND	ND
PBDE 32	ND	ND	ND	ND	ND	ND
PBDE 33	ND	ND	ND	ND	ND	ND
PBDE 35	ND	ND	ND	ND	ND	ND
PBDE 37	ND	ND	ND	ND	ND	ND
Tetra-						
PBDE 47	982	846	1190	1550	1200 ± 350	213
PBDE 49	46.0	46.9	59.4	93.8	66.7 ± 24.3	20.7
PBDE 66	15.6	21.9	30.2	36.1	29.4 ± 7.12	13.8
PBDE 71	ND	ND	ND	ND	ND	ND
PBDE 75	6.05	4.22	6.39	14.3	8.31 ± 5.32	2.26
PBDE 77	ND	ND	ND	ND	ND	ND
Penta-						
PBDE 85	7.50	9.44	11.4	16.4	12.4 ± 3.59	4.93
PBDE 99	169	201	276	345	274 ± 72.0	105
PBDE 100	76.3	85.3	109	135	110 ± 24.9	33.5
PBDE 116	5.24	3.70	9.48	15.6	9.59 ± 5.95	4.35
PBDE 118	ND	ND	ND	ND	ND	ND
PBDE 119	ND	ND	ND	ND	ND	ND
PBDE 126	ND	ND	ND	ND	ND	ND
Hexa-						
PBDE 138	ND	ND	ND	ND	ND	ND
PBDE 153	6.19	8.01	8.74	13.6	10.1 ± 3.04	3.93
PBDE 154	5.70	7.36	9.39	12.3	9.67 ± 2.46	3.97
PBDE 155	ND	ND	ND	ND	ND	ND
PBDE 166	ND	ND	ND	ND	ND	ND
Hepta-						
PBDE 181	ND	ND	ND	ND	ND	ND
PBDE 183	ND	ND	ND	ND	ND	ND
PBDE 190	ND	ND	ND	ND	ND	ND
Octa-						
PBDE 203	ND	ND	ND	ND	ND	ND
Deca-						
PBDE 209	2.22	56.7	61.7	77.4	65.3 ± 10.8	63.1

Table 4.3 Total PBDE concentrations (pg/m^3) in indoor air samples for a computer laboratory in a public office building during the February 1 - 4, 2004 sampling campaign. “ND” indicates that the compound was not detected.

	Sampling Day / Computer State				Mean ± SD	Difference
	1	2	3	4		
Compound	Off	On	On	On	On	On - Off
Tri-						
PBDE 17	33.5	37.0	40.8	37.7	38.5 ± 2.01	4.96
PBDE 25	2.93	9.36	8.07	6.28	7.90 ± 1.55	4.97
PBDE 28	78.1	83.6	89.7	83.1	85.5 ± 3.69	7.41
PBDE 30	ND	ND	ND	ND	ND	ND
PBDE 32	ND	ND	ND	ND	ND	ND
PBDE 33	ND	ND	ND	ND	ND	ND
PBDE 35	ND	ND	ND	ND	ND	ND
PBDE 37	ND	ND	ND	ND	ND	ND
Tetra-						
PBDE 47	819	916	940	935	930 ± 12.7	112
PBDE 49	42.0	49.0	49.9	52.4	50.4 ± 1.78	8.41
PBDE 66	19.9	26.6	27.2	31.6	28.5 ± 2.70	8.59
PBDE 71	ND	ND	ND	ND	ND	ND
PBDE 75	1.99	3.98	3.97	6.98	4.98 ± 1.73	2.99
PBDE 77	ND	ND	ND	ND	ND	ND
Penta-						
PBDE 85	9.68	12.1	11.5	15.3	13.0 ± 2.06	3.28
PBDE 99	141	209	194	210	204 ± 8.77	63.5
PBDE 100	65.3	90.2	87.9	90.7	89.6 ± 1.47	24.4
PBDE 116	15.1	17.2	22.4	19.8	19.8 ± 2.59	4.73
PBDE 118	ND	ND	ND	ND	ND	ND
PBDE 119	ND	ND	ND	ND	ND	ND
PBDE 126	ND	ND	ND	ND	ND	ND
Hexa-						
PBDE 138	ND	ND	ND	ND	ND	ND
PBDE 153	9.24	10.1	11.4	13.5	11.7 ± 1.68	2.42
PBDE 154	12.5	16.2	15.3	17.3	16.3 ± 1.04	3.82
PBDE 155	ND	ND	ND	ND	ND	ND
PBDE 166	ND	ND	ND	ND	ND	ND
Hepta-						
PBDE 181	ND	ND	ND	ND	ND	ND
PBDE 183	ND	ND	ND	ND	ND	ND
PBDE 190	ND	ND	ND	ND	ND	ND
Octa-						
PBDE 203	ND	ND	ND	ND	ND	ND
Deca-						
PBDE 209	17.7	47.6	47.1	55.9	50.2 ± 4.95	32.6

In all cases, the air concentrations were higher when the computers were turned on compared to when the computers were turned off. The differences were the greatest for PBDE

47, 99, 100 and 209. The high concentrations of PBDE 47 and 99 combined with the presence of PBDE 209 suggests that these compounds volatilized from “penta” and “deca” formulations present in the computers. For comparison, other researchers[17] have measured indoor concentrations of PBDEs as high as 1,800 pg/m^3.

The air concentrations of PBDEs were used to calculate the source strength from all 13 computers in the laboratory. An emission rate (in pg/h) was then calculated on a “per computer” basis. These calculations are presented in Appendix G. Since these calculations estimate emission rates from the observed air concentrations of PBDEs, the trends observed in the source strength and emission rates mirror the observed air concentration trends.

4.6 PBDE concentrations in dust samples

In contrast to indoor air, PBDE 209 was the dominant congener measured in the dust obtained from vacuuming the carpet, followed by PBDE 99 and 47 (Table 4.4). Interestingly, the concentrations farther from the door were higher than near the door.

Certain congeners were present in the dust samples that were not present in the indoor air samples. The congeners, namely PBDE 203, PBDE 183, PBDE 155, PBDE 138 and PBDE 77, were present in the dust sample but not in the air. PBDE 203 and 183 were cogeners in the octa-PBDE formulations. The reason for the presence of these compounds in the dust samples, but not in the air samples, was not clear. However, it may have been attributed to differences in analytical detection limits due to a larger mass of extracted dust material compared to the relatively small mass present in the airborne particulate matter. Mono- and di-PBDEs were not determined because of interferences from dust sample impurities.

Table 4.4. PBDEs concentrations (ng/g) in dust samples from computer laboratory. “ND” indicates that the compound was not detected.

Congener	Sample 1 Left Side of Room	Sample 2 Right Side of Room
Tri-		
PBDE 17	6.05	4.90
PBDE 25	2.78	1.28
PBDE 28	16.5	12.1
PBDE 30	ND	ND
PBDE 32	ND	ND
PBDE 33	ND	ND
PBDE 35	ND	ND
PBDE 37	ND	ND
Tetra-		
PBDE 47	502	411
PBDE 49	ND	ND
PBDE 66	21.3	19.4
PBDE 71	ND	ND
PBDE 75	ND	ND
PBDE 77	1.51	ND

Table 4.4 (cont.)

Penta-		
PBDE 85	47.3	55.6
PBDE 99	856	695
PBDE 100	148	122
PBDE 116	297	161
PBDE 118	65.7	75.0
PBDE 119	15.5	9.36
PBDE 126	ND	ND
Hexa-		
PBDE 138	15.1	14.7
PBDE 153	178	111
PBDE 154	99.3	91.8
PBDE 155	4.33	12.0
PBDE 166	ND	ND
Hepta-		
PBDE 181	ND	ND
PBDE 183	158	101
PBDE 190	48.7	ND
Octa-		
PBDE 203	113	104
Deca-		
PBDE 209	7,560	2,800
Total PBDEs	10,200	4,800

The total concentration of tri- through deca-PBDEs found in the fine dust from the computer laboratory was about 10,200 ng/g for the left side of the room and 4,800 ng/g for the right side, with a PBDE 209 concentration of 7,560 and 2,800 ng/g. The values were rather consistent with concentrations observed by other researchers.

The sum of PBDEs measured in house dust from a study conducted in United Kingdom ranged from 4,254 to 20,505 ng/g (average value of 10,543 ng/g). The concentration of PBDE 209 found in the dust was from 3,800 up to 19,900 ng/g, with an average value 9,820 ng/g. The analysis of house dust from Germany found total PBDEs concentrations to range from 145 to 27,008 ng/g (the average value was 1,807 ng/g). PBDE 209 was found at concentrations ranging from 137 to 19,100 ng/g (average value was 1,394 ng/g).[4]

The Environmental Working Group (EWG) in the USA reported the total PBDEs concentrations in house dust to be between 614 to 16,366 ng/g, with an average value of 3,699 ng/g (EWG: Toxic fire retardants in American homes in the dust. http://www.ewg.org). The PBDE 209 concentration reached the level <400 up to 7,150 ng/g, with an average value of 2,394 ng/g. The high levels of total PBDEs (1,412-11,426 ng/g, with an average value 3,699 ng/g) were also found in dust in Cape Cod (Mass.) homes (EWG: Toxic fire retardants in American homes in the dust. http://www.ewg.org). In this study, the concentration of PBDE 209 ranged from 916 up to 1,472 ng/g, with an average value 1,232 ng/g.

High concentrations of PBDE 209 have been also found in the dust from buildings in the Netherlands, Finland, Sweden, Italy and Denmark with concentrations ranging from 330 to 6,900 ng/g (EWG: Toxic fire retardants in American homes in the dust. http://www.ewg.org). The total PBDEs concentrations ranged from 437 to 7,100 ng/g with an average value of 2,371 ng/g.

4.7 Carpet extraction results

To decrease the effects of a very high organic background of carpet sample, the sample extract was diluted (1:1) and the internal standard added prior to the analysis. In the case of mono- through hepta-PBDEs analysis, a very high background was observed and no PBDEs were identified. Also, the peak of the internal standard PCB 209 was affected by the high background (Figure 4.2) and so PBDEs quantification was impossible. In the case of deca-PBDE analysis, the compound was identified in both the blank and carpet samples (Figure 4.3). The internal standard was not affected by the high background and quantification of PBDE 209 was possible. The concentration of PBDE 209 in this single sample was 116 ng/g of carpet (361.0 ng per 2.5×2.5 cm square of carpet with a weight of 3.1 g). This value was significantly higher than the blank sample (12.2 ng per sample) processed at the same time. Octa- and nona-PBDEs could not be determined due to analytical difficulties arising from interferences observed in BDE 209 calibration curve standard.

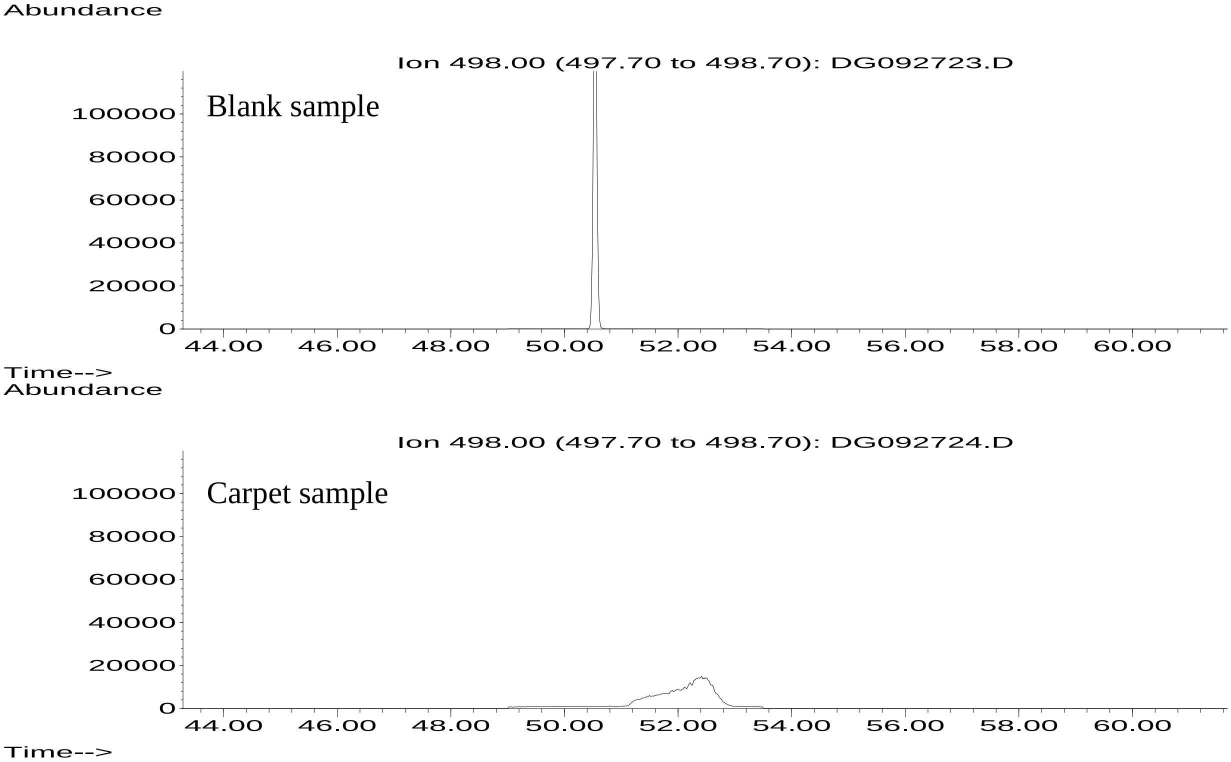

Figure 4.2. Internal standard PCB 209 in the blank and carpet samples. This chromatogram shows the degradation of the internal standard peak shape due to interfering chemicals.

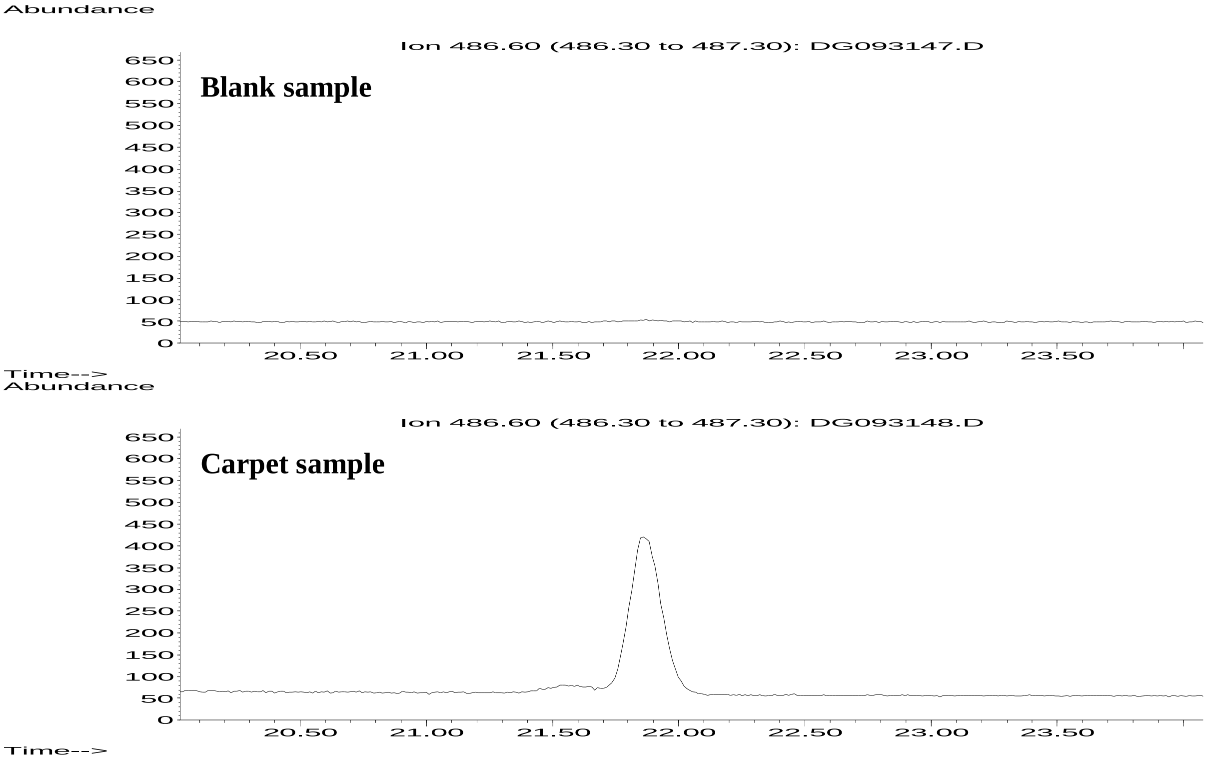

Figure 4.3. Chromatograms of PBDE 209 in the blank and carpet samples. In this case, PBDE 209 could be identified and quantified.

5. Near-Source and Indoor Air Monitoring of PBDEs at an Electronics Recycling Facility

Since PBDEs were used in electronics, the highest indoor air concentrations are likely to occur in industries that handle electronics, particularly older electronic equipment corresponding to a time when the use of PBDEs was more prevalent. The electronics recycling industry generally fits this description and was therefore viewed as one of the primary sampling sites for this study.

A specific electronics recycling facility was selected for the sampling site. This plant focused on dismantling discarded electronic equipment such as computers, printers, TV sets and other electronic goods. The electronic equipment was ground into small pieces by a shredder and then the material was compacted for shipment to other locations for recovery of metals. Plastic cases and cabinets were compacted and shipped for plastics recycling. The physical grinding of the plastics and electronics was expected to release PBDEs, both as vapors and as particulate matter. The large amount of electronic equipment on site at any given time probably also contributed to elevated concentrations of PBDEs. Although the purpose of the research was near-source outdoor air monitoring, indoor air samples were also collected at the facility to compare with outdoor air concentrations of PBDEs.

5.1 Site description and sample collection

Both indoor and outdoor air samples were conducted at this site for 8 hours per day during three consecutive days from June 2-4, 2004. During the first day, recycling operations at the facility consisted of both shredding old electronics and compacting old plastic cases. Activities at the facility were very light on the second day with no shredding activities and minimal compaction activity. Both shredding and compaction activity were the heaviest on the last sampling day.

For outdoor air sampling, four high volume air samplers were used. Two of them were located at the upwind side (S2 and S3) and two samplers were located downwind (S1 and S4) of the building (Figure 5.1). The back gate shown on Figure 5.1 consisted of a roll-up door that remained open during operations.

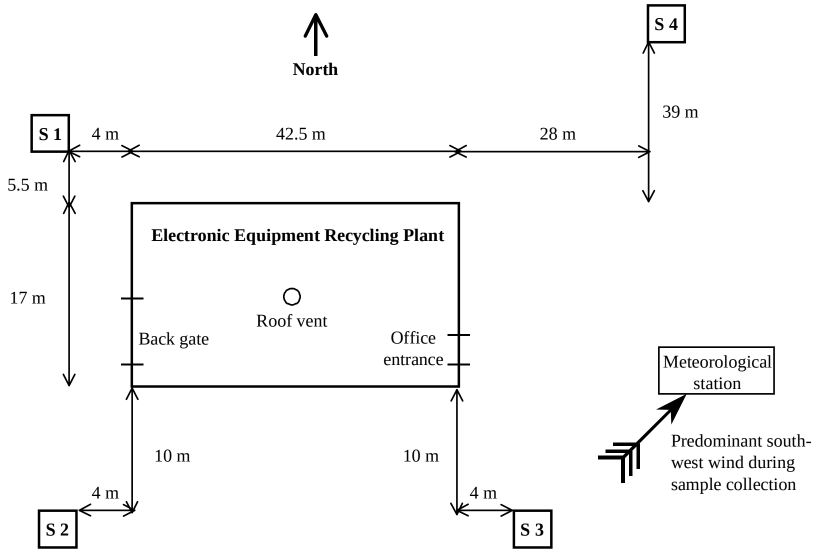

Figure 5.1. Schematic of outdoor air sampling sites at the electronics recycling facility. The position of the four high-volume air samplers are marked by “S1” to “S4”.

The outdoor samplers were equipped with a quartz filter followed by approximately 90g of XAD-2 adsorbent. The air samplers were operated for 8 hours during business hours at a flow rate 30.8 – 34.2 m^3/h giving total of 246 – 274 m^3 of air sampled. The meteorological data for outdoor air sampling are presented in Appendix H (data reported in Pacific Standard Time). The predominant wind direction was from the southwest on all three of the sampling days. Table 5.1 includes data on the amount of adsorbent (XAD-2) used per sample, total sampling time, flow rate and total volume of sampled air, temperature, and relative humidity.

Table 5.1. Details of outdoor air sampling at an electronics recycling facility.

Date	Sampler No.	XAD-2 (g)	Total sampling time (h)	Air Flow (m^3/hr)	Total sampled air (m^3)	Range of Temperature (°C)	Relative Humidity (%)
6/02/04	1	90.05	8	32.5	260	18.7 –33.7	62.6 – 27.3
	2	90.09	8	34.2	274		
	3	90.10	8	32.5	260		
	4	90.07	8	30.8	246		
6/03/04	1	90.09	8	34.2	274	15.3 – 30.0	78.2 – 31.0
	2	90.05	8	34.2	274		
	3	90.05	8	34.2	274		
	4	90.09	8	34.2	274		
6/04/04	1	90.09	8	34.2	274	16.1 – 30.3	73.4 – 32.2
	2	90.03	8	34.2	274		
	3	90.05	8	34.2	274		
	4	90.02	8	34.2	274		

The indoor air sampling consisted of two air samplers located in the dismantling hall between the shredder and the compactor (Figure 5.2). The air intake of the samplers was about 4 feet above the floor. The recycling plant contained two major areas: a dismantling hall (including a shredder and a compactor) and offices. The flow rate for these “low volume” samplers was 12.0 – 18.0 L/min, with a total air volume of 5.95 – 8.64 m^3 during the 8-hour sample collection period (8:00 am to 4:00 pm). The temperature and humidity of the air in the dismantling hall were measured by a sensor probe IAQ-CALC, model 8762 (TSI, Inc., Shoreview, MN). The sample collection details are shown in Table 5.2.

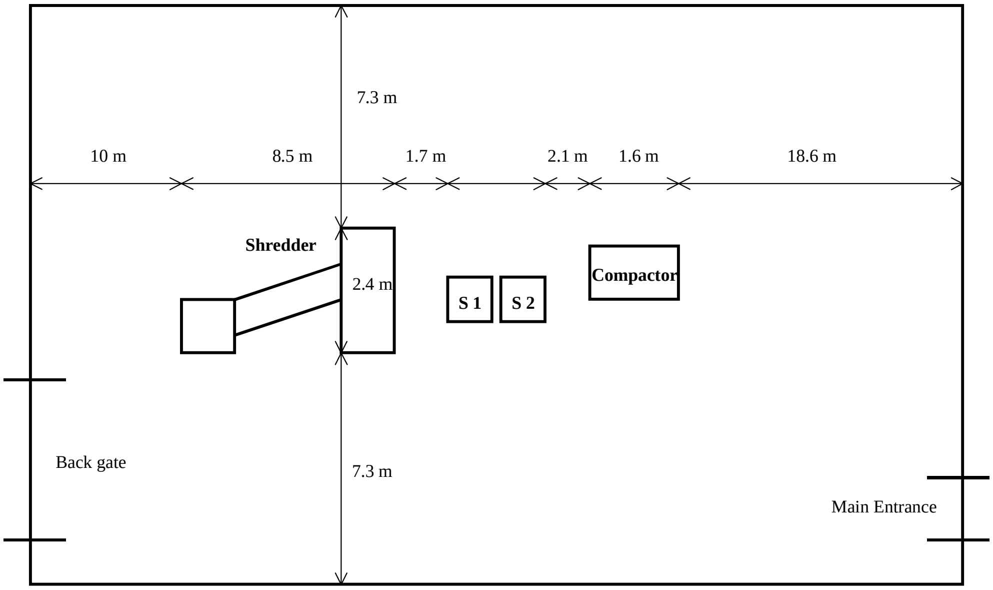

Figure 5.2. Schematic of indoor air sampling at an electronics recycling facility. The two samplers were located at S1 and S2.

Table 5.2. Sampling details for indoor air sampling at an electronics recycling facility.

Date	Sampler No.	XAD-2 (g)	Total sampling time (h)	Air Flow (L/min)	Total sampled air (m^3)	Range of Temperature (°C)	Relative Humidity (%)
6/02/04	1	6.03	8	12.4	5.95	23.6 – 32.3	47.8 – 33.8
	2	6.06	8	17.6	8.35		
6/03/04	1	6.05	8	12.4	5.95	20.6 – 29.1	55.0 – 37.1
	2	6.07	8	18.0	8.64		
6/04/04	1	6.08	8	12.4	5.95	22.5 – 28.9	47.8 – 41.2
	2	6.08	8	18.0	8.64		

To ensure that the sampling matrices were free of contamination, three sampling matrices of each type (from the same batch used for sampling) were analyzed. The “blank” matrices were stored in amber glass jars and transported to the sampling site and back to the laboratory in an ice chest. Prior a sample’s treatment, the “blank” matrices were stored in the refrigerator at -20°C. Therefore, these “travel” blanks were exposed to the same conditions as the samples were, including transport to the field and storage upon return to the laboratory.

In addition, three replicates of each sampling media were enriched with a known amount of PBDEs to verify the extraction efficiency of PBDEs from the sampling matrices used in this sampling episode. These "spiked" sampling substrates were sealed in glass jars, transported to and from the sampling site and stored in the refrigerator at -20°C. These enriched substrates were then extracted and analyzed in the same fashion as the field samples. Results are presented in Appendix I (Tables I.3 – I.6).

Sample extraction was conducted as described in Section 2.4 and the PBDEs in the sample extracts were quantified by GC-ECNCI-MS as described in Sections 2.5.1 and 2.5.2.

5.2 Outdoor air concentrations at an electronics recycling facility

The quality assurance samples, including matrices blanks and spikes, showed that the sampling substrates were effectively free of contamination and that PBDEs were efficiently recovered from the sampling substrates by the extraction procedures. The results of these quality assurance/quality control samples are presented in Appendix I.

The concentrations of PBDEs detected with four high-volume air samplers are summarized in Table 5.3 while the full details, such as mass collected on filter and mass collected on XAD-2, are presented in Appendix J. The octa- and nona-PBDEs could not be accurately determined due to interference observed in PBDE 209 calibration curve standard. This interference is detailed in Appendix K. Again, mono- and di-PBDEs were not determine because of interferences from sample's impurities (bromo-chloro- organic compounds).

Table 5.3. Total atmospheric concentrations of PBDEs (pg/m^3) collected by four high-volume air samplers outside an electronics recycling facility. The values represent the sum of the particulate and XAD-2 collected mass. The results for the three individual sampling days are presented. "ND" indicates that the chemical was not detected while values for octa- and nona-PBDE were not reported due to analytical interferences.

Congener	Sampling day	Sampler 1	Sampler 2	Sampler 3	Sampler 4
Tri-					
PBDE 17	06/02/04	5.37	5.57	4.26	4.44
	06/03/04	4.26	2.32	1.67	1.73
	06/04/04	3.37	2.93	2.40	1.53
PBDE 25	06/02/04	4.67	4.12	2.38	0.66
	06/03/04	3.79	1.37	0.66	0.35
	06/04/04	2.77	2.24	0.85	0.79
PBDE 28	06/02/04	16.3	17.8	7.91	10.4
	06/03/04	13.7	6.02	2.59	3.47
	06/04/04	10.5	9.07	3.98	2.87
PBDE 30	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 32	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 33	06/02/04	1.23	1.28	1.36	0.93
	06/03/04	1.36	0.95	0.89	ND
	06/04/04	0.96	1.07	ND	ND
PBDE 35	06/02/04	1.07	1.11	1.11	ND
	06/03/04	1.13	0.70	ND	ND
	06/04/04	0.83	0.85	0.79	ND
PBDE 37	06/02/04	6.17	8.10	3.10	1.73
	06/03/04	8.35	3.06	1.50	1.34
	06/04/04	7.75	6.88	2.33	1.42

Table 5.3.(cont.)

Tetra-					
PBDE 47	06/02/04	125	104.7	83.0	128
	06/03/04	77.5	35.5	30.2	41.6
	06/04/04	92.5	60.1	36.4	32.5
PBDE 49	06/02/04	33.2	31.6	12.8	11.8
	06/03/04	27.8	11.3	6.32	5.31
	06/04/04	36.7	23.0	7.49	4.55
PBDE 66	06/02/04	9.97	9.83	6.78	6.50
	06/03/04	9.47	4.27	3.15	3.45
	06/04/04	12.7	9.08	4.16	2.94
PBDE 71	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 75	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 77	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
Penta-					
PBDE 85	06/02/04	2.56	2.16	1.66	ND
	06/03/04	2.47	ND	ND	ND
	06/04/04	5.98	2.92	ND	ND
PBDE 99	06/02/04	41.9	30.1	19.9	25.9
	06/03/04	33.3	9.05	8.87	13.0
	06/04/04	84.9	32.3	9.86	9.19
PBDE 100	06/02/04	11.4	9.63	6.99	9.24
	06/03/04	7.68	3.24	3.04	4.07
	06/04/04	16.7	7.24	3.34	3.02
PBDE 116	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 118	06/02/04	2.58	2.57	1.42	ND
	06/03/04	3.30	ND	ND	ND
	06/04/04	5.27	3.37	ND	ND
PBDE 119	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 126	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND

Table 5.3. (cont.)

Hexa-					
PBDE 138	06/02/04	3.98	4.25	ND	ND
	06/03/04	5.71	ND	ND	ND
	06/04/04	6.75	ND	ND	ND
PBDE 153	06/02/04	67.2	60.4	9.22	7.84
	06/03/04	90.3	7.36	3.71	3.31
	06/04/04	150	47.7	6.40	3.47
PBDE 154	06/02/04	13.2	12.8	3.49	2.82
	06/03/04	86.7	3.71	1.37	3.70
	06/04/04	53.5	22.8	2.43	1.47
PBDE 155	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 166	06/02/04	1.43	ND	ND	ND
	06/03/04	2.50	ND	ND	ND
	06/04/04	2.19	1.47	ND	ND
Hepta-					
PBDE 181	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 183	06/02/04	171	165	19.2	7.21
	06/03/04	366	15.8	6.39	6.18
	06/04/04	456	165	8.84	6.63
PBDE 190	06/02/04	6.74	8.50	ND	ND
	06/03/04	13.6	ND	ND	ND
	06/04/04	16.2	8.28	ND	ND
Deca-					
PBDE 209	06/02/04	4390	3170	524	171
	06/03/04	7790	433	140	300
	06/04/04	11400	4180	487	183

The outdoor PBDE concentration data showed a few trends. First, the PBDE concentrations determined from samplers #1 and #2 were almost always higher than samplers #3 and #4. This was not surprising since samplers #1 and #2 were located closest to the loading dock of the facility, which was almost always open during the hours of operation. PBDEs, both particulate and gas-phase, may be emitted from the facility from the open loading area. The east side of the building contains the offices and a normal-size door for people to enter the building, but this door was much smaller than the loading zone and it was typically shut during the hours of operation. Although there was a small vent on the roof of the dismantling hall which could allow for gases and particulate matter to leave the building, it would appear that the loading dock was a significant, if not main, ventilation exit from the dismantling hall.

The most prevalent PBDEs were 209, 183, 154, 153, 100, 99, 60, 49 and 47, with PBDE 209 being found in the highest concentrations that were typically at least an order of magnitude higher than the other PBDEs. This implies that the “deca” formulation may be the most important in terms of PBDEs in the old electronic equipment handled by this facility. It also should be noted that PBDE 209 has a very low volatility, so all the chemical mass was collected on the filter and almost no mass was present on the XAD-2 adsorbent (Appendix J). Since PBDE 209 was particulate associated, then its concentrations may be more sensitive to creation of airborne particulate matter during the grinding operations. It is interesting to note that the concentrations of PBDE 209 are ≥ 40-fold different between the samplers on the two sides of the building. This suggests that airborne particulate matter may be formed, but they may settle rather rapidly and may not disperse much. The outdoor air samplers were total suspended particulate (TSP) samplers, hence they had no size selective inlet. This allows rather coarse particulate matter (such as dust) to be collected by the sampler and analyzed.

The concentrations of PBDEs in outdoor air were relatively consistent between the three sampling days. This contrasts sharply with the indoor air samples that were highly dependent on the sampling day since the second sampling day was conducted when no electronics shredding was taking place.

The concentration of PBDEs in outside air at the recycling facility were significantly elevated compared to PBDEs observed in Davis, CA during the field test of the sampling methodology. Even the lowest observed concentration of PBDE 209 (140 pg/m^3) at the recycling facility was higher than the concentrations observed at Davis (4.4 to 17.8 pg/m^3). Although the sampling was conducted 3 months apart, it still suggests that the recycling facility has elevated concentrations around it compared to a control site.

5.3 Indoor air concentrations of PBDEs at an electronics recycling facility

The indoor air concentrations of PBDEs (Table 5.4) in the recycling were considerably higher than the outdoor air concentrations in almost all cases. This clearly showed that the dismantling facility was a source of PBDEs. Once again PBDE 209 was present in the highest concentrations, which ranged up to 0.83 μg/m^3. These concentrations were essentially completely due to particulate matter. This result was expected since the samplers were located adjacent (within 2 m) to the circuit board shredder. Therefore, airborne particulate matter generation from the shredding operations was expected and the samplers were placed in this location to be representative of this "worst case scenario". It should be noted that the "low volume" air sampler did not have any size-selective inlets on the sampling apparatus, thus large particles could (and probably were) collected by the sampler. The presence of large particles could significantly add to the high PBDE concentrations that were observed.

The indoor air sampling showed highly variable PBDE concentrations depending on the amount of shredding activity that occurred on that sampling day. The second sampling day, namely June 3, 2004, showed significantly lower concentrations compared to the other two days. The concentrations on this day were typically about 3 to 4-fold lower than the other sampling days. The most probable reason for the difference was that there was no shredding activity on that day. The concentrations in the dismantling hall in the absence of shredding activity were still about 10-fold higher than the outdoor concentrations from the sampler closest to the loading dock. The high concentration even on "non-shredding" days was most probably due to dust generated on previous days with shredding activity that was then re-suspended by other activity in the dismantling hall.

The indoor air concentrations of PBDE 209 determined in this study were higher than those reported in the literature for an electronics recycling plant.[9] The reported dismantling hall concentrations ranged from 12,000 to 70,000 pg/m^3, which are a little lower than our "no shredding" day values of 79,700 to 80,100 pg/m^3. The concentrations near the shredder in the literature ranged from 150,000 to 200,000 pg/m^3, while our observed concentrations ranged from 316,000 to 833,000 pg/m^3.

The indoor concentrations of PBDE 209 in the dismantling hall on the “non-shredding” days exceeded the air concentrations of PBDEs in the computer laboratory by approximately 10-fold. This suggests that the mere presence of a large amount of electronic equipment on site is not necessarily the source of PBDEs in the recycling facility but the actual shredding activity and the resulting dust formation is mostly responsible for the elevated PBDE concentrations.

Mono- and di-PBDEs were not determined because of the interferences from sample’s impurities coeluting with studied PBDEs.

Table 5.4. Concentrations of PBDEs (pg/m^3) in indoor air samples collected in the dismantling hall of an electronics recycling facility. “ND” indicates that the analyte was not detected. Values are not reported for octa- and nona-PBDEs due to an analytical interference.

		Sampler				Total	
		1	2	1	2		
Congener	Sampling day	Filter	Filter	XAD-2	XAD-2	Sampler 1	Sampler 2
Tri-							
PBDE 17	06/02/04	45.9	50.7	30.2	42.6	76.1	93.3
	06/03/04	14.8	11.1	23.8	24.1	38.6	35.3
	06/04/04	65.3	56.6	41.0	36.5	106	93.1
PBDE 25	06/02/04	44.8	45.0	29.2	41.5	74.0	86.5
	06/03/04	ND	ND	16.3	20.4	16.3	20.4
	06/04/04	62.6	57.6	40.2	37.4	103	95.0
PBDE 28	06/02/04	149	195	100	142	250	337
	06/03/04	36.6	33.4	65.8	70.0	102	103
	06/04/04	258	222	114	120	372	341
PBDE 30	06/02/04	ND	ND	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND	ND	ND
PBDE 32	06/02/04	ND	ND	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND	ND	ND
PBDE 33	06/02/04	ND	ND	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND	ND	ND
PBDE 35	06/02/04	ND	15.1	ND	ND	ND	15.1
	06/03/04	ND	ND	ND	ND	ND	ND
	06/04/04	18.1	16.9	ND	ND	18.1	16.9
PBDE 37	06/02/04	97.2	94.1	122	142	219	236
	06/03/04	ND	42.7	ND	ND	ND	42.7
	06/04/04	288	270	180	120	468	390

Table 5.4. (cont.)

Tetra-							
PBDE 47	06/02/04	1480	1800	295	325	1780	2120
	06/03/04	594	518	52.5	85.8	647	604
	06/04/04	2750	2450	101	184	2850	2630
PBDE 49	06/02/04	1730	2120	82.0	159	1810	2280
	06/03/04	473	391	40.4	58.8	513	449
	06/04/04	2780	2520	76.6	143	2860	2670
PBDE 66	06/02/04	355	406	35.4	33.8	390	440
	06/03/04	103	93.1	ND	22.1	103	115
	06/04/04	717	660	33.1	35.6	750	695
PBDE 71	06/02/04	ND	ND	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND	ND	ND
PBDE 75	06/02/04	98.9	129	ND	12.4	98.9	142
	06/03/04	ND	ND	ND	ND	ND	ND
	06/04/04	194	157	ND	ND	194	157
PBDE 77	06/02/04	48.3	47.3	ND	ND	48.3	47.3
	06/03/04	28.3	22.1	ND	ND	28.3	22.1
	06/04/04	75.5	70.6	ND	ND	75.5	70.6
Penta-							
PBDE 85	06/02/04	201	195	ND	ND	201	195
	06/03/04	127	87.4	ND	ND	127	87.4
	06/04/04	284	242	ND	ND	284	242
PBDE 99	06/02/04	1570	1980	ND	ND	1570	1980
	06/03/04	483	402	ND	ND	483	402
	06/04/04	3210	2980	ND	ND	3210	2980
PBDE 100	06/02/04	229	292	ND	ND	229	292
	06/03/04	86.9	69.2	ND	ND	86.9	69.2
	06/04/04	448	392	ND	ND	448	392
PBDE 116	06/02/04	ND	ND	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND	ND	ND
PBDE 118	06/02/04	191	223	ND	ND	191	223
	06/03/04	78.8	63.7	ND	ND	78.8	63.7
	06/04/04	343	317	ND	ND	343	317
PBDE 119	06/02/04	ND	ND	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND	ND	ND
PBDE 126	06/02/04	ND	ND	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND	ND	ND

Table 5.4. (cont.)

Hexa-							
PBDE 138	06/02/04	280	319	ND	ND	280	319
	06/03/04	128	95.4	ND	ND	128	95.4
	06/04/04	346	340	ND	ND	346	340
PBDE 153	06/02/04	8040	6600	ND	ND	8040	6600
	06/03/04	1260	1120	ND	ND	1260	1120
	06/04/04	8900	7820	ND	ND	8900	7820
PBDE 154	06/02/04	1230	2210	ND	ND	1230	2210
	06/03/04	3630	3430	ND	ND	3630	3430
	06/04/04	5260	4970	ND	ND	5260	4970
PBDE 155	06/02/04	ND	ND	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND	ND	ND
PBDE 166	06/02/04	97.6	149	ND	ND	97.6	149
	06/03/04	88.9	34.7	ND	ND	88.9	34.7
	06/04/04	463	403	ND	ND	463	403
Hepta-							
PBDE 181	06/02/04	ND	ND	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND	ND	ND
PBDE 183	06/02/04	24300	34000	ND	ND	24300	34000
	06/03/04	6070	5610	ND	ND	6070	5610
	06/04/04	36700	36200	ND	ND	36700	36200
PBDE 190	06/02/04	905	1260	ND	ND	905	1260
	06/03/04	355	288	ND	ND	355	288
	06/04/04	1300	1210	ND	ND	1300	1210
Deca-							
PBDE 209	06/02/04	316000	534000	433	108	316000	534000
	06/03/04	79500	80100	134	ND	79700	80100
	06/04/04	832000	698000	305	130	833000	698000

6. PBDEs in Air Samples from an Automotive Shredding and Metal Recycling Facility

PBDEs are common fire retardants in polyurethane foam such as used in seat cushions and some plastics. Therefore, the last sampling episode focused on an automotive shredding/metal recycling facility that recycles cars and large appliances for metal recovery.

6.1 Site description and sample collection

The shredding operations were conducted outdoors, so only outdoor air sampling was conducted using high-volume air samplers. To determine the contribution of the shredding to fenceline concentrations of PBDEs, one sampler was located on the expected upwind side of the facility (S1) and two samplers (S2, S3) were located on the expected downwind side of the plant (Figure 6.1). The shredding facility was not in operation on the first sampling day (September 13, 2004), so higher concentrations were expected on the second and third sampling days. Crushed cars and metal for recycling are received by the facility during the day while the shredder operates during the night.

Outdoor air sampling was conducted using high-volume air samplers as described in Section 2.2. Outdoor air samples were collected for 24 h for three days (September 13, 21 and 22, 2004) at a rate 30.8 – 35.9 m^3/h giving a total of 725 – 865 m^3 of sampled air. The exact sampling time, the amount of XAD-2 adsorbent, the flow rate and the total air sampled for outdoor air samples are shown in Table 6.1. After sample collection, the filters were folded individually in aluminum foil and sealed in glass jars and XAD-2 resins were removed from the aluminum holders and placed in amber glass jars for transport to the lab in the ice chest. Prior to sample extraction, the samples were stored in a freezer at -20°C.

To determine background concentrations of PBDEs in the sampling matrices, three blanks for each sampling matrix, from the same batch used for sampling, were analyzed. The "blank" matrices were stored in the amber glass jars and transported to the sampling site and back to the laboratory in an ice chest along with the samples.

Additionally, a set of spiked filter and XAD-2 substrates were prepared to verify the extraction efficiency of PBDEs during the current sampling episode. Three replicates of each sampling substrate were enriched with a known amount of PBDEs, stored in amber glass jars and transported to the sampling site and back to the laboratory in an ice chest.

Sample extraction was conducted as described in Section 2.4 and the extracts were quantified by GC-ECNCI-MS as described in Section 2.5.

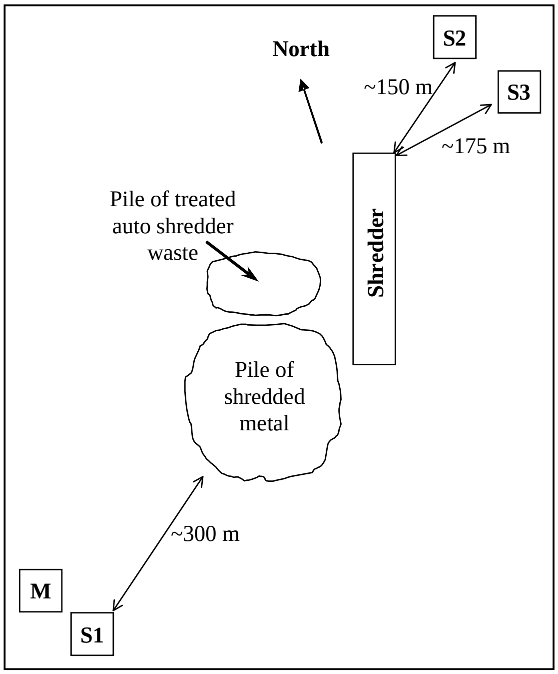

Figure 6.1. Schematic of sampling sites at automotive shredding facility. “S1” indicates the expected upwind sampling site, while “S2” and “S3” represent the expected downwind side of the site. “M” marks the location of the meteorological station.

Table 6.1. Sampling details for outdoor air sampling conducted at an automotive shredding facility.

Sampling Day	Sampler No.	Amount of XAD-2 (g)	Total sampling time (h)	Air Flow (m^3/h)	Total sampled air (m^3)
09/13/2004	1	90.06	23.68	34.2	810
	2	90.37	23.57	30.8	725
	3	90.04	23.67	35.9	850
09/21/2004	1	90.07	24.23	35.1	850
	2	90.11	24.23	30.8	746
	3	90.06	24.10	35.9	865
09/22/2004	1	90.06	24.33	34.2	832
	2	90.02	24.13	30.8	743
	3	90.12	24.03	35.9	863

6.2 PBDE concentrations at the automotive shredding facility

The concentration of PBDEs at the automotive shredding facility (presented in Table 6.2) showed three main trends. The first of which was that the concentrations on the first day of sampling, which corresponded to the day when there was no shredding activity, were typically lower than the days when there was activity at the site. The difference was congener specific, but it was generally a factor of 2-fold different or less. This is similar to the situation in the electronics recycling facility where days of light activity resulted in lower PBDE concentrations.

The second trend was that the PBDE concentrations were considerably higher downwind (see Appendix L for meteorological data, reported in Pacific Standard Time, during sample collection periods) of the shredding operation compared to the upwind side. Once again, the differences were congener specific, but the differences typically ranged from a 50% increase to a 4-fold increase. The elevated PBDE concentrations downwind of the site were still observed even when there was no activity at the site, which implies that PBDEs were being emitted by either off-gassing or dust re-suspension.

Results of the monitoring data should be interpreted along with the meteorological data. While there was no shredding on the first day of sampling (September 13, 2004 to September 14, 2004), samplers S2 and S3 were downwind for more of the sampling period than sampler S1 so the S2 and S3 samplers showed higher concentrations of PBDEs. On the second day of sampling (September 21, 2004 to September 22, 2004), samplers S2 and S3 were downwind of the site for more of the sampling time than sampler S1 and higher concentrations were observed in these samplers compared to sampler S1. During the night when the shredder would have been operating, the wind was mostly out of the north and north-northwest, which would take any emissions to the south or southeast fenceline of the facility where higher concentrations might have occurred. Unfortunately, there were no suitable monitoring sites in that portion of the facility. Similarly, on the third day of sampling, the winds were mostly from the northwest. Samplers S2 and S3 were downwind more than sampler S1 and they measured higher concentrations than S1. Higher concentrations would have been expected along the southeast fenceline of the facility during this sampling period.

The last major trend was that the concentrations of PBDEs at the upwind site were still higher than the concentrations observed in Davis, CA, which served as a control site. The elevated concentrations may be from other sources or it might be from the automotive shredding site itself if the wind switched directions. The concentrations, using PBDE 209 as an example, were comparable to the more remote samplers at the electronics recycling facility.

The quality assurance samples (blanks, limit of detection and extraction efficiencies) are presented in Appendix M. The octa- and nona- PBDEs were not quantified due to interferences observed in BDE 209 calibration curve standard. See Appendix K for the details of this analytical problem. Again, mono- and di-PBDEs were not determine because of interferences from the sample’s impurities coeluting with studied PBDEs.

Table 6.2. PBDE concentrations (pg/m^3) in outdoor air samples at an automotive shredding facility in September 2004. “ND” indicates that the analyte was not detected. The octa- and nona-PBDEs could not be quantified due to an analytical interference.

		Sampler								
		1	**2**	**3**	**1**	**2**	**3**	**Total**		
Congener	**Sampling day**	**Filter**	**Filter**	**Filter**	**XAD-2**	**XAD-2**	**XAD-2**	**Sampler 1**	**Sampler 2**	**Sampler 3**
Tri-										
PBDE 17	09/13/04	0.38	0.76	0.25	0.66	ND	ND	1.04	0.76	0.25
	09/21/04	0.92	1.28	1.16	2.42	4.09	4.09	3.34	5.37	5.25
	09/22/04	1.02	1.24	1.20	2.15	4.58	4.30	3.17	5.82	5.50
PBDE 25	09/13/04	ND	0.29	ND	0.45	2.71	1.87	0.45	3.00	1.87
	09/21/04	ND	ND	0.89	1.25	1.96	2.24	1.25	1.96	3.13
	09/22/04	0.96	1.07	0.92	1.15	2.00	1.89	2.11	3.07	2.81
PBDE 28	09/13/04	0.43	2.04	1.16	ND	ND	ND	0.43	2.04	1.16
	09/21/04	5.66	7.44	6.67	ND	ND	ND	5.66	7.44	6.67
	09/22/04	5.78	7.23	6.38	ND	ND	ND	5.78	7.23	6.38
PBDE 30	09/13/04	ND	ND	ND	ND	0.31	0.17	ND	0.31	0.17
	09/21/04	ND	ND	ND	0.84	0.87	0.84	0.84	0.87	0.84
	09/22/04	ND	ND	ND	0.72	0.74	ND	0.72	0.74	ND
PBDE 32	09/13/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/21/04	0.63	0.86	0.81	ND	ND	ND	0.63	0.86	0.81
	09/22/04	0.66	0.71	0.67	ND	ND	ND	0.66	0.71	0.67
PBDE 33	09/13/04	ND	0.90	0.79	0.80	17.3	13.3	0.80	18.2	14.0
	09/21/04	ND	ND	ND	0.69	34.6	22.4	0.69	34.6	22.4
	09/22/04	0.30	ND	0.33	0.47	18.3	15.2	0.77	18.3	15.6
PBDE 35	09/13/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/21/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/22/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
PBDE 37	09/13/04	ND	ND	ND	0.60	2.30	1.67	0.60	2.30	1.67
	09/21/04	ND	ND	ND	0.93	2.42	0.86	0.93	2.42	0.86
	09/22/04	ND	ND	ND	0.86	0.64	0.68	0.86	0.64	0.68
Tetra-										
PBDE 47	09/13/04	12.0	45.3	31.3	21.2	41.2	45.5	33.1	86.5	76.9
	09/21/04	11.4	44.9	47.6	18.9	39.7	40.8	30.3	84.6	88.3
	09/22/04	8.6	30.5	30.4	18.3	44.0	41.7	27.0	74.5	72.1
PBDE 49	09/13/04	0.96	4.20	3.13	1.77	4.52	5.09	2.73	8.72	8.22
	09/21/04	1.59	5.13	5.54	2.08	5.16	4.95	3.67	10.3	10.5
	09/22/04	1.34	4.20	4.03	1.90	5.41	4.98	3.24	9.61	9.01
PBDE 66	09/13/04	1.09	2.48	1.95	1.21	2.03	2.01	2.30	4.51	3.96
	09/21/04	1.37	2.63	2.75	1.32	2.37	2.34	2.69	5.00	5.09
	09/22/04	1.23	2.23	2.14	1.39	2.80	2.55	2.62	5.03	4.69
PBDE 71	09/13/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/21/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/22/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
PBDE 75	09/13/04	ND	0.69	0.56	0.50	0.77	0.81	0.50	1.46	1.37
	09/21/04	0.83	1.29	1.21	0.85	0.85	0.74	1.68	2.14	1.95
	09/22/04	0.78	1.08	1.02	0.83	1.32	0.72	1.61	2.40	1.74
PBDE 77	09/13/04	ND	1.06	0.92	ND	1.37	ND	ND	2.43	0.92
	09/21/04	0.98	1.16	1.05	ND	ND	0.92	0.98	1.16	1.97
	09/22/04	ND	ND	0.95	ND	1.06	ND	ND	1.06	0.95

Table 6.2. (cont.)

Penta-										
PBDE 85	09/13/04	3.56	6.41	4.61	2.38	2.63	2.30	5.94	9.04	6.91
	09/21/04	2.48	6.28	6.73	ND	ND	ND	2.48	6.28	6.73
	09/22/04	2.11	4.74	4.77	ND	1.41	1.22	2.11	6.15	5.99
PBDE 99	09/13/04	23.9	85.9	55.5	3.19	4.45	6.07	27.1	90.3	61.5
	09/21/04	23.5	94.7	105	2.41	4.95	5.29	25.9	99.7	111
	09/22/04	18.4	66.4	67.0	2.62	6.39	5.63	21.0	72.8	72.6
PBDE 100	09/13/04	4.32	10.4	10.1	1.23	1.96	2.45	5.55	12.4	12.5
	09/21/04	4.87	17.7	18.9	1.33	2.48	2.61	6.20	20.2	21.5
	09/22/04	3.70	11.8	11.7	1.45	3.18	2.82	5.15	15.0	14.5
PBDE 116	09/13/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/21/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/22/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
PBDE 118	09/13/04	1.08	1.81	1.31	ND	1.02	ND	1.08	2.83	1.31
	09/21/04	1.68	2.68	2.56	ND	ND	ND	1.68	2.68	2.56
	09/22/04	1.56	2.23	2.10	ND	1.63	ND	1.56	3.86	2.10
PBDE 119	09/13/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/21/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/22/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
PBDE 126	09/13/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/21/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/22/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexa-										
PBDE 138	09/13/04	1.27	2.08	1.55	ND	ND	ND	1.27	2.08	1.55
	09/21/04	2.88	3.93	3.92	ND	ND	ND	2.88	3.93	3.92
	09/22/04	2.83	3.71	3.38	ND	ND	ND	2.83	3.71	3.38
PBDE 153	09/13/04	3.64	32.2	10.4	0.94	1.06	0.97	4.58	33.2	11.3
	09/21/04	4.91	16.6	23.1	ND	1.99	1.70	4.91	18.6	24.8
	09/22/04	4.18	12.9	14.3	ND	1.94	ND	4.18	14.9	14.3
PBDE 154	09/13/04	3.79	23.8	17.1	ND	ND	0.27	3.79	23.8	17.4
	09/21/04	5.06	24.0	35.6	0.96	1.32	1.31	6.02	25.3	36.9
	09/22/04	4.58	17.7	21.8	0.96	1.28	1.11	5.54	18.9	22.9
PBDE 155	09/13/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/21/04	0.19	0.50	0.62	ND	ND	ND	0.19	0.50	0.62
	09/22/04	ND	0.29	0.53	ND	ND	ND	ND	0.29	0.53
PBDE 166	09/13/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/21/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/22/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hepta-										
PBDE 181	09/13/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/21/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
	09/22/04	ND	ND	ND	ND	ND	ND	ND	ND	ND
PBDE 183	09/13/04	1.67	19.3	16.1	ND	ND	0.25	1.67	19.3	16.3
	09/21/04	6.34	16.9	32.6	ND	ND	ND	6.34	16.94	32.55
	09/22/04	3.96	14.7	20.2	ND	ND	ND	3.96	14.7	20.2
PBDE 190	09/13/04	1.95	3.46	2.92	ND	ND	ND	1.95	3.46	2.92
	09/21/04	ND	2.72	3.83	ND	ND	ND	ND	2.72	3.83
	09/22/04	ND	2.40	2.48	ND	ND	ND	ND	2.40	2.48
Deca-										
PBDE 209	09/13/04	43.0	249	185	2.41	2.65	3.42	45.5	252	189
	09/21/04	285	449	1940	1.13	2.35	3.58	286	452	1940
	09/22/04	122	260	317	ND	1.04	1.67	123	261	319

7. Comparisons between Sampling Sites

The large number of permutations of different PBDE congeners and different sampling conditions makes the raw data tables difficult to read. Therefore, the data are summarized below for three of the most important PBDE congeners, namely PBDE 47, 99 and 209.

The results for outdoor air samples, summarized in Table 7.1, showed that the down-wind side at the automotive shredding site and the "near loading dock" sites had significantly elevated PBDE concentrations ($p< 0.05$) compared to the control site at UC Davis for all congeners. The level of statistical significance was not as great as expected due to the very high standard deviation associated with the measurements, which was particularly large for PBDE 209. A larger sample size would have been able to achieve a higher level of statistical power, but the trends were still clear. The upwind site at the automotive shredding facility and the "far from loading dock" samplers at the electronics recycling facility showed elevated PBDE concentrations, but the concentrations were frequently not statistically significant due to the high variation in the data sets. The "near" and "far" from loading dock data sets at the electronics recycling facility were significantly different from each other for PBDE 209 (Mann-Whitney test, $p < 0.05$), but this trend was not repeated at the automotive shredding facility due to the high variability in the PBDE 209 concentrations. In general, it appears from the data that the electronic recycling facility and the automotive shredding facility are both point sources of PBDEs to the air.

Table 7.1. Comparison of outdoor air concentrations (pg/m^3) for three selected PBDE congeners in Davis, the electronics recycling facility and the automotive shredding facility. The mean ± SD are presented for each congener even though data from multiple days are combined and the data may not conform to a normal distribution if there is daily variation in concentrations. A student's t-test was used for the determination of statistical significance for PBDE 47 and 99 while a Mann-Whitney test was used for PBDE 209 due to its non-normally distributed data.

Site	*n*	PBDE 47	PBDE 99	PBDE 209
UC Davis (control)	4	34.3 ± 11.9	11.8 ± 4.20	10.6 ± 6.57
Electronics recycling facility, far from loading dock	6	58.6 ± 39.2	14.4 ± 6.97	301 ± 168$^{\mathbf{b}}$
Electronics recycling facility, near loading dock	6	82.6 ± 32.0$^{\mathbf{b}}$	38.6 ± 25.2$^{\mathbf{b}}$	5230 ± 3840$^{\mathbf{b}}$
Auto shredding facility, upwind site	3	30.1 ± 3.05	24.7 ± 3.23$^{\mathbf{b}}$	152 ± 123
Auto shredding facility, downwind site	6	80.5 ± 6.82$^{\mathbf{a}}$	84.7 ± 18.8$^{\mathbf{a}}$	569 ± 678$^{\mathbf{b}}$

$^{\mathbf{a}}$ Concentrations were significantly different from control site at UC Davis (p<0.05).
$^{\mathbf{b}}$ Concentrations were significantly different from control site at UC Davis (p<0.01).

The comparison between indoor air samples collected from different locations suffered from low statistical power due to very few samples (n=2), particularly for the control conditions (computers off in the computer laboratory and no shredding at the electronics recycling facility). However, the computer laboratory with the computers "on" had significantly higher concentrations than the outdoor air concentrations at the control site of UC Davis (Table 7.2). Whether the elevated concentrations were due mainly to the computers or other sources in the building (e.g. foam chairs) was not evident since the PBDE concentrations between computers "on" and "off" did not vary significantly for PBDEs 47 and 99. The data show that PBDE 209 increased the most (about 6 fold) between the computers "off" and "on" conditions, but once again, the small data set lacked the statistical power to provide a reasonable level of confidence. The concentration of PBDEs in the electronics recycling facility during shredding operations was clearly higher than the control conditions for all congeners. In particular, the concentrations of PBDE 209 were exceptionally high compared to all other conditions and locations. Evidently, the shredding operations generate airborne particulate matter consisting of plastics that contain high amounts of PBDE 209. This was not particularly surprising since the samplers were located within 2 meters of the shredding equipment, so the samplers collected a worst case scenario in terms of measuring PBDEs arising from particulate matter.

Table 7.2. Comparison of indoor air concentrations (pg/m^3) for three selected PBDE congeners in the computer laboratory and the electronics recycling facility. The mean ± SD are presented for each congener. A student's t-test was used for the determination of statistical significance for PBDE 47 and 99 while a Mann-Whitney test was used for PBDE 209 due to its non-normally distributed data.

Site	*n*	PBDE 47	PBDE 99	PBDE 209
UC Davis (control, outdoor air)	4	34.3 ± 11.9	11.8 ± 4.20	10.6 ± 6.57
Computer laboratory, computers off	2	901 ± 115	117 ± 73.3	9.96 ± 10.9
Computer laboratory, computers on	6	1060 ± 266$^{\mathbf{b}}$	182 ± 111$^{\mathbf{a}}$	57.7 ± 11.2$^{\mathbf{a}}$
Electronics recycling, no shredding	2	626 ± 30.4$^{\mathbf{a}}$	443 ± 57.3	79900 ± 283
Electronics recycling, shredding	4	2350 ± 485$^{\mathbf{b}}$	2440 ± 786$^{\mathbf{b}}$	595000 ± 222000$^{\mathbf{a}}$

[a] Concentrations are significantly different from control site at UC Davis (p<0.05).
[b] Concentrations are significantly different from control site at UC Davis (p<0.01).

8. Summary and Conclusions

The objective of this research was to determine the airborne concentrations of PBDEs near suspected sources of PBDEs. Therefore, PBDE sampling focused on three sites where elevated PBDE concentrations were expected: namely 1) a computer room in a public office building; 2) an electronics recycling facility; and 3) an automotive shredding/metal recovery facility. In addition, outdoor air samples were also collected at the University of California, Davis, both as a test of the analytical procedures as well as serving as a control site to compare the concentrations observed at the three test sites.

Both indoor and outdoor air samples were collected during this research. The outdoor air samples were collected with an Andersen High-Volume TSP air sampler, with a flow rate of approximately 30 m^3/h, equipped with a quartz microfiber filter followed by ~90 g of XAD-2 resin as an adsorbent. The indoor air samples were collected with a "low volume" sampler, with flow rates of about 15 to 20 l/min, which was also equipped with a quartz filter followed by XAD-2 resin. The filters and XAD-2 resin were extracted by Soxhlet extraction for 24 hours with dichloromethane. After extraction, the samples were concentrated by rotoevaporation and then passed through a silica gel column.

The determination of PBDEs in the sample extracts was conducted by an Agilent gas chromatography coupled to a quadrupole mass spectrometer. Both electron ionization (EI) and electron-capture negative chemical ionization (ECNCI) were evaluated for the analysis of PBDEs. We determined that greater sensitivity was obtained with ECNCI, so this was the preferred ionization mode. Several instrumental conditions were optimized to improve the sensitivity of the analysis, such as source temperature (150^oC), ionization gas pressure (methane at 2.5×10^{-4} torr; 0.0333 Pa), electron energy (130 eV) and emission current (300 μA). In addition, selected ion monitoring (SIM) was used to further improve the sensitivity of the analysis. These instrumental conditions were able to provide detection limits from 0.08 to 2.18 pg/μl of sample extract depending on the congener.

The first sampling campaign was designed to determine the emissions of PBDEs from computers in a computer room in a public office building. In this case, indoor air samples were collected under two conditions, namely with the computers on and with the computers turned off. The difference between "computers on" and "computers off" gave an indication of the contribution of computers to the PBDE levels in the indoor environment. While the concentrations of all detected PBDEs increased when the computers were on, the increase compared to the "computers off" condition was minimal (<2-fold) with the exception of PBDE 209 which showed a 5-fold increase in concentrations when the computers were turned on. This implies that there may be other significant sources of the lower brominated diphenyl ethers in the office environment, such as foam chairs, etc. while computers were a significant factor for the decabromodiphenyl ether. Considering that PBDE 209 is a relatively non-volatile PBDE, it was not surprising that the emissions were higher when the computers were on and warmed up. The concentrations of PBDEs in the computer laboratory air were clearly higher than outdoor air concentrations at the control site of UC Davis, although the small (n=2) sample size of the "computers off" condition resulted in low statistical power that effectively prevented statistical verification of the observed differences. In contrast, the "computers on" condition had a sufficiently large sample set which could be statistically proven to be different from the outdoor air concentrations at UC Davis.

The second sampling campaign focused on an electronics recycling facility where old computers, televisions, etc. were dismantled, shredded and compacted for shipment off-site for metal recovery and plastics recycling. Since PBDEs were commonly used in electronics equipment, this facility was expected to have significantly elevated concentrations of PBDEs in the air. Both indoor and outdoor air samples were collected during this sampling campaign to assess both indoor concentrations in the dismantling hall and the impact of the facility on near-source outdoor PBDE. The outdoor air samplers showed that the facility did contribute to the near-source PBDE loading, but its effects appeared to be localized. The two outdoor air samplers located farthest from the loading dock area, which was a large ventilation mechanism for the dismantling hall, had concentrations that were fairly similar to the control site at UC Davis with the exception of PBDE 209, which had about 30-fold higher concentrations at the electronics recycling facility. In contrast, the two samplers located closest to the loading dock door had significantly higher PBDE concentrations for most PBDEs, but PBDE 209 had the greatest increase with about 500-fold higher PBDE 209 concentrations compared to the control site. The PBDE 209 was essentially completely particulate-associated, which suggested that airborne particulate matter generated in the dismantling hall escaped the building and were collected by the air samplers.

The indoor air samples from the electronics recycling facility showed an even more pronounced increase in air PBDE concentrations. In this case, the samplers were located within about 2 m of the electronics shredder, so the samplers would represent the “worst case scenario” for indoor air concentrations. The indoor samplers lacked any size selective inlets, so relatively coarse particulate matter could be collected by the samplers. The concentrations of PBDEs in the air of the dismantling hall were 20 to 60,000-fold higher than the control site at UC Davis. There were also differences between the three sampling days. There was no shredding activity in the facility on one of the sampling days, which resulted in lower PBDE concentrations on that day. Even these concentrations were highly elevated compared to the control site. The concentrations of PBDEs on days where there was shredding activity were dramatically higher, with PBDE 209 showing the greatest increase. This suggests that airborne particulate matter generated during shredding was collected by the samplers.

The last sampling campaign focused on an automotive shredding facility, where the PBDEs were expected to arise from foam used in car seats and other plastics used in cars. Since the operations at this facility were conducted outdoors, only outdoor air samples were collected for this part of the project. For this project, two air samplers were deployed in an area expected to be downwind of the site while one was set on the expected upwind side of the site. The concentrations of PBDEs on the upwind side of the site were not very different from the control site, although PBDE 209 was about 15 fold higher. The downwind side of the site showed significantly elevated PBDE concentrations compared to the UC Davis control site. The downwind concentrations were about 3 to 4 fold greater than the upwind side of the site, which shows that the automotive shredding facility was a source of airborne PBDEs.

In all three sampling campaigns, the suspected point sources of PBDEs were shown to contribute to the atmospheric loading of PBDEs. However, the actual impact of the facilities seemed to be localized with relatively little effect at the upwind sites. In almost all cases, PBDE 209 was the PBDE that showed the greatest increase compared to the control site at UC Davis. Since this compound was most often particulate-associated, we suspect that the air samplers were simply collecting airborne particulate matter, which consisted of plastics and PBDEs, that were generated at the sites. This was clearly the case in the indoor electronics recycling facility. If the

PBDEs, and PBDE 209 in particular, are associated with coarse particulate matter generated from shredding or dismantling operations, then the residence time of these PBDEs in the air column may be rather short since the settling velocity of coarse particles is rather rapid. The short residence times in the air column would indicate that the chemicals are not likely to move too far from the site before settling out. Therefore, the impact of the sites would be expected to be localized. The lower brominated PBDEs are semi-volatile and thus exist in both the gas and particulate phases, so they would be more likely to move farther from the site since they can move into the gas phase and escape the coarse particles.

These near-source results and the results from the indoor air monitoring at the electronics recycling facility point to the need to further evaluate the health effects from exposure to PBDEs.

Future studies should include field spikes, in which spiked samples have air drawn through them during field sampling conditions to evaluate collection efficiency and breakthrough. This would help to supplement information about the accuracy of the method obtained during method development.

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Glossary of Abbreviations

ECNCI	electron-capture negative chemical ionization
EI	electron ionization (also called electron impact)
eV	electron volts
K_{OW}	octanol-water partition coefficient
LOD	limit of detection
m/z	mass to charge ratio (in mass spectrometry)
ND	not detected
PBDDs	polybrominated dibenzo-p-dioxins
PBDEs	polybrominated diphenyl ethers
PBDFs	polybrominated dibenzofurans
PCBs	polychlorinated biphenyls
PUF	polyurethane foam
SIM	selected ion monitoring
S/N	signal to noise ratio
SPMD	semi-permeable membrane device
TSP	total suspended particulates
XAD-2	a trade name for a styrene divinylbenzene adsorbent

APPENDIX A
Concentrations of PBDEs in Calibration Curves

Table A.1. Concentration (pg/µl) of calibration standards and internal standards for the quantification of mono- through hepta- PBDEs.

	Calibration Level				
Congener	1	2	3	4	5
Mono-					
PBDE 1	0.49	4.90	9.80	49.02	98.04
PBDE 2	0.49	4.90	9.80	49.02	98.04
PBDE 3	0.49	4.90	9.80	49.02	98.04
Di-					
PBDE 7	0.49	4.90	9.80	49.02	98.04
PBDE 8	0.49	4.90	9.80	49.02	98.04
PBDE 10	0.49	4.90	9.80	49.02	98.04
PBDE 11	0.49	4.90	9.80	49.02	98.04
PBDE 12	0.49	4.90	9.80	49.02	98.04
PBDE 13	0.49	4.90	9.80	49.02	98.04
PBDE 15	0.49	4.90	9.80	49.02	98.04
Tri-					
PBDE 17	0.49	4.90	9.80	49.02	98.04
PBDE 25	0.49	4.90	9.80	49.02	98.04
PBDE 28	0.49	4.90	9.80	49.02	98.04
PBDE 30	0.49	4.90	9.80	49.02	98.04
PBDE 32	0.49	4.90	9.80	49.02	98.04
PBDE 33	0.49	4.90	9.80	49.02	98.04
PBDE 35	0.49	4.90	9.80	49.02	98.04
PBDE 37	0.49	4.90	9.80	49.02	98.04
Tetra-					
PBDE 47	0.49	4.90	9.80	49.02	98.04
PBDE 49	0.49	4.90	9.80	49.02	98.04
PBDE 66	0.49	4.90	9.80	49.02	98.04
PBDE 71	0.49	4.90	9.80	49.02	98.04
PBDE 75	0.49	4.90	9.80	49.02	98.04
PBDE 77	0.49	4.90	9.80	49.02	98.04
Penta-					
PBDE 85	0.74	7.35	14.71	73.53	147.06
PBDE 99	0.74	7.35	14.71	73.53	147.06
PBDE 100	0.74	7.35	14.71	73.53	147.06
PBDE 116	0.74	7.35	14.71	73.53	147.06
PBDE 118	0.74	7.35	14.71	73.53	147.06
PBDE 119	0.74	7.35	14.71	73.53	147.06
PBDE 126	0.74	7.35	14.71	73.53	147.06

Table A.1. (cont.)

Hexa-					
PBDE 138	0.98	9.80	19.61	98.04	196.08
PBDE 153	0.98	9.80	19.61	98.04	196.08
PBDE 154	0.98	9.80	19.61	98.04	196.08
PBDE 155	0.98	9.80	19.61	98.04	196.08
PBDE 166	0.98	9.80	19.61	98.04	196.08
Hepta-					
PBDE 181	1.23	12.26	24.51	122.55	245.10
PBDE 183	1.23	12.26	24.51	122.55	245.10
PBDE 190	1.23	12.26	24.51	122.55	245.10
Internal Standard					
PCB 65	2,376	2,376	2,376	2,376	2,376
PCB 209	112.47	112.47	112.47	112.47	112.47

Table A.2. Concentration (pg/µl) of calibration standards and internal standards for the quantification of octa- through deca-PBDEs.

Congener	Calibration Level				
	1	2	3	4	5
Octa-					
PBDE 196	0.93	4.67	9.34	93.37	466.85
PBDE 197	0.93	4.67	9.34	93.37	466.85
PBDE 203	1.04	5.19	10.37	103.37	518.67
Nona-					
PBDE 206	0.93	4.67	9.34	93.37	466.85
PBDE 207	0.93	4.67	9.34	93.37	466.85
PBDE 208	0.93	4.67	9.34	93.37	466.85
Deca-					
PBDE 209	0.94	4.69	9.38	93.76	468.78
Internal Standard					
$^{13}C_{12}$-PBDE 209	490.19	490.19	490.19	490.19	490.19

APPENDIX B
Electron Ionization (EI) Optimization and Parameterization

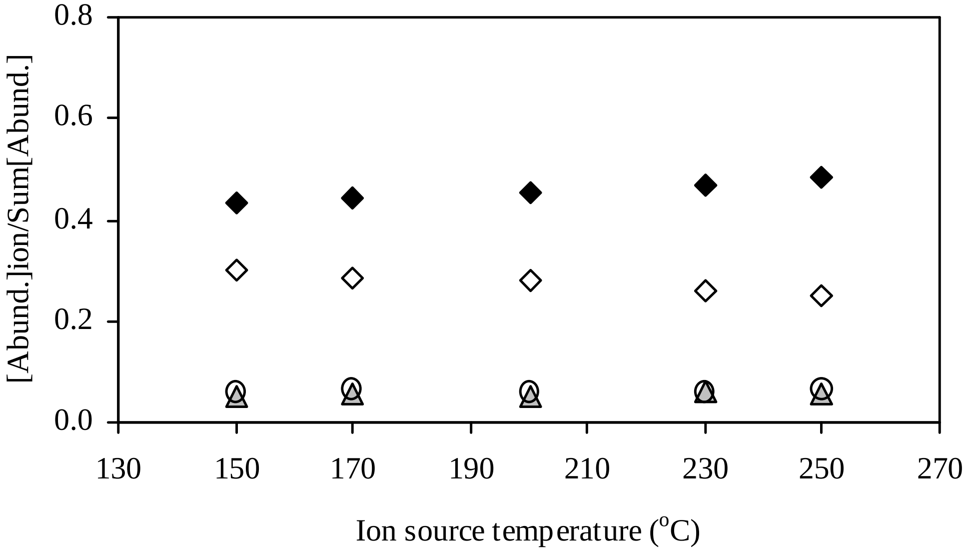
Optimization of Ion Source Temperature and Electron Energy:

For EI-MS analysis, experiments focused on finding optimal conditions, such as ion source temperature and electron energy. The ion source temperature was varied from 150° to 250°C while the electron energy was held constant at 75 eV. Next, the electron energy was varied from 30 to 100 eV while the ion source temperature was held at 230°C.

The ion source temperature has a slight effect on the ratio of fragmentation ions $[M]^+$ and $[M-2Br]^+$ (Figure B.1). While increasing ion source temperature decreased the ratio of $[M]^+$ ion (from 0.300 to 0.248) in EI-MS spectra, the ratio of $[M-2Br]^+$ ion intensity to the total intensities increased from 0.433 to 0.485 (Figure B.2). While the ion source temperature did not affect the amount of fragmentation, it did affect the ion intensities where source temperatures greater than 200°C gave the highest ion intensities(Figure B.2).

For example, the electron energy significantly affected the fragmentation of PBDE 153 congener. As the electron energy increased from 40 to 100 eV, the $[M]^+$ and $[M-2Br]^+$ ions increased in EI-MS spectra. The ratio of $[M]^+$ ion increased from 0.147 to 0.302 and $[M-2Br]^+$ ion ratio increased from 0.387 to 0.475 (Figure B.1). The ions intensities increased with increasing electron energies up to a maximum of 70 to 80 eV, and then the ion intensities decreased (Figure B.2).

Although the results from PBDE 153 are presented herein, but the same trends were observed in the spectra of other studied mono- through hepta-PBDEs. The highest intensity of ions in EI-MS spectra of PBDEs congeners was achieved at the ion source temperature 200°C and the electron energy 70 eV to 80 eV. The optimal instrumental parameters found for the PBDEs analysis in EI-MS mode again differ from the results of Eljarrat et al.[47] where the maximum total abundance was obtained at the ion source temperature 250°C and the electron energy 35 eV.



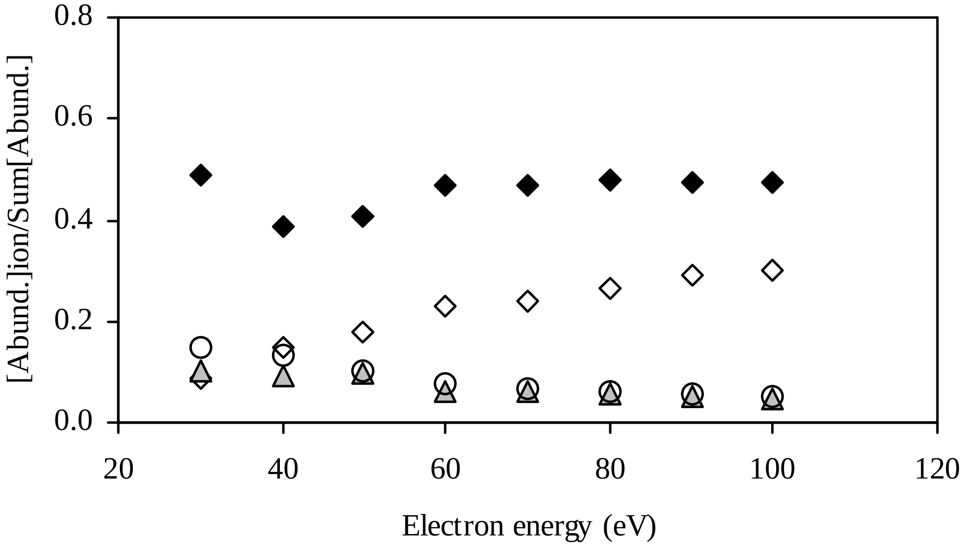


Figure B.1. Effect of the studied instrumental parameters on the fragmentation of BDE 153 in EI-MS spectra.◊ - $[M]^+$, ♦ - $[M\text{-}2Br]^+$, Δ- $[M\text{-}3Br\text{-}CO]^+$, ○ - $[M\text{-}4Br]^+$

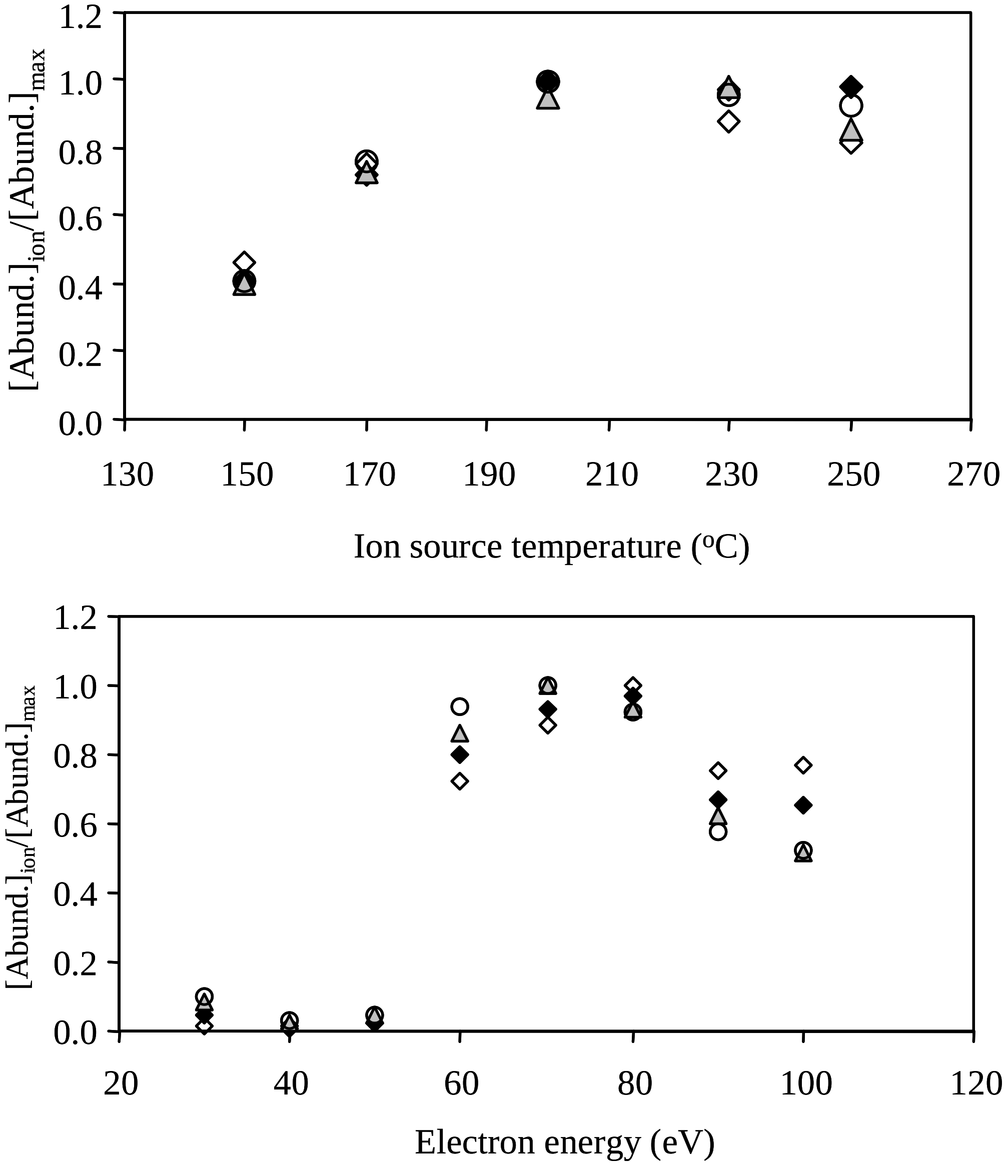


Figure B.2. Effect of the ion source temperature and electron energy on the intensity of PBDE 153 ions in EI-MS spectra. ◊ = $[M]^+$, ♦ = $[M\text{-}2Br]^+$, Δ= $[M\text{-}3Br\text{-}CO]^+$, ○ = $[M\text{-}4Br]^+$

Mass Spectra Characterization of Electron Ionization (EI) Analyses:

The major ions of selected mono- through hepta-PBDEs (relative intensity >10%) in EI-MS spectra are presented in Table B.1. In comparison with ECNCI-MS spectra, EI-MS spectra of PBDEs gave $[M]^+$ ion with very high intensity (42-100%). In spectra of di-, tetra- and penta-PBDEs, the $[M]^+$ ion is dominant. The dominant ion observed in spectra of mono- PBDEs is $[M\text{-}Br]^+$ while the spectra of the tri-, hexa- and hepta-PBDEs had a $[M\text{-}2Br]^+$ fragment as the base ion.

The relative intensity of ion $[M\text{-}2Br]^+$ in the spectra of di-, tetra- and penta-PBDEs ranged from 25% up to 90%. Another common ion presented in the EI mass spectra of mono- and di-PBDEs is a fragment $[M\text{-}Br\text{-}CO]^+$ with the relative intensity 39% and 10%.

The spectra of higher brominated diphenyl ethers (tri- up to hepta-PBDE) had a $[M-3Br-CO]^+$ ion with relative intensity of 12-25%. Tetra-PBDEs EI mass spectra also showed an $[M-4Br-CO]^+$ ion with the relative intensity 10%. In the spectra of penta- and hexa-PBDE, a $[M-5Br-CO]^+$ fragment with relative intensity of 16% and 7%, respectively, was observed. Lastly, the hexa- and hepta-PBDEs had an $[M-4Br]^+$ ion with the relative intensity 13% and 12%, respectively.

Table B.1. The major ions of selected mono- through hepta-PBDEs (relative intensity >10%) in EI-MS spectra.

# of Br	Congener	% Relative Intensity of Fragmentation Ions							
		$[M]^+$	$[M-Br]^+$	$[M-Br_2-CO]^+$	$[M-2Br]^+$	$[M-3Br-CO]^+$	$[M-4Br]^+$	$[M-4Br-CO]^+$	$[M-5Br-CO]^+$
Mono-	PBDE 1	63	100	39					
Di-	PBDE 15	100		10	25				
Tri-	PBDE 30	56			100	25			
Tetra-	PBDE 47	100			90	15		10	
Penta-	PBDE 100	100			85	20			16
Hexa-	PBDE 153	62			100	12	13		7
Hepta-	PBDE 190	42			100	17	12		

APPENDIX C
Identification and Quantification Ions for PBDEs

Table C.1. Identifying and quantifying ions for PBDEs in field samples. The table is divided into three groups depending on which internal standard was used for the calculation of the relative retention time (RRT). The first group (the lighter compounds) used PCB 65 as the RRT marker; the intermediate compounds used PCB 209 and the heaviest compounds used $^{13}C_{12}$-deca-PBDE.

Compound	Relative Retention Time	Identifying and Quantifying Ions	Theoretical Ratio	Confirming Ions	Theoretical Ratio
PCB 65 [a]	1.000	35.0 / 37.0	100 : 33		
Mono-					
PBDE 1	0.551	78.9 / 80.9	100 : 98		
PBDE 2	0.573	78.9 / 80.9	100 : 98		
PBDE 3	0.595	78.9 / 80.9	100 : 98		
Di-					
PBDE 7	0.964	78.9 / 80.9	100 : 98		
PBDE 8 + 11	1.019	78.9 / 80.9	100 : 98		
PBDE 10	0.861	78.9 / 80.9	100 : 98		
PBDE 12 + 13	1.048	78.9 / 80.9	100 : 98		
PBDE 15	1.101	78.9 / 80.9	100 : 98		
Tri-					
PBDE 17	1.476	78.9 / 80.9	100 : 98		
PBDE 25	1.496	78.9 / 80.9	100 : 98		
PBDE 28	1.557	78.9 / 80.9	100 : 98		
PBDE 30	1.288	78.9 / 80.9	100 : 98		
PBDE 32	1.437	78.9 / 80.9	100 : 98		
PBDE 33	1.551	78.9 / 80.9	100 : 98		
PBDE 35	1.607	78.9 / 80.9	100 : 98		
PBDE 37	1.660	78.9 / 80.9	100 : 98		
PCB 209 [a]	1.000	497.7 / 499.8	100 : 87		
Tetra-					
PBDE 47	0.809	78.9 / 80.9	100 : 98	404.8 / 406.8	100 : 98
PBDE 49	0.784	78.9 / 80.9	100 : 98	404.8 / 406.8	100 : 98
PBDE 66	0.836	78.9 / 80.9	100 : 98	404.8 / 406.8	100 : 98
PBDE 71	0.789	78.9 / 80.9	100 : 98	404.8 / 406.8	100 : 98
PBDE 75	0.769	78.9 / 80.9	100 : 98	404.8 / 406.8	100 : 98
PBDE 77	0.874	78.9 / 80.9	100 : 98	404.8 / 406.8	100 : 98
Penta-					
PBDE 85	1.012	78.9 / 80.9	100 : 98	402.8 / 404.8	100 : 98
PBDE 99	0.957	78.9 / 80.9	100 : 98	402.8 / 404.8	100 : 98
PBDE 100	0.922	78.9 / 80.9	100 : 98	402.8 / 404.8	100 : 98
PBDE 116	0.967	78.9 / 80.9	100 : 98	402.8 / 404.8	100 : 98
PBDE 118	0.986	78.9 / 80.9	100 : 98	402.8 / 404.8	100 : 98

Table C.1 (cont.)

PBDE 119	0.937	78.9 / 80.9	100 : 98	402.8 / 404.8	100 : 98
PBDE 126	1.026	78.9 / 80.9	100 : 98	402.8 / 404.8	100 : 98
Hexa-					
PBDE 138	1.134	78.9 / 80.9	100 : 98	401.8 / 403.8	100 : 98
PBDE 153	1.082	78.9 / 80.9	100 : 98	401.8 / 403.8	100 : 98
PBDE 154	1.038	78.9 / 80.9	100 : 98	401.8 / 403.8	100 : 98
PBDE 155	1.014	78.9 / 80.9	100 : 98	401.8 / 403.8	100 : 98
PBDE 166	1.138	78.9 / 80.9	100 : 98	401.8 / 403.8	100 : 98
Hepta-					
PBDE 181	1.249	78.9 / 80.9	100 : 98	479.7 / 481.7	68 : 100
PBDE 183	1.192	78.9 / 80.9	100 : 98	479.7 / 481.7	68 : 100
PBDE 190	1.260	78.9 / 80.9	100 : 98	479.7 / 481.7	68 : 100
$^{13}C_{12}$-PBDE 209[a]	1.000	494.6 / 496.6	98 : 48	78.9 / 80.9	100 : 98
Octa-					
PBDE 196	0.720	559.6 / 561.6	100 : 98	78.9 / 80.9	100 : 98
PBDE 197	0.707	406.7 / 408.7	68 : 100	78.9 / 80.9	100 : 98
PBDE 203	0.715	559.6 / 561.6	100 : 98	78.9 / 80.9	100 : 98
Nona-					
PBDE 206	0.835	486.6 / 488.6	100 : 98	78.9 / 80.9	100 : 98
PBDE 207	0.813	486.6 / 488.6	100 : 98	78.9 / 80.9	100 : 98
PBDE 208	0.802	486.6 / 488.6	100 : 98	78.9 / 80.9	100 : 98
Deca-					
PBDE 209	1.000	484.6 / 486.6	51 : 100	78.9 / 80.9	100 : 98

[a] Internal standard and relative retention time marker.

APPENDIX D
Selected Ion Monitoring Conditions for PBDEs

Table D.1. Selected ion monitoring for mono- through hepta-PBDEs, including brominated dibenzofurans and dibenzo-p-dioxins.

Group	Formula	MW	Retention Time Window (min)	Ion	*m/z*	Isotope
Mono-PBDE	$C_{12}H_9BrO$	247.98	11:00 – 15:00	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
Di-PBDE	$C_{12}H_8Br_2O$	325.89	15:00 – 37:00	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
Tri-PBDE	$C_{12}H_7Br_3O$	403.80		$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[M\text{-}Br]^-$	325	$[A]^-$
					327	$[A+2]^-$
PCB 65	$C_{12}H_6Cl_4$	289.92		$[Cl]^-$	35	$[A]^-$
(internal standard)					37	$[A+2]^-$
Tetra-PBDE	$C_{12}H_6Br_4O$	481.72	37:00 – 45:00	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[M\text{-}Br]^-$	405	$[A+2]^-$
					407	$[A+4]^-$
Penta-PBDE	$C_{12}H_5Br_5O$	559.63	45:00 – 49:00	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[M\text{-}HBr_2]^-$	403	$[A+2]^-$
					405	$[A+4]^-$
Tetra-BDF	$C_{12}H_4Br_4O$	479.70		$[M]^-$	482	$[M+2]^-$
					484	$[M+4]^-$
Penta-PBDE	$C_{12}H_5Br_5O$	559.63	49:00 – 53:50	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[M\text{-}HBr_2]^-$	403	$[A+2]^-$
					405	$[A+4]^-$
Hexa-PBDE	$C_{12}H_4Br_6O$	637.54		$[M\text{-}H\text{-}3Br]^-$	402	$[A+2]^-$
					404	$[A+4]^-$
PCB 209	$C_{12}Cl_{10}$	493.69		$[M]^-$	498	$[M+4]^-$
(internal standard)					500	$[M+6]^-$
Hexa-PBDE	$C_{12}H_4Br_6O$	637.54	53:50 – 59:00	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[M\text{-}H\text{-}3Br]^-$	402	$[A+2]^-$
					404	$[A+4]^-$
Penta-BDF	$C_{12}H_3Br_5O$	557.61		$[M]^-$	562	$[M+4]^-$
					564	$[M+6]^-$
Penta-BDD	$C_{12}H_3Br_5O_2$	573.60		$[M]^-$	578	$[M+4]^-$
					580	$[M+6]^-$

Table D.1. (cont.)

Hepta-PBDE	$C_{12}H_3Br_7O$	715.45	59:00 – 65:00	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[M-H-3Br]^-$	480	$[A+2]^-$
					482	$[A+4]^-$
Hexa-BDF	$C_{12}H_2Br_6O$	635.52		$[M]^-$	640	$[M+4]^-$
					642	$[M+6]^-$
Hexa-BDD	$C_{12}H_2Br_6O_2$	651.52		$[M]^-$	656	$[M+4]^-$
					658	$[M+6]^-$
Octa-PBDE	$C_{12}H_2Br_8O$	793.36	65:00 – 75:00	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[M-3Br-H]^-$	560	$[A+4]^-$
					562	$[A+6]^-$
Hepta-BDF	$C_{12}HBr_7O$	713.43		$[M]^-$	719	$[M+6]^-$
					721	$[M+8]^-$

Table D.2. Selected ion monitoring conditions for octa- through deca- PBDEs, including brominated dibenzofurans and dibenzo-p-dioxins.

Group	Formula	MW	Retention Time Window (min)	Ion	*m/z*	Isotope
Tetra-BDF	$C_{12}H_4Br_4O$	479.70	8:00 – 13:00	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[M]^-$	482	$[M+2]^-$
					484	$[M+4]^-$
Penta-BDF	$C_{12}H_3Br_5O$	557.61	13:00 – 14:50	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[M]^-$	562	$[M+4]^-$
					564	$[M+6]^-$
Penta-BDD	$C_{12}H_3Br_5O_2$	573.60		$[M]^-$	578	$[M+4]^-$
					580	$[M+6]^-$
Octa-PBDE	$C_{12}H_2Br_8O$	793.36	14:50 – 16:70	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[C_6Br_4HO]^-$	407	$[A+2]^-$
					409	$[A+4]^-$
				$[M-3Br-H]^-$	560	$[A+4]^-$
					562	$[A+6]^-$
Hexa-BDF	$C_{12}H_2Br_6O$	635.52		$[M]^-$	640	$[M+4]^-$
					642	$[M+6]^-$
Hexa-BDD	$C_{12}H_2Br_6O_2$	651.52		$[M]^-$	656	$[M+4]^-$
					658	$[M+6]^-$
Nona-PBDE			16:70 – 20:00	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[C_6Br_5O]^-$	487	$[A+4]^-$
					489	$[A+6]^-$
Hepta-BDF	$C_{12}HBr_7O$	713.43		$[M]^-$	719	$[M+6]^-$
					721	$[M+8]^-$
Deca-PBDE	$C_{12}Br_{10}O$	949.18	20:00 – 25.00	$[Br]^-$	79	$[A]^-$
					81	$[A+2]^-$
				$[C_6Br_5O]^-$	485	$[A+2]^-$
					487	$[A+4]^-$
$^{13}C_{12}$ Deca-PBDE	$^{13}C_{12}Br_{10}O$	961.22		$[^{13}C_6Br_5O]^-$	495	$[A+6]^-$
(internal standard)					497	$[A+8]^-$

APPENDIX E
Blank, Limit of Detection and Recovery Efficiency Results for Ambient Air Samples in Davis, California

Table E.1. PBDE concentrations in blank sample matrices (pg/m^3 ± SD for an 841m^3 sample, n = 2) from the ambient PBDE measurements in Davis California. "ND" indicates that the chemical was not detected.

Compound	Matrix		
	Filter	XAD-2	PUF
Tri-			
PBDE 17	ND	ND	ND
PBDE 25	ND	ND	ND
PBDE 28	ND	ND	ND
PBDE 30	ND	ND	ND
PBDE 32	ND	ND	ND
PBDE 33	ND	ND	ND
PBDE 35	ND	ND	ND
PBDE 37	ND	ND	ND
Tetra-			
PBDE 47	0.84 ± 0.12	0.29 ± 0.04	1.20 ± 0.25
PBDE 49	ND	ND	ND
PBDE 66	ND	ND	ND
PBDE 71	ND	ND	ND
PBDE 75	ND	ND	ND
PBDE 77	ND	ND	ND
Penta-			
PBDE 85			
PBDE 99	0.75 ± 0.15	0.46 ± 0.00	1.53 ± 0.28
PBDE 100	0.33 ± 0.03	0.25 ± 0.01	0.51 ± 0.05
PBDE 116	ND	ND	ND
PBDE 118	ND	ND	ND
PBDE 119	ND	ND	ND
PBDE 126	ND	ND	ND
Hexa-			
PBDE 138	ND	ND	ND
PBDE 153	0.07 ± 0.02	ND	0.11 ± 0.01
PBDE 154	0.13 ± 0.01	ND	0.20 ± 0.00
PBDE 155	ND	ND	ND
PBDE 166	ND	ND	ND
Hepta-			
PBDE 181	ND	ND	ND
PBDE 183	ND	ND	ND
PBDE 190	ND	ND	ND
Octa-			
BDE 203	ND	ND	ND
Deca-			
PBDE 209	0.90 ± 0.24	0.12 ± 0.03	[a]

[a] problem with detection

Table E.2. Limit of Detection (LOD) for Davis air sampling expressed in pg/m^3 for a 841 m^3 air sample (n = 2).

Congener	Mean ± SD
Tri-	
PBDE 17	0.10 ± 0.07
PBDE 25	0.11 ± 0.08
PBDE 28	0.09 ± 0.07
PBDE 30	0.06 ± 0.04
PBDE 32	0.11 ± 0.08
PBDE 33	0.10 ± 0.08
PBDE 35	0.12 ± 0.11
PBDE 37	0.11 ± 0.09
Tetra-	
PBDE 47	0.09 ± 0.07
PBDE 49	0.10 ± 0.07
PBDE 66	0.10 ± 0.08
PBDE 71	0.07 ± 0.05
PBDE 75	0.07 ± 0.05
PBDE 77	0.08 ± 0.08
Penta-	
PBDE 85	0.08
PBDE 99	0.09 ± 0.04
PBDE 100	0.07 ± 0.02
PBDE 116	0.10 ± 0.03
PBDE 118	0.10 ± 0.05
PBDE 119	0.08 ± 0.03
PBDE 126	0.11 ± 0.08
Hexa-	
PBDE 138	0.09 ± 0.02
PBDE 153	0.08 ± 0.03
PBDE 154	0.07 ± 0.01
PBDE 155	0.10
PBDE 166	0.17 ± 0.02
Hepta-	
PBDE 181	0.39 ± 0.05
PBDE 183	0.14 ± 0.02
PBDE 190	0.53 ± 0.02
Octa-	
PBDE 203	0.23 ± 0.02
Deca-	
PBDE 209	0.25 ± 0.13

Table E.3. PBDE extraction efficiencies (n = 1) from different sample collection substrates during the ambient PBDE determination in Davis, California.

Compound	Matrix	Enriched Amount (ng)	Amount Measured (ng)	Background (ng)	Total Mass (ng)	Recovery (%)
PBDE 47	Filter	50.00	42.0	0.70	41.3	82.6
	XAD-2	50.00	37.7	0.24	37.4	74.9
	PUF	50.00	41.5	1.01	40.5	80.9
PBDE 99	Filter	50.00	42.0	0.63	41.4	82.8
	XAD-2	50.00	40.7	0.38	40.3	80.6
	PUF	50.00	31.6	1.29	30.3	60.6
PBDE 100	Filter	50.00	44.6	0.28	44.3	88.6
	XAD-2	50.00	40.7	0.21	40.5	81.1
	PUF	50.00	36.3	0.42	35.8	71.7
PBDE 153	Filter	50.00	45.3	0.06	45.3	90.6
	XAD-2	50.00	41.4	0.00	41.4	82.8
	PUF	50.00	19.1	0.09	19.0	37.9
PBDE 154	Filter	50.00	45.4	0.11	45.3	90.6
	XAD-2	50.00	41.9	0.00	41.9	83.7
	PUF	50.00	26.6	0.17	26.5	52.9
PBDE 209	Filter	63.93	75.5	0.75	74.8	116.9
	XAD-2	63.93	71.8	0.10	71.7	112.2
	PUF	63.93	[a]	[a]	[a]	[a]

[a] problem with detection

APPENDIX F

Blank, Limit of Detection and Recovery Efficiency Results for the Computer Laboratory Sampling Episode.

Table F.1. PBDE concentrations in blank sample matrices (pg/m^3 ± SD, n =3) from the first computer lab sampling episode in January 2004. "ND" indicates that the chemical was not detected.

	Matrix (25.9 m^3)	
Compound	Filter	XAD-2
Tri-		
PBDE 17	ND	ND
PBDE 25	ND	ND
PBDE 28	ND	ND
PBDE 30	ND	ND
PBDE 32	ND	ND
PBDE 33	ND	ND
PBDE 35	ND	ND
PBDE 37	ND	ND
Tetra-		
PBDE 47	1.82 ± 0.92	2.08 ± 1.08
PBDE 49	ND	ND
PBDE 66	ND	ND
PBDE 71	ND	ND
PBDE 75	ND	ND
PBDE 77	ND	ND
Penta-		
PBDE 85	ND	ND
PBDE 99	ND	1.01 ± 1.76
PBDE 100	ND	ND
PBDE 116	ND	ND
PBDE 118	ND	ND
PBDE 119	ND	ND
PBDE 126	ND	ND
Hexa-		
PBDE 138	ND	ND
PBDE 153	ND	ND
PBDE 154	ND	ND
PBDE 155	ND	ND
PBDE 166	ND	ND
Hepta-		
PBDE 181	ND	ND
PBDE 183	ND	ND
PBDE 190	ND	ND
Octa-		
PBDE 203	ND	ND
Deca-		
PBDE 209	5.54 ± 1.82	7.04 ± 4.48

Table F.2. PBDE concentrations in blank sample matrices (pg/m^3 ± SD, n =3) from the second computer lab sampling episode in February 2004. "ND" indicates that the chemical was not detected.

Compound	Matrix (25.9 m^3)	
	Filter	XAD-2
Tri-		
PBDE 17	ND	ND
PBDE 25	ND	ND
PBDE 28	ND	ND
PBDE 30	ND	ND
PBDE 32	ND	ND
PBDE 33	ND	ND
PBDE 35	ND	ND
PBDE 37	ND	ND
Tetra-		
PBDE 47	2.50 ± 1.02	1.50 ± 0.14
PBDE 49	ND	ND
PBDE 66	ND	ND
PBDE 71	ND	ND
PBDE 75	ND	ND
PBDE 77	ND	ND
Penta-		
PBDE 85	ND	ND
PBDE 99	0.95 ± 0.83	0.49 ± 0.43
PBDE 100	0.59 ± 0.52	ND
PBDE 116	ND	ND
PBDE 118	ND	ND
PBDE 119	ND	ND
PBDE 126	ND	ND
Hexa-		
PBDE 138	ND	ND
PBDE 153	ND	ND
PBDE 154	ND	ND
PBDE 155	ND	ND
PBDE 166	ND	ND
Hepta-		
PBDE 181	ND	ND
PBDE 183	ND	ND
PBDE 190	ND	ND
Octa-		
PBDE 203	ND	ND
Deca-		
PBDE 209	4.90 ± 3.31	4.48 ± 0.52

Table F.3. Limit of Detection (LOD, pg/ m^3 for an 25.9 m^3 of air sample) for PBDEs during the computer laboratory sampling campaign in January and February 2004. The values represent mean ± SD of 4 LOD estimations, two of them from the January episode and two from the February episode.

Congener	Mean ± SD
Di-	
PBDE 10	2.51 ± 0.90
PBDE 7	2.48 ± 1.02
PBDE 11 + 8	2.20 ± 0.60
PBDE 12 + 13	1.82 ± 0.68
PBDE 15	2.44 ± 0.78
Tri-	2.41 ± 0.88
PBDE 30	2.37 ± 0.74
PBDE 32	2.33 ± 0.82
PBDE 17	
PBDE 25	2.08 ± 0.42
PBDE 33	2.51 ± 0.82
PBDE 28	2.39 ± 0.64
PBDE 35	2.35 ± 0.58
PBDE 37	2.22 ± 0.56
Tetra-	1.82 ± 0.48
PBDE 75	
PBDE 49	3.05 ± 0.70
PBDE 71	2.31 ± 0.60
PBDE 47	2.27 ± 0.67
PBDE 66	3.03 ± 1.20
PBDE 77	2.50 ± 0.53
Penta-	2.44 ± 0.76
PBDE 100	2.92 ± 0.91
PBDE 119	
PBDE 99	2.56 ± 0.85
PBDE 116	2.51 ± 0.78
PBDE 118	2.55 ± 0.77
PBDE 155 + 85	2.67 ± 0.82
PBDE 126	4.98 ± 1.41
Hexa-	
PBDE 154	7.67 ± 2.75
PBDE 153	3.92 ± 1.30
PBDE 138	9.10 ± 3.54
PBDE 166	
Hepta-	3.45 ± 0.49
PBDE 183	
PBDE 181	2.68 ± 0.48
PBDE 190	
Octa-	2.51 ± 0.90
PBDE 203 (n=1)	2.48 ± 1.02
Deca-	2.20 ± 0.60
PBDE 209	1.82 ± 0.68

Table F.4. PBDE extraction efficiencies from filters used in the first computer laboratory sampling episode in January 2004. “ND” indicates that the compound was not detected.

Compound	**Enriched Amount (ng)**	**Amount Measured (ng)**	**Background (ng)**	**Total Mass (ng)**	**Recovery (%)**
PBDE 47	20.00	14.6	0.05	14.6	72.9
	20.00	12.1	0.05	12.0	60.1
	20.00	10.8	0.05	10.8	53.9
	Mean ± SD	12.5 ± 1.9		12.5 ± 1.9	62.3 ± 9.7
PBDE 99	20.00	16.0	ND	16.0	79.9
	20.00	13.7	ND	13.7	68.7
	20.00	12.3	ND	12.3	61.3
	Mean ± SD	14.0 ± 1.9		14.0 ± 1.9	70.0 ± 9.4
PBDE 100	20.00	18.3	ND	18.3	91.4
	20.00	14.9	ND	14.9	74.3
	20.00	13.1	ND	13.1	65.4
	Mean ± SD	15.4 ± 2.6		15.4 ± 2.6	77.0 ± 13.2
PBDE 153	20.00	17.5	ND	17.5	87.4
	20.00	15.7	ND	15.7	78.5
	20.00	13.8	ND	13.8	69.0
	Mean ± SD	15.7 ± 1.9		15.7 ± 1.9	78.3 ± 9.2
PBDE 154	20.00	17.6	ND	17.6	88.1
	20.00	15.1	ND	15.1	75.3
	20.00	13.3	ND	13.3	66.5
	Mean ± SD	15.3 ± 2.2		15.3 ± 2.2	76.6 ± 10.9
PBDE 209	20.95	15.0	0.14	14.8	70.7
	20.95	17.0	0.14	16.9	80.7
	20.95	16.2	0.14	16.0	76.5
	Mean ± SD	16.1 ± 1.1		15.9 ± 1.1	75.9 ± 5.0

Table F.5. PBDE extraction efficiencies from filters used in the second computer laboratory sampling episode in February 2004. “ND” indicates that the compound was not detected.

Compound	Enriched Amount (ng)	Amount Measured (ng)	Background (ng)	Total Mass (ng)	Recovery (%)
PBDE 47	20.00	16.1	0.06	16.1	80.4
	20.00	16.3	0.06	16.2	81.0
	20.00	13.5	0.06	13.4	67.3
	Mean ± SD	15.3 ± 1.5		15.2 ± 1.5	76.2 ± 7.7
PBDE 99	20.00	17.9	0.02	17.9	89.4
	20.00	17.7	0.02	17.7	88.6
	20.00	15.2	0.02	15.2	75.9
	Mean ± SD	16.9 ± 1.5		16.9 ± 1.5	84.6 ± 7.6
PBDE 100	20.00	21.5	0.01	21.4	107.2
	20.00	21.5	0.02	21.4	107.2
	20.00	18.1	0.02	18.0	90.2
	Mean ± SD	20.3 ± 1.7		20.3 ± 1.7	102 ± 9.8
PBDE 153	20.00	19.9	0.00	19.9	99.4
	20.00	19.5	0.00	19.5	97.6
	20.00	16.8	0.00	16.8	84.2
	Mean ± SD	18.8 ± 1.7		18.8 ± 1.7	93.7 ± 8.3
PBDE 154	20.00	19.1	0.00	19.1	95.4
	20.00	18.9	0.00	18.9	94.3
	20.00	16.5	0.00	16.5	82.4
	Mean ± SD	18.14 ± 1.4		18.1 ± 1.4	90.7 ± 7.2
PBDE 209	22.10	23.4	0.12	23.3	105.5
	22.10	23.1	0.13	23.0	103.9
	22.10	22.7	0.13	22.6	102.1
	Mean ± SD	23.1 ± 0.4		23.0 ± 0.4	104 ± 1.7

Table F.6. PBDE extraction efficiencies from XAD-2 adsorbent used in the first computer laboratory sampling episode in January 2004. “ND” indicates that the compound was not detected.

Compound	**Enriched Amount (ng)**	**Amount Measured (ng)**	**Background (ng)**	**Total Mass (ng)**	**Recovery (%)**
PBDE 47	20.00	12.3	0.05	12.3	61.2
	20.00	11.5	0.05	11.5	57.4
	20.00	13.0	0.05	13.0	64.5
	Mean ± SD	12.3 ± 0.7		12.3 ± 0.7	61.1 ± 3.6
PBDE 99	20.00	13.8	0.03	13.7	68.8
	20.00	13.3	0.03	13.2	66.1
	20.00	14.8	0.03	14.8	73.8
	Mean ± SD	13.9 ± 0.8		13.9 ± 0.8	69.6 ± 3.9
PBDE 100	20.00	14.7	ND	14.7	73.3
	20.00	14.2	ND	14.2	71.2
	20.00	15.9	ND	15.9	79.6
	Mean ± SD	14.9 ± 0.9		14.9 ± 0.9	74.7 ± 4.4
PBDE 153	20.00	14.9	ND	14.9	74.3
	20.00	15.1	ND	15.1	75.7
	20.00	16.9	ND	16.9	84.7
	Mean ± SD	15.6 ± 1.1		15.6 ± 1.1	78.2 ± 5.6
PBDE 154	20.00	14.7	ND	14.7	73.7
	20.00	14.7	ND	14.7	73.3
	20.00	16.3	ND	16.3	81.6
	Mean ± SD	15.2 ± 0.9		15.2 ± 0.9	76.2 ± 4.7
PBDE 209	20.95	14.1	0.18	13.9	66.5
	20.95	15.9	0.18	15.7	74.9
	20.95	20.1	0.18	19.9	95.0
	Mean ± SD	16.7 ± 3.1		16.5 ± 3.1	78.8 ± 14.6

Table F.7. PBDE extraction efficiencies from XAD-2 adsorbent used in the second computer laboratory sampling episode in February 2004. “ND” indicates that the compound was not detected.

Compound	**Enriched Amount (ng)**	**Amount Measured (ng)**	**Background (ng)**	**Total Mass (ng)**	**Recovery (%)**
PBDE 47	20.00	13.4	0.04	13.3	66.6
	20.00	12.2	0.04	12.2	60.9
	20.00	14.9	0.04	14.9	74.3
	Mean ± SD	13.5 ± 1.4		13.5 ± 1.4	67.3 ± 6.8
PBDE 99	20.00	15.4	0.00	15.4	77.2
	20.00	14.1	0.00	14.1	70.3
	20.00	17.3	0.00	17.3	86.3
	Mean ± SD	15.6 ± 1.6		15.6 ± 1.6	77.9 ± 8.02
PBDE 100	20.00	17.9	0.00	17.9	89.5
	20.00	16.3	0.00	16.3	81.4
	20.00	20.3	0.00	20.3	101.3
	Mean ± SD	18.2 ± 2.0		18.2 ± 2.0	90.7 ± 10.0
PBDE 153	20.00	16.6	0.00	16.6	83.1
	20.00	15.4	0.00	15.4	76.8
	20.00	18.5	0.00	18.5	92.7
	Mean ± SD	16.8 ± 1.6		16.8 ± 1.6	84.2 ± 8.0
PBDE 154	20.00	16.2	0.00	16.2	80.9
	20.00	15.1	0.00	15.1	75.4
	20.00	18.0	0.00	18.0	89.9
	Mean ± SD	16.4 ± 1.5		16.4 ± 1.5	82.1 ± 7.4
PBDE 209	22.10	24.1	0.12	24.0	108.3
	22.10	21.4	0.12	21.3	96.4
	22.10	22.0	0.12	21.8	98.8
	Mean ± SD	22.5 ± 1.4		22.4 ± 1.4	101 ± 6.3

APPENDIX G
Source Strength Calculation of PBDEs from Computers

The source strength was calculated using the air exchange rate (ACH) and a simple first order kinetics model. The calculations are as follows:

Room Size: 2.7 m × 9.4 m × 4.5 m = 114.21 m^3 (V)
Concentration of CO_2 after 3 hours, 1 person in the room, ventilation turned off: 708 ppm (C_{eq})
CO_2 generation rate per person for office buildings = 5.3×10^{-6} m^3/s per person (G_p)
Assuming outdoor CO_2 is 400 ppm (C_{out})
Outdoor Airflow Rate into the building (Q):

$$Q = \frac{\text{Number of building occupants} \times G_p}{(C_{eq} - C_{out})}$$

$$Q = \frac{(1) \times (5.3 \times 10^{-6}\ m^3/s)}{(708\ \text{ppm} - 400\ \text{ppm})} = \frac{5.3\ m^3/s \times 3600\ s/h}{308} = 61.948\ m^3/h$$

$$ACH = \frac{Q}{V} = \frac{61.948\ m^3/h}{114.21\ m^3} = 0.54\ h^{-1}$$

Source Strength (S, pg/$m^3 \cdot h^{-1}$) Calculation

$$C_o \times ACH - C_i \times ACH + S - k = \frac{dC}{dt}$$

<u>Assumptions:</u>
$C_o = C(PBDE)_{off}$
$C_i = C(PBDE)_{on}$
k (decay rate) = 0
dC / dt = 0

$$ACH \times (C_o - C_i) + S - 0 = 0$$

$$S = ACH \times (C_i - C_o)$$

Personal computer Emission Rate (pg/h PC) Calculation:

$$\text{Emission Rate} = \frac{S \times V}{13\ \text{(number of PCs)}}$$

Table G.1. Source strength of PBDEs in a computer laboratory containing 13 computers sampled for six days. The source strength was defined as = ACH (air exchange rate 0.54) × C_{BDE}. Days with concentrations that were less than the control samples (computers off) are marked by "---" implying no significant emissions from the computers on that day.

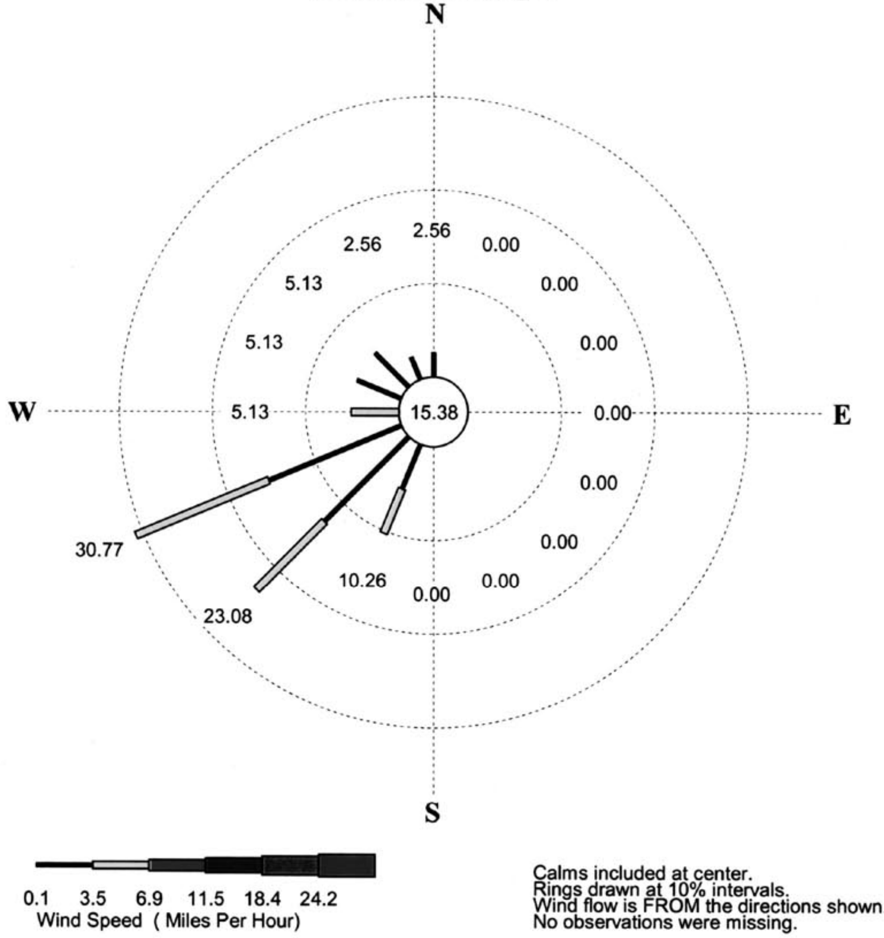
	Source strength (pg/m^3·h)						
Congener	1/25/04	1/26/04	1/27/04	2/02/04	2/03/04	2/04/04	Mean±S.D.
Tri-							
PBDE 17	---	---	14.0	1.86	3.91	2.26	5.52±5.75
PBDE 25	---	---	34.8	3.47	2.78	1.81	10.7±16.1
PBDE 28	---	---	20.4	3.00	6.30	2.71	8.09±8.34
PBDE 30	ND	ND	ND	ND	ND	ND	ND
PBDE 32	ND	ND	ND	ND	ND	ND	ND
PBDE 33	ND	ND	ND	ND	ND	ND	ND
PBDE 35	ND	ND	ND	ND	ND	ND	ND
PBDE 37	ND	ND	ND	ND	ND	ND	ND
Tetra-							
PBDE 47	ND	114	304	52.5	65.6	62.9	120±106
PBDE 49	0.49	7.23	25.8	3.74	4.27	5.61	7.86±9.08
PBDE 66	3.40	7.87	11.1	3.63	3.97	6.31	6.04±3.02
PBDE 71	ND	ND	ND	ND	ND	ND	ND
PBDE 75	---	0.18	4.47	1.07	1.07	2.69	1.90±1.70
PBDE 77	ND	ND	ND	ND	ND	ND	ND
Penta-							
PBDE 85	1.05	2.13	4.81	1.28	0.99	3.05	2.22±1.49
PBDE 99	17.5	57.9	95.2	36.6	28.8	37.4	45.6±27.7
PBDE 100	4.84	17.6	31.8	13.5	12.3	13.7	15.6±8.94
PBDE 116	---	2.29	5.59	1.15	3.95	2.56	3.11±1.71
PBDE 118	ND	ND	ND	ND	ND	ND	ND
PBDE 119	ND	ND	ND	ND	ND	ND	ND
PBDE 126	ND	ND	ND	ND	ND	ND	ND
Hexa-							
PBDE 138	ND	ND	ND	ND	ND	ND	ND
PBDE 153	0.98	1.38	4.00	0.48	1.17	2.28	1.72±1.27
PBDE 154	0.90	1.99	3.54	2.03	1.52	2.64	3.10±0.91
PBDE 155	ND	ND	ND	ND	ND	ND	ND
PBDE 156	ND	ND	ND	ND	ND	ND	ND
Hepta-							
PBDE 181	ND	ND	ND	ND	ND	ND	ND
PBDE 183	ND	ND	ND	ND	ND	ND	ND
PBDE 190	ND	ND	ND	ND	ND	ND	ND
Octa-							
PBE 203	ND	ND	ND	ND	ND	ND	ND
Deca-							
PBDE 209	29.4	32.1	40.6	16.2	15.9	20.7	25.8±9.90
Sum of PBDEs	58.6	244	601	141	152	167	227±192

Table G.2. Emission rates of PBDEs calculated on a "per computer" basis. Days with concentrations that were less than the control samples (computers off) are marked by "---" implying no significant emissions from the computers on that day.

Congener	Source strength (pg/h) 1/25/04	1/26/04	1/27/04	2/02/04	2/03/04	2/04/04	Mean±S.D.
Tri-							
PBDE 17	---	---	123	16.3	34.4	19.9	48.5±50.5
PBDE 25	---	---	306	30.5	24.4	15.9	94.2±141
PBDE 28	---	---	179	26.4	55.3	23.8	71.1±73.3
PBDE 30	ND	ND	ND	ND	ND	ND	ND
PBDE 32	ND	ND	ND	ND	ND	ND	ND
PBDE 33	ND	ND	ND	ND	ND	ND	ND
PBDE 35	ND	ND	ND	ND	ND	ND	ND
PBDE 37	ND	ND	ND	ND	ND	ND	ND
Tetra-							
PBDE 47	ND	998	2680	462	576	553	1050±930
PBDE 49	4.27	63.5	227	32.9	37.5	49.2	69.1±79.8
PBDE 66	29.8	69.1	97.1	31.9	34.9	55.4	53.1±26.5
PBDE 71	ND	ND	ND	ND	ND	ND	ND
PBDE 75	---	1.61	39.2	9.44	9.39	23.7	16.7±14.9
PBDE 77	ND	ND	ND	ND	ND	ND	ND
Penta-							
PBDE 85	9.20	18.7	42.3	11.2	8.68	26.8	19.5±13.1
PBDE 99	153	509	837	322	253	328	400±243
PBDE 100	42.5	155	279	119	108	121	137±78.6
PBDE 116	---	20.1	49.1	10.1	34.7	22.5	27.3±15.0
PBDE 118	ND	ND	ND	ND	ND	ND	ND
PBDE 119	ND	ND	ND	ND	ND	ND	ND
PBDE 126	ND	ND	ND	ND	ND	ND	ND
Hexa-							
PBDE 138	ND	ND	ND	ND	ND	ND	ND
PBDE 153	8.63	12.1	35.2	4.17	10.3	20.0	15.1±11.1
PBDE 154	7.88	17.5	31.1	17.8	13.4	23.2	8.47±8.01
PBDE 155	ND	ND	ND	ND	ND	ND	ND
PBDE 156	ND	ND	ND	ND	ND	ND	ND
Hepta-							
PBDE 181	ND	ND	ND	ND	ND	ND	ND
PBDE 183	ND	ND	ND	ND	ND	ND	ND
PBDE 190	ND	ND	ND	ND	ND	ND	ND
Octa-							
PBE 203	ND	ND	ND	ND	ND	ND	ND
Deca-							
PBDE 209	259	282	357	142	140	182	227±87.0
Sum of PBDEs	514	2150	5280	1230	1340	1460	2000±1690

APPENDIX H
Meteorological Data for the Electronics Recycling Facility Sampling Episode

Wind Rose Data for Site 1
Polybrominated Diphenyl Ethers (PBDE)
June 2, 2004 from 0700 to 1500 hours PST
15 minute averages



Calms included at center.
Rings drawn at 10% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
N	2.56	0.00	0.00	0.00	0.00	0.00
NNE	0.00	0.00	0.00	0.00	0.00	0.00
NE	0.00	0.00	0.00	0.00	0.00	0.00
ENE	0.00	0.00	0.00	0.00	0.00	0.00
E	0.00	0.00	0.00	0.00	0.00	0.00
ESE	0.00	0.00	0.00	0.00	0.00	0.00
SE	0.00	0.00	0.00	0.00	0.00	0.00
SSE	0.00	0.00	0.00	0.00	0.00	0.00

TOTAL OBS = 39 MISSING OBS = 0

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

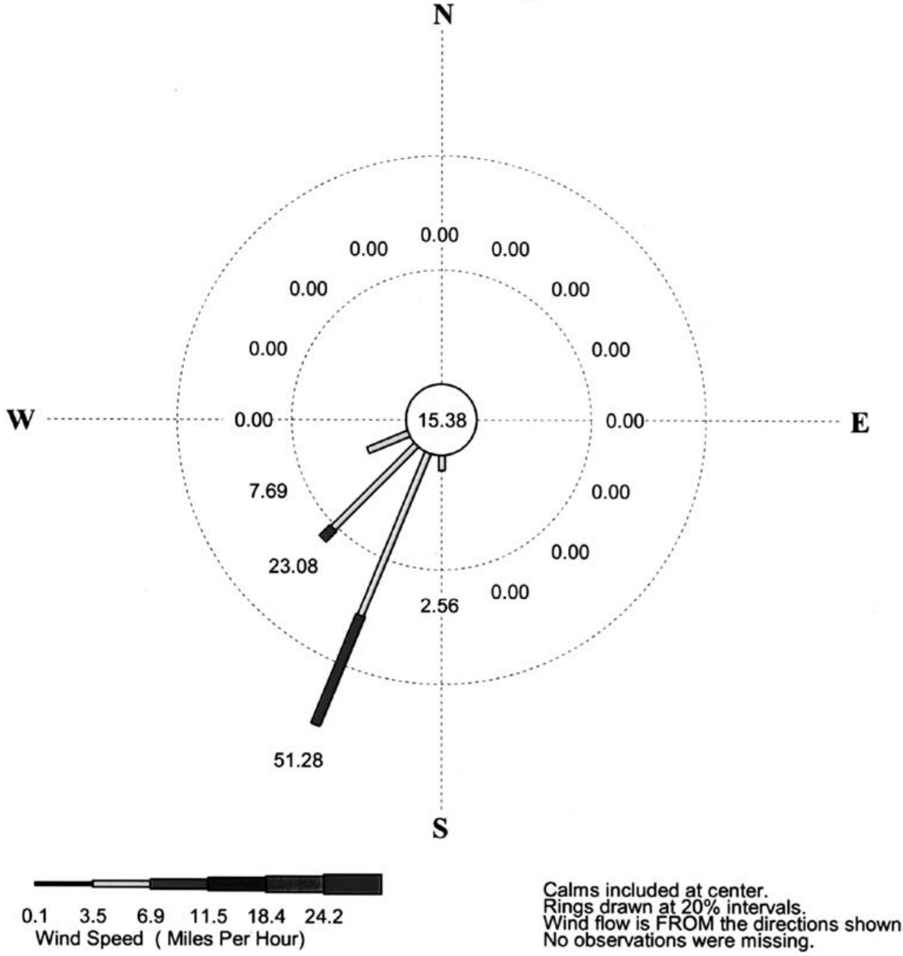
DIR	0.1	3.5	6.9	11.5	18.4	24.2
S	0.00	0.00	0.00	0.00	0.00	0.00
SSW	5.13	5.13	0.00	0.00	0.00	0.00
SW	12.82	10.26	0.00	0.00	0.00	0.00
WSW	15.38	15.38	0.00	0.00	0.00	0.00
W	0.00	5.13	0.00	0.00	0.00	0.00
WNW	5.13	0.00	0.00	0.00	0.00	0.00
NW	5.13	0.00	0.00	0.00	0.00	0.00
NNW	2.56	0.00	0.00	0.00	0.00	0.00

CALM OBS = 6 PERCENT CALM = 15.38

Table H1. Raw meteorological data for the June 2, 2004 sampling event at the electronics recycling facility.

Time (minutes)	Wind speed (MPH)	Wind Direction (degrees)	Temperature (C)	Relative Humidity (%)
7:00	3.6	212.7	18.7	62.6
7:15	3.7	217	19	62.3
7:30	3.4	226.5	19.4	61
7:45	3.3	235.4	20	59.4
8:00	3	250.4	20.2	59.3
8:15	2.6	194	21.3	56.9
8:30	2	242.8	22.1	54.6
8:45	2.7	295.4	22.6	53.2
9:00	2.6	245	23.1	51.6
9:15	2.9	241.6	23.7	49.4
9:30	2.5	227.9	24.7	46.9
9:45	3.1	229.7	25	44.9
10:00	2.7	208.4	25.9	43.6
10:15	2.5	256	26.9	41
10:30	2.9	292.8	27.3	38.9
10:45	3	331.8	28	37.6
11:00	3.4	316.7	28.4	34.6
11:15	2.8	236.5	29.1	33.4
11:30	3.1	354.7	29.7	32.8
11:45	3.5	226.6	30.2	31.8
12:00	3.7	261.7	30.8	30.3
12:15	3.6	224.9	31.1	30.2
12:30	3.7	206.6	32	29
12:45	3.2	307	31.9	28.8
13:00	4.4	252.9	32.5	28.4
13:15	4.5	238.7	32.9	27
13:30	4.5	272.4	32.8	25.9
13:45	4	241.1	33	25.8
14:00	5.6	219.2	33.5	24.7
14:15	4.6	256	33.4	25.5
14:30	6.2	226.7	33.7	25
14:45	5.3	258.6	33.6	26.4
15:00	5.2	247.9	33.7	27.3

Wind Rose Data for Site 1
Polybrominated Diphenyl Ethers (PBDE)
June 3, 2004 from 0700 to 1500 hours PST
15 minute averages



Calms included at center.
Rings drawn at 20% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
N	0.00	0.00	0.00	0.00	0.00	0.00
NNE	0.00	0.00	0.00	0.00	0.00	0.00
NE	0.00	0.00	0.00	0.00	0.00	0.00
ENE	0.00	0.00	0.00	0.00	0.00	0.00
E	0.00	0.00	0.00	0.00	0.00	0.00
ESE	0.00	0.00	0.00	0.00	0.00	0.00
SE	0.00	0.00	0.00	0.00	0.00	0.00
SSE	0.00	0.00	0.00	0.00	0.00	0.00

TOTAL OBS = 39 MISSING OBS = 0

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

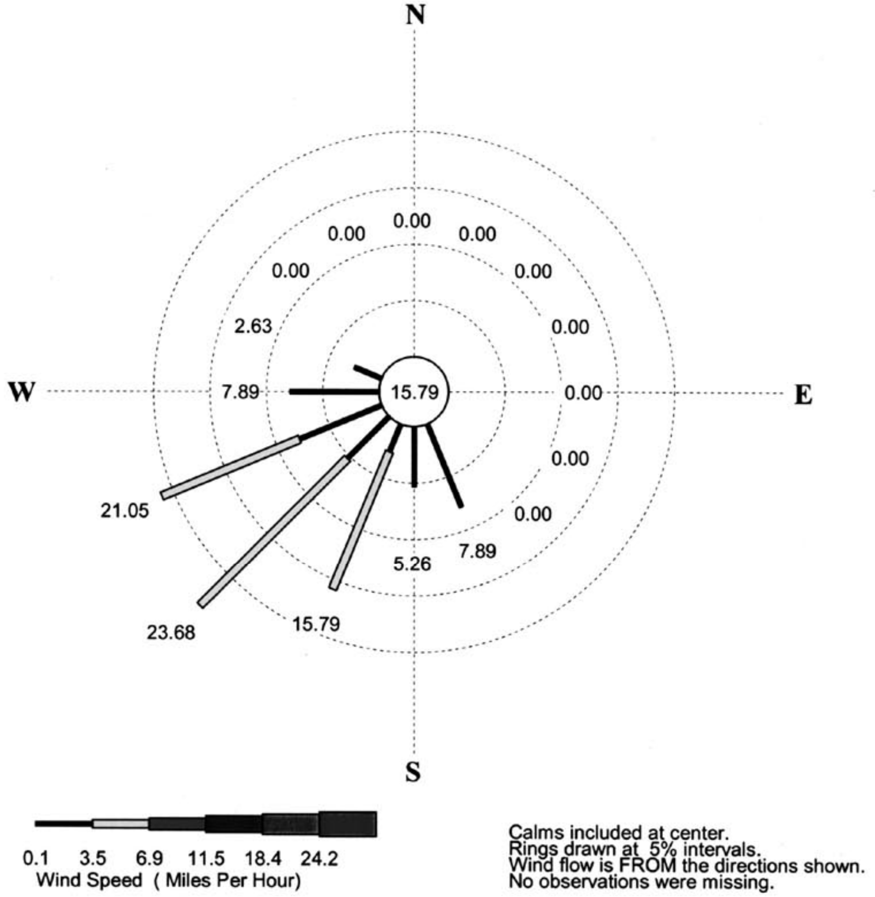
DIR	0.1	3.5	6.9	11.5	18.4	24.2
S	0.00	2.56	0.00	0.00	0.00	0.00
SSW	0.00	30.77	20.51	0.00	0.00	0.00
SW	0.00	20.51	2.56	0.00	0.00	0.00
WSW	0.00	7.69	0.00	0.00	0.00	0.00
W	0.00	0.00	0.00	0.00	0.00	0.00
WNW	0.00	0.00	0.00	0.00	0.00	0.00
NW	0.00	0.00	0.00	0.00	0.00	0.00
NNW	0.00	0.00	0.00	0.00	0.00	0.00

CALM OBS = 6 PERCENT CALM = 15.38

Table H2. Raw meteorological data for the June 3, 2004 sampling event at the electronics recycling facility.

Time (minutes)	Wind speed (MPH)	Wind Direction (degrees)	Temperature (C)	Relative Humidity (%)
7:00	8.3	210.8	15.3	78.2
7:15	8.6	202.9	15.7	76.5
7:30	7	215.2	16.2	74.8
7:45	7.9	207.2	16.6	72.6
8:00	6.9	193.8	17.6	70
8:15	7.1	198.1	18.3	66.5
8:30	7	203.6	18.5	66
8:45	7.9	203.9	18.6	65.5
9:00	6.8	213.8	19.2	63
9:15	7.2	207.2	19.4	62.1
9:30	6.8	200.7	20.1	58.7
9:45	6.9	214.9	20.2	58.8
10:00	7.3	197.8	20.8	56.6
10:15	6.5	207.9	21.3	55.3
10:30	6.7	202.1	21.7	53.1
10:45	6.2	199.9	22.1	52.4
11:00	5.7	201.5	22.9	49.8
11:15	5.6	211.4	23.4	48.8
11:30	5.1	201.4	23.9	46.2
11:45	5.6	207.1	24.7	43.9
12:00	5	211	25.2	42.4
12:15	4.5	217.1	25.7	40.3
12:30	4.3	181.5	26.6	39.1
12:45	5.5	206.4	27	35.8
13:00	5.5	206.2	27.9	34.1
13:15	5.9	216.1	28.2	34.2
13:30	5.7	231.9	28.8	33.6
13:45	6.3	218.6	29.1	31.9
14:00	6.6	237.1	29	32.6
14:15	6.2	236.9	29.2	31.1
14:30	5.7	213.8	29.8	30.6
14:45	5.7	220.3	30.2	29.7
15:00	6.8	241.3	30	31

Wind Rose Data for Site 1
Polybrominated Diphenyl Ethers (PBDE)
June 4, 2004 from 0700 to 1445 hours PST
15 minute averages



Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
N	0.00	0.00	0.00	0.00	0.00	0.00
NNE	0.00	0.00	0.00	0.00	0.00	0.00
NE	0.00	0.00	0.00	0.00	0.00	0.00
ENE	0.00	0.00	0.00	0.00	0.00	0.00
E	0.00	0.00	0.00	0.00	0.00	0.00
ESE	0.00	0.00	0.00	0.00	0.00	0.00
SE	0.00	0.00	0.00	0.00	0.00	0.00
SSE	7.89	0.00	0.00	0.00	0.00	0.00

TOTAL OBS = 38 MISSING OBS = 0

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
S	5.26	0.00	0.00	0.00	0.00	0.00
SSW	2.63	13.16	0.00	0.00	0.00	0.00
SW	5.26	18.42	0.00	0.00	0.00	0.00
WSW	7.89	13.16	0.00	0.00	0.00	0.00
W	7.89	0.00	0.00	0.00	0.00	0.00
WNW	2.63	0.00	0.00	0.00	0.00	0.00
NW	0.00	0.00	0.00	0.00	0.00	0.00
NNW	0.00	0.00	0.00	0.00	0.00	0.00

CALM OBS = 6 PERCENT CALM = 15.79

Table H3. Raw meteorological data for the June 4, 2004 sampling event at the electronics recycling facility.

Time (minutes)	Wind speed (MPH)	Wind Direction (degrees)	Temperature (C)	Relative Humidity (%)
7:00	2.8	154.3	16.1	73.4
7:15	2.5	182.5	16.3	71.8
7:30	2.2	154.2	16.8	70.1
7:45	3.1	170.6	17.2	68.5
8:00	3.2	146.5	17.9	65.9
8:15	2.8	216	18.5	63.7
8:30	3.1	212.5	18.9	62.1
8:45	3.6	200.5	19.8	59.8
9:00	3.7	245	20	59.1
9:15	3.8	240.9	20.4	59.8
9:30	3.4	226.9	21	58.5
9:45	3.7	244.1	21.7	56.9
10:00	2.6	250.6	21.9	56.3
10:15	3.3	260.7	22.2	55.1
10:30	2.7	244.6	22.7	54.3
10:45	3.2	264.3	23.4	51.9
11:00	3.3	269.6	23.9	49.3
11:15	3.3	284.9	24.5	48
11:30	3.3	246.7	25.2	45.2
11:45	3.6	227	25.7	43.5
12:00	3.6	206.9	26.1	42.6
12:15	3.8	240.6	26.8	41.3
12:30	4.1	257.3	27.2	40.3
12:45	4.9	235.5	27.7	40.9
13:00	4.5	227.6	27.7	38.8
13:15	5.8	222.5	27.9	39.4
13:30	6.2	201.5	28	41.4
13:45	5.6	217.3	28.4	37.9
14:00	4.9	231.4	28.8	34.6
14:15	5.6	226.7	29.5	33.2
14:30	5.7	210.8	30	33.9
14:45	6.5	213.1	30.3	32.2
7:00	2.8	154.3	16.1	73.4

APPENDIX I
Blank, Limit of Detection and Recovery Efficiency Results for the Electronics Recycling Facility Sampling Episode.

Table I.1. Background PBDE concentrations (pg/m^3) in the sampling matrices (n= 3) from the electronics recycling facility. "ND" indicates that the chemical was not detected.

Congener	Indoor Air Sampler (7.30 m^3)		Outdoor Air Sampler (265.8 m^3)	
	Filter	XAD-2	Filter	XAD-2
Tri-				
PBDE 17	ND	ND	ND	ND
PBDE 25	ND	ND	ND	ND
PBDE 28	ND	ND	ND	ND
PBDE 30	ND	ND	ND	ND
PBDE 32	ND	ND	ND	ND
PBDE 33	ND	ND	ND	ND
PBDE 35	ND	ND	ND	ND
PBDE 37	ND	ND	ND	ND
Tetra-				
PBDE 47	6.75 ± 0.32	7.70 ± 2.04	0.70 ± 0.37	0.77 ± 0.10
PBDE 49	ND	ND	ND	ND
PBDE 66	ND	ND	ND	ND
PBDE 71	ND	ND	ND	ND
PBDE 75	ND	ND	ND	ND
PBDE 77	ND	ND	ND	ND
Penta-				
PBDE 85	ND	ND	ND	ND
PBDE 99	ND	ND	0.90 ± 0.92	0.35 ± 0.06
PBDE 100	ND	ND	0.17 ± 0.19	0.11 ± 0.04
PBDE 116	ND	ND	ND	ND
PBDE 118	ND	ND	ND	ND
PBDE 119	ND	ND	ND	ND
PBDE 126	ND	ND	ND	ND
Hexa-				
PBDE 138	ND	ND	ND	ND
PBDE 153	ND	ND	ND	ND
PBDE 154	ND	ND	ND	ND
PBDE 155	ND	ND	ND	ND
PBDE 166	ND	ND	ND	ND
Hepta				
PBDE 181	ND	ND	ND	ND
PBDE 183	ND	ND	ND	ND
PBDE 190	ND	ND	ND	ND

Table I.1. (cont.)

Octa-				
PBDE 196	ND	ND	ND	ND
PBDE 197	ND	ND	ND	ND
PBDE 203	ND	ND	ND	ND
Nona-				
PBDE 206	ND	ND	ND	ND
PBDE 207	ND	ND	ND	ND
PBDE 208	ND	ND	ND	ND
Deca-				
PBDE 209	ND	ND	0.73 ± 1.12	ND

Table I.2. Limit of Detection for PBDEs (expressed as pg/m^3) for the indoor and outdoor air samplers used in the electronics recycling facility sampling episode. The values represent the mean ± SD of three determinations.

Congener	Indoor Air (7.30 m^3)	Outdoor Air (265.8 m^3)
Tri-		
PBDE 17	6.78 ± 3.01	0.186 ± 0.083
PBDE 25	8.25 ± 3.52	0.226 ± 0.097
PBDE 28	7.20 ± 2.68	0.198 ± 0.074
PBDE 30	5.06 ± 2.27	0.139 ± 0.062
PBDE 32	6.78 ± 3.01	0.186 ± 0.083
PBDE 33	8.26 ± 3.49	0.227 ± 0.096
PBDE 35	9.60 ± 2.67	0.264 ± 0.073
PBDE 37	11.5 ± 3.78	0.317 ± 0.104
Tetra-		
PBDE 47	6.28 ± 2.33	0.172 ± 0.064
PBDE 49	7.11 ± 3.22	0.195 ± 0.088
PBDE 66	8.90 ± 3.44	0.244 ± 0.095
PBDE 71	5.95 ± 2.62	0.163 ± 0.072
PBDE 75	5.11 ± 1.40	0.142 ± 0.038
PBDE 77	6.37 ± 1.67	0.175 ± 0.046
Penta-		
PBDE 85 (n = 1)	9.91	0.272
PBDE 99	7.03 ± 3.02	0.193 ± 0.083
PBDE 100	5.39 ± 2.20	0.148 ± 0.060
PBDE 116	7.21 ± 2.83	0.198 ± 0.078
PBDE 118	10.3 ± 6.30	0.282 ± 0.173
PBDE 119	5.98 ± 2.34	0.164 ± 0.064
PBDE 126	9.85 ± 3.02	0.271 ± 0.087
Hexa-		
PBDE 138	7.90 ± 3.07	0.217 ± 0.084
PBDE 153	6.80 ± 2.50	0.187 ± 0.069
PBDE 154	6.00 ± 2.52	0.165 ± 0.069
PBDE 155 (n = 1)	6.38	0.175
PBDE 166	12.8 ± 2.83	0.350 ± 0.078
Hepta-		
PBDE 181	21.8 ± 9.25	0.599 ± 0.254
PBDE 183	11.2 ± 2.76	0.306 ± 0.076
PBDE 190	27.8 ± 10.0	0.765 ± 0.275
Deca-		
PBDE 209	26.1 ± 11.5	0.718 ± 0.317

Table I.3. PBDE extraction efficiency from outdoor air sampler filters. "ND" indicates that the analyte was not detected.

Compound	Enriched Amount (ng)	Amount Measured (ng)	Background (ng)	Total Mass (ng)	Recovery (%)
PBDE 1	15.00	12.4	ND	12.4	82.8
	15.00	9.76	ND	9.76	65.1
	15.00	11.6	ND	11.6	77.4
	Mean ± SD	11.3 ± 1.4		11.3 ± 1.4	75.1 ± 9.07
PBDE 15	14.01	11.9	ND	11.9	85.2
	14.01	11.0	ND	11.0	78.7
	14.01	11.1	ND	11.1	79.3
	Mean ± SD	11.4 ± 0.5		11.4 ± 0.5	81.1± 3.6
PBDE 30	15.00	14.0	ND	14.0	93.0
	15.00	13.4	ND	13.4	89.2
	15.00	13.7	ND	13.7	91.6
	Mean ± SD	13.7 ± 0.3		13.7 ± 0.3	91.3 ± 1.9
PBDE 47	15.00	12.4	0.19	12.2	81.6
	15.00	13.0	0.19	12.8	85.2
	15.00	13.1	0.19	12.9	86.2
	Mean ± SD	12.8 ± 0.4		12.7 ± 0.4	84.4 ± 2.4
PBDE 99	15.00	13.3	0.24	13.0	86.7
	15.00	13.7	0.24	13.5	89.7
	15.00	14.0	0.24	13.7	91.5
	Mean ± SD	13.6 ± 0.4		13.4 ± 0.4	89.3 ± 2.4
PBDE 100	15.00	15.0	0.05	15.0	99.7
	15.00	15.8	0.05	15.8	105.3
	15.00	15.9	0.05	15.9	105.9
	Mean ± SD	15.6 ± 0.5		15.6 ± 0.5	104 ± 3.4
PBDE 153	15.00	14.2	ND	14.2	94.7
	15.00	15.5	ND	15.5	103.1
	15.00	15.3	ND	15.3	102.1
	Mean ± SD	15.0 ± 0.7		15.0 ± 0.7	100 ± 4.6
PBDE 154	15.00	14.6	ND	14.6	97.0
	15.00	15.6	ND	15.6	103.7
	15.00	15.6	ND	15.6	104.1
	Mean ± SD	15.2 ± 0.6		15.2 ± 0.6	102 ± 4.0
PBDE 190	15.00	13.2	ND	13.2	87.7
	15.00	15.4	ND	15.4	102.6
	15.00	14.9	ND	14.9	99.5
	Mean ± SD	14.5 ± 1.2		14.5 ± 1.2	96.6 ± 7.9
PBDE 203	15.00	13.3	ND	13.3	88.9
	15.00	13.1	ND	13.1	87.2
	15.00	12.6	ND	12.6	84.3
	Mean ± SD	13.0 ± 0.4		13.0 ± 0.4	86.8 ± 2.3
PBDE 208	15.00	12.4	ND	12.4	82.3
	15.00	12.1	ND	12.1	80.9
	15.00	11.5	ND	11.5	76.8
	Mean ± SD	12.0 ± 0.4		12.0 ± 0.44	80.0 ± 2.9
PBDE 209	15.15	15.4	0.19	15.4	100.7
	15.15	16.2	0.19	16.2	105.7
	15.15	15.9	0.19	15.9	103.8
	Mean ± SD	15.9 ± 0.4		15.9 ± 0.4	103 ± 2.5

Table I.4. PBDE extraction efficiency from outdoor air sampler XAD-2. “ND” indicates that the analyte was not detected.

Compound	Enriched Amount (ng)	Amount Measured (ng)	Background (ng)	Total Mass (ng)	Recovery (%)
PBDE 1	15.00	8.93	ND	8.93	59.5
	15.00	10.4	ND	10.4	69.2
	15.00	9.64	ND	9.64	64.2
	Mean ± SD	9.65 ± 0.73		9.65 ± 0.73	64.3 ± 4.8
PBDE 15	14.01	12.5	ND	12.5	89.4
	14.01	12.2	ND	12.2	87.0
	14.01	13.4	ND	13.4	95.9
	Mean ± SD	12.7 ± 0.7		12.7 ± 0.7	90.8± 4.6
PBDE 30	15.00	14.1	ND	14.1	94.3
	15.00	13.7	ND	13.7	91.0
	15.00	15.4	ND	15.4	103
	Mean ± SD	14.4 ± 0.9		14.4 ± 0.9	95.9 ± 5.9
PBDE 47	15.00	13.5	0.21	13.3	88.7
	15.00	11.0	0.21	10.8	71.8
	15.00	14.3	0.21	14.1	94.1
	Mean ± SD	12.9 ± 1.8		12.9 ± 1.8	84.9 ± 11.6
PBDE 99	15.00	13.7	0.09	13.6	90.9
	15.00	11.3	0.09	11.2	74.8
	15.00	15.1	0.09	15.0	100
	Mean ± SD	13.4 ± 1.9		13.3 ± 1.9	88.7 ± 12.8
PBDE 100	15.00	15.3	0.03	15.3	102
	15.00	12.3	0.03	12.3	81.9
	15.00	16.5	0.03	16.5	110
	Mean ± SD	14.7 ± 2.2		14.7 ± 2.2	98.0 ± 14.5
PBDE 153	15.00	13.8	ND	13.8	91.9
	15.00	11.3	ND	11.3	75.2
	15.00	15.8	ND	15.8	105.4
	Mean ± SD	13.6 ± 2.3		13.6 ± 2.3	90.8 ± 15.1
PBDE 154	15.00	14.3	ND	14.3	95.1
	15.00	11.7	ND	11.7	77.6
	15.00	16.1	ND	16.1	107
	Mean ± SD	14.0 ± 2.2		14.0 ± 2.2	93.3 ± 14.8
PBDE 190	15.00	8.86	ND	8.86	59.1
	15.00	9.08	ND	9.08	60.5
	15.00	12.1	ND	12.1	81.0
	Mean ± SD	10.0 ± 1.8		10.0 ± 1.8	66.8 ± 12.2
PBDE 203	15.00	17.6	ND	17.6	118
	15.00	16.8	ND	16.8	112
	15.00	20.6	ND	20.6	137
	Mean ± SD	12.0 ± 2.0		12.0 ± 2.0	122 ± 13.3
PBDE 208	15.00	12.8	ND	12.8	85.0
	15.00	12.0	ND	12.0	80.2
	15.00	14.4	ND	14.4	95.8
	Mean ± SD	13.1 ± 1.2		13.1 ± 1.2	87.0 ± 8.0
PBDE 209	15.15	17.9	ND	17.9	118
	15.15	16.0	ND	16.0	105
	15.15	17.7	ND	17.7	117
	Mean ± SD	17.2 ± 1.1		17.2 ± 1.1	113 ± 6.9

Table I.5. PBDE extraction efficiency from indoor air sampler filters. "ND" indicates that the analyte was not detected.

Compound	Enriched Amount (ng)	Amount Measured (ng)	Background (ng)	Total Mass (ng)	Recovery (%)
PBDE 1	10.00	6.8	ND	6.8	68.1
	10.00	9.9	ND	9.9	99.4
	10.00	10.0	ND	10.0	99.5
	Mean ± SD	8.90 ± 1.81		8.90 ± 1.81	89.0 ± 18.1
PBDE 15	9.34	8.32	ND	8.32	89.1
	9.34	7.06	ND	7.06	75.6
	9.34	10.0	ND	10.0	108
	Mean ± SD	8.47 ± 1.50		8.47 ± 1.50	90.7± 16.0
PBDE 30	10.00	10.1	ND	10.1	101
	10.00	11.5	ND	11.5	115
	10.00	12.4	ND	12.4	124
	Mean ± SD	11.3 ± 1.1		11.3 ± 1.1	113 ± 11.4
PBDE 47	10.00	9.34	0.05	9.29	92.9
	10.00	3.99	0.05	3.94	39.4
	10.00	8.09	0.05	8.04	80.4
	Mean ± SD	7.14 ± 2.80		7.09 ± 2.80	70.9 ± 27.9
PBDE 99	10.00	10.5	ND	10.5	105
	10.00	4.46	ND	4.46	44.6
	10.00	9.01	ND	9.01	90.1
	Mean ± SD	7.99 ± 3.15		7.99 ± 3.15	79.9 ± 31.5
PBDE 100	10.00	11.2	ND	11.2	112
	10.00	4.96	ND	4.96	49.6
	10.00	9.61	ND	9.61	96.1
	Mean ± SD	8.59 ± 3.25		8.59 ± 3.25	85.9 ± 32.5
PBDE 153	10.00	10.9	ND	10.9	109
	10.00	5.06	ND	5.06	50.6
	10.00	9.75	ND	9.75	97.5
	Mean ± SD	8.56 ± 3.09		8.56 ± 3.09	85.6 ± 30.9
PBDE 154	10.00	11.4	ND	11.4	114
	10.00	4.98	ND	4.98	49.8
	10.00	9.71	ND	9.71	97.1
	Mean ± SD	8.69 ± 3.32		8.69 ± 3.32	86.9 ± 33.2
PBDE 190	10.00	9.50	ND	9.50	95.0
	10.00	12.2	ND	12.2	122
	10.00	15.4	ND	15.4	154
	Mean ± SD	12.4 ± 2.9		12.4 ± 2.9	124 ± 29.4
PBDE 203	10.00	9.57	ND	9.57	95.7
	10.00	7.69	ND	7.69	76.9
	10.00	8.24	ND	8.24	82.4
	Mean ± SD	8.50 ± 0.97		8.50 ± 0.97	85.0 ± 9.7
PBDE 208	10.00	8.95	ND	8.95	89.5
	10.00	7.28	ND	7.28	72.8
	10.00	7.70	ND	7.70	77.0
	Mean ± SD	7.97 ± 0.87		7.97 ± 0.87	79.8 ± 8.7
PBDE 209	10.10	11.3	ND	11.3	112
	10.10	8.22	ND	8.22	81.4
	10.10	10.6	ND	10.6	105
	Mean ± SD	10.1 ± 1.6		10.1 ± 1.6	99.7 ± 16.2

Table I.6. PBDE extraction efficiency from indoor air sampler XAD-2. “ND” indicates that the analyte was not detected.

Compound	Enriched Amount (ng)	Amount Measured (ng)	Background (ng)	Total Mass (ng)	Recovery (%)
PBDE 1	10.00	8.68	ND	8.68	86.8
	10.00	7.98	ND	7.98	79.8
	10.00	10.5	ND	10.5	105
	Mean ± SD	9.04 ± 1.27		9.04 ± 1.27	90.4 ± 12.7
PBDE 15	9.34	8.95	ND	8.95	95.8
	9.34	9.19	ND	9.19	98.4
	9.34	9.99	ND	9.99	107
	Mean ± SD	9.38 ± 0.54		9.38 ± 0.54	100 ± 5.8
PBDE 30	10.00	11.5	ND	11.5	115
	10.00	11.4	ND	11.4	114
	10.00	12.2	ND	12.2	122
	Mean ± SD	11.7 ± 0.5		11.7 ± 0.5	117 ± 4.6
PBDE 47	10.00	9.84	0.06	9.79	97.9
	10.00	10.6	0.06	10.6	106
	10.00	10.8	0.06	10.7	107
	Mean ± SD	10.4 ± 0.5		10.4 ± 0.5	104 ± 4.9
PBDE 99	10.00	10.7	ND	10.7	107
	10.00	11.7	ND	11.7	117
	10.00	11.8	ND	11.8	118
	Mean ± SD	11.4 ± 0.6		11.4 ± 0.6	114 ± 6.2
PBDE 100	10.00	11.6	ND	11.6	116
	10.00	12.8	ND	12.8	128
	10.00	12.8	ND	12.8	128
	Mean ± SD	12.4 ± 0.7		12.4 ± 0.7	124 ± 7.1
PBDE 153	10.00	11.4	ND	11.4	114
	10.00	12.5	ND	12.5	125
	10.00	12.3	ND	12.3	123
	Mean ± SD	12.1 ± 0.6		12.1 ± 0.6	121 ± 5.6
PBDE 154	10.00	11.6	ND	11.6	116
	10.00	12.7	ND	12.7	127
	10.00	12.7	ND	12.7	127
	Mean ± SD	12.3 ± 0.7		12.3 ± 0.7	123 ± 6.6
PBDE 190	10.00	11.0	ND	11.0	110
	10.00	11.7	ND	11.7	117
	10.00	10.8	ND	10.8	108
	Mean ± SD	11.2± 0.5		11.2± 0.5	112 ± 4.5
PBDE 203	10.00	11.8	ND	11.8	118
	10.00	12.5	ND	12.5	125
	10.00	9.96	ND	9.96	99.6
	Mean ± SD	11.4 ± 1.3		11.4 ± 1.3	114 ± 12.9
PBDE 208	10.00	11.5	ND	11.5	115
	10.00	11.5	ND	11.5	115
	10.00	9.06	ND	9.06	90.6
	Mean ± SD	10.7 ± 1.4		10.7 ± 1.4	107 ± 14.1
PBDE 209	10.10	12.1	ND	12.1	120
	10.10	12.3	ND	12.3	122
	10.10	11.4	ND	11.4	113
	Mean ± SD	11.9 ± 0.5		11.9 ± 0.5	118 ± 4.5

APPENDIX J
Particulate and Adsorbent Concentrations from High-Volume Air Samplers at an Electronics Recycling Facility.

Table J.1. Filter-collected concentrations of PBDEs (pg/m^3) collected by four high-volume air samplers outside an electronics recycling facility. The results for the three individual sampling days are presented. "ND" indicates that the chemical was not detected. Octa- and nona-PBDEs could not be quantified due to an analytical interference.

Congener	Sampling day	Filter 1	Filter 2	Filter 3	Filter 4
Tri-					
PBDE 17	06/02/04	0.62	0.39	0.96	0.30
	06/03/04	0.40	0.36	0.45	0.25
	06/04/04	1.02	0.43	0.52	0.26
PBDE 25	06/02/04	0.67	ND	0.84	ND
	06/03/04	0.26	ND	0.23	ND
	06/04/04	0.77	0.33	ND	0.41
PBDE 28	06/02/04	0.95	1.02	ND	ND
	06/03/04	1.22	ND	ND	ND
	06/04/04	2.57	1.21	ND	ND
PBDE 30	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 32	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 33	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 35	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 37	06/02/04	ND	ND	ND	ND
	06/03/04	1.48	ND	ND	ND
	06/04/04	2.60	1.50	ND	ND

Table J.1. (cont.)

Tetra-					
PBDE 47	06/02/04	17.1	15.4	7.26	8.67
	06/03/04	18.6	4.77	3.74	6.53
	06/04/04	50.4	20.0	3.49	4.24
PBDE 49	06/02/04	11.9	9.72	3.05	1.99
	06/03/04	12.5	3.17	1.88	1.63
	06/04/04	25.0	11.6	1.55	1.26
PBDE 66	06/02/04	3.62	3.54	1.92	2.05
	06/03/04	4.46	1.37	1.07	1.40
	06/04/04	9.03	5.28	1.33	1.26
PBDE 71	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 75	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 77	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
Penta-					
PBDE 85	06/02/04	2.56	2.16	1.66	ND
	06/03/04	2.47	ND	ND	ND
	06/04/04	5.98	2.92	ND	ND
PBDE 99	06/02/04	22.5	16.9	8.31	9.73
	06/03/04	22.8	4.39	4.11	8.36
	06/04/04	77.5	26.2	4.06	4.93
PBDE 100	06/02/04	4.03	3.67	1.75	2.29
	06/03/04	3.78	1.03	1.03	2.00
	06/04/04	13.9	4.44	0.92	1.18
PBDE 116	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 118	06/02/04	2.58	2.57	1.42	ND
	06/03/04	3.30	ND	ND	ND
	06/04/04	5.27	3.37	ND	ND
PBDE 119	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 126	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND

Table J.1. (cont.)

Hexa-					
PBDE 138	06/02/04	3.98	4.25	ND	ND
	06/03/04	5.71	ND	ND	ND
	06/04/04	6.75	ND	ND	ND
PBDE 153	06/02/04	63.5	56.9	9.22	6.37
	06/03/04	88.5	6.03	3.71	3.31
	06/04/04	148	46.0	5.05	3.47
PBDE 154	06/02/04	11.4	11.2	2.70	2.03
	06/03/04	86.3	3.16	1.37	3.70
	06/04/04	52.3	21.7	1.80	1.47
PBDE 155	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 166	06/02/04	1.43	ND	ND	ND
	06/03/04	2.50	ND	ND	ND
	06/04/04	2.19	1.47	ND	ND
Hepta-					
PBDE 181	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 183	06/02/04	163	157	19.2	7.21
	06/03/04	362	15.8	6.39	6.18
	06/04/04	456	162	8.84	6.63
PBDE 190	06/02/04	6.74	8.50	ND	ND
	06/03/04	13.6	ND	ND	ND
	06/04/04	16.2	8.28	ND	ND
Deca-					
PBDE 209	06/02/04	4370	3130	516	167
	06/03/04	7730	424	140	290
	06/04/04	11300	4120	478	179

Table J.2. XAD-2 collected concentrations of PBDEs (pg/m^3) collected by four high-volume air samplers outside an electronics recycling facility. The XAD-2 concentrations represent PBDEs present in the gas phase as well as PBDEs that were associated with particulate matter, but then volatilized from the particulate matter during sample collection. The results for the three individual sampling days are presented. "ND" indicates that the chemical was not detected. Octa- and nona-PBDEs could not be quantified due to an analytical interference.

Congener	Sampling day	XAD-2 adsorbent Sampler #1	XAD-2 adsorbent Sampler #2	XAD-2 adsorbent Sampler #3	XAD-2 adsorbent Sampler #4
Tri-					
PBDE 17	06/02/04	4.75	5.18	3.30	4.14
	06/03/04	3.86	1.96	1.22	1.48
	06/04/04	2.35	2.50	1.88	1.27
PBDE 25	06/02/04	4.00	4.12	1.54	0.66
	06/03/04	3.53	1.37	0.43	0.35
	06/04/04	2.00	1.91	0.85	0.38
PBDE 28	06/02/04	15.4	16.8	7.91	10.4
	06/03/04	12.5	6.02	2.59	3.47
	06/04/04	7.95	7.86	3.98	2.87
PBDE 30	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 32	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 33	06/02/04	1.23	1.28	1.36	0.93
	06/03/04	1.36	0.95	0.89	ND
	06/04/04	0.96	1.07	ND	ND
PBDE 35	06/02/04	1.07	1.11	1.11	ND
	06/03/04	1.13	0.70	ND	ND
	06/04/04	0.83	0.85	0.79	ND
PBDE 37	06/02/04	6.17	8.10	3.10	1.73
	06/03/04	6.87	3.06	1.50	1.34
	06/04/04	5.15	5.38	2.33	1.42

Table J.2. (cont.)

Tetra-					
PBDE 47	06/02/04	108	89.3	75.8	119
	06/03/04	58.9	30.8	26.5	35.1
	06/04/04	42.2	40.1	32.9	28.3
PBDE 49	06/02/04	21.3	21.9	9.70	9.85
	06/03/04	15.3	8.13	4.44	3.68
	06/04/04	11.7	11.4	5.94	3.29
PBDE 66	06/02/04	6.35	6.29	4.86	4.45
	06/03/04	5.01	2.90	2.08	2.05
	06/04/04	3.66	3.80	2.83	1.68
PBDE 71	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 75	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 77	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
Penta-					
PBDE 85	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 99	06/02/04	19.4	13.2	11.6	16.2
	06/03/04	10.5	4.66	4.75	4.64
	06/04/04	7.44	6.10	5.80	4.27
PBDE 100	06/02/04	7.32	5.97	5.24	6.94
	06/03/04	3.90	2.21	2.01	2.07
	06/04/04	2.82	2.80	2.42	1.85
PBDE 116	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 118	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 119	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 126	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND

Table J.2. (cont.)

Hexa-					
PBDE 138	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 153	06/02/04	3.70	3.51	ND	1.47
	06/03/04	1.77	1.34	ND	ND
	06/04/04	1.43	1.61	1.35	ND
PBDE 154	06/02/04	1.86	1.64	0.79	0.79
	06/03/04	0.43	0.55	ND	ND
	06/04/04	1.28	1.07	0.63	ND
PBDE 155	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 166	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
Hepta-					
PBDE 181	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
PBDE 183	06/02/04	7.57	7.98	ND	ND
	06/03/04	3.25	ND	ND	ND
	06/04/04	ND	3.05	ND	ND
PBDE 190	06/02/04	ND	ND	ND	ND
	06/03/04	ND	ND	ND	ND
	06/04/04	ND	ND	ND	ND
Deca-					
PBDE 209	06/02/04	20.4	41.1	8.16	3.35
	06/03/04	52.0	8.54	8.99	9.42
	06/04/04	19.4	65.4	8.61	3.95

APPENDIX K
Octa- and Nona-PBDE Detection Problems with Field Samples

The analysis of field-collected high-volume air samples showed a problem with the detection of octa- and nona-PBDEs. This problem was not observed with the high-volume air samples collected at UC Davis prior to the sampling campaigns because of the lack of the octa- and nona-PBDEs standards.

Figure K.1 demonstrates the present of impurities in BDE 209 standard observed in each analysis of this compound. These impurities were, due to octa- and nona-PBDEs standard, identified as octa-PBDEs 196, 197 and 203 and nona-PBDEs 206, 207 and 208 together with heptabrominated dibenzofuran. Figure K.2 represents a chromatogram of calibration standards (level 3): octa-, nona-PBDEs and polybrominated dibenzofurans used to identify impurities in PBDE 209 standard.

The concentration of octa- and nona-PBDEs in the sample depended on the concentration of PBDE 209 presented in the sample. Higher concentration of PBDE 209, higher concentration of octa- and nona-PBDEs. The same is applied for heptabrominated dibenzofuran. Therefore it was complicated to determine the concentration of mentioned compounds originated from air samples. The ratio of octa- and nona-PBDEs to PBDE 209 was not calculated.

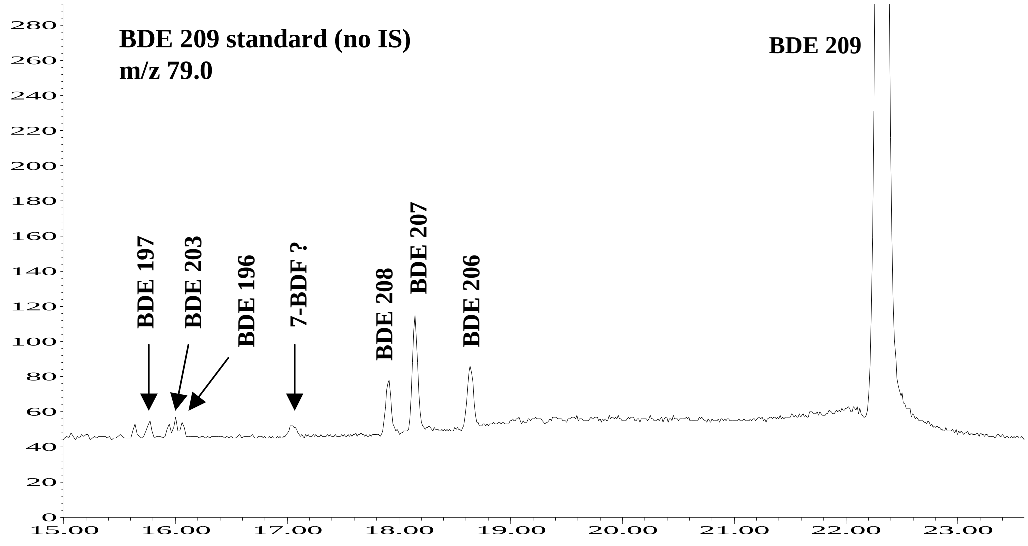


Figure K.1. Chromatogram of a standard of PBDE 209 where ion m/z 79 $[Br]^-$ was monitored. The impurities were identified as octa-, nona-PBDEs and heptabrominated dibenzofuran.

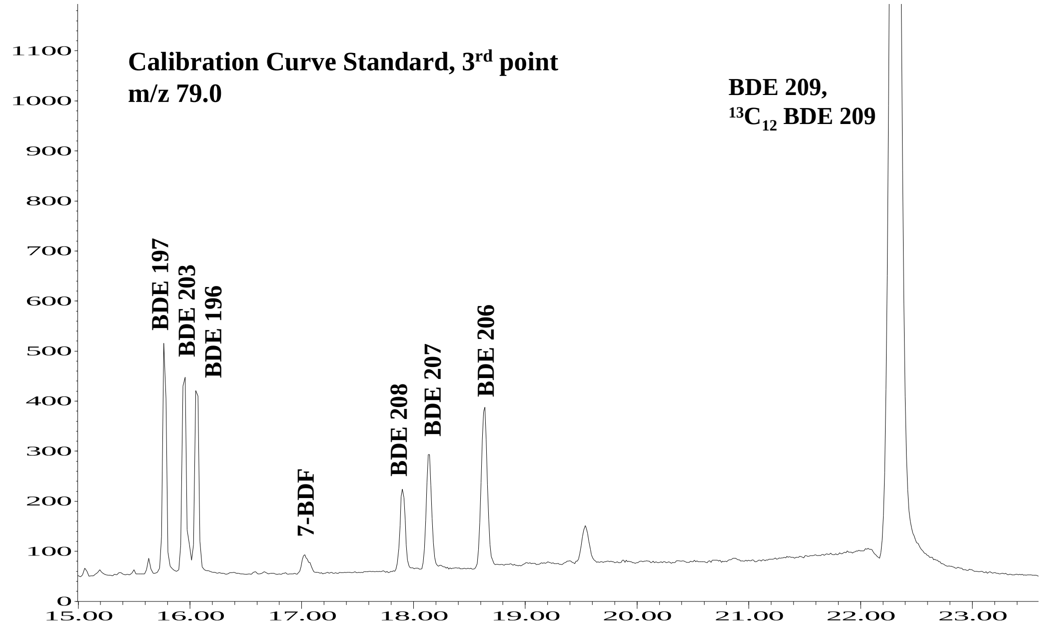
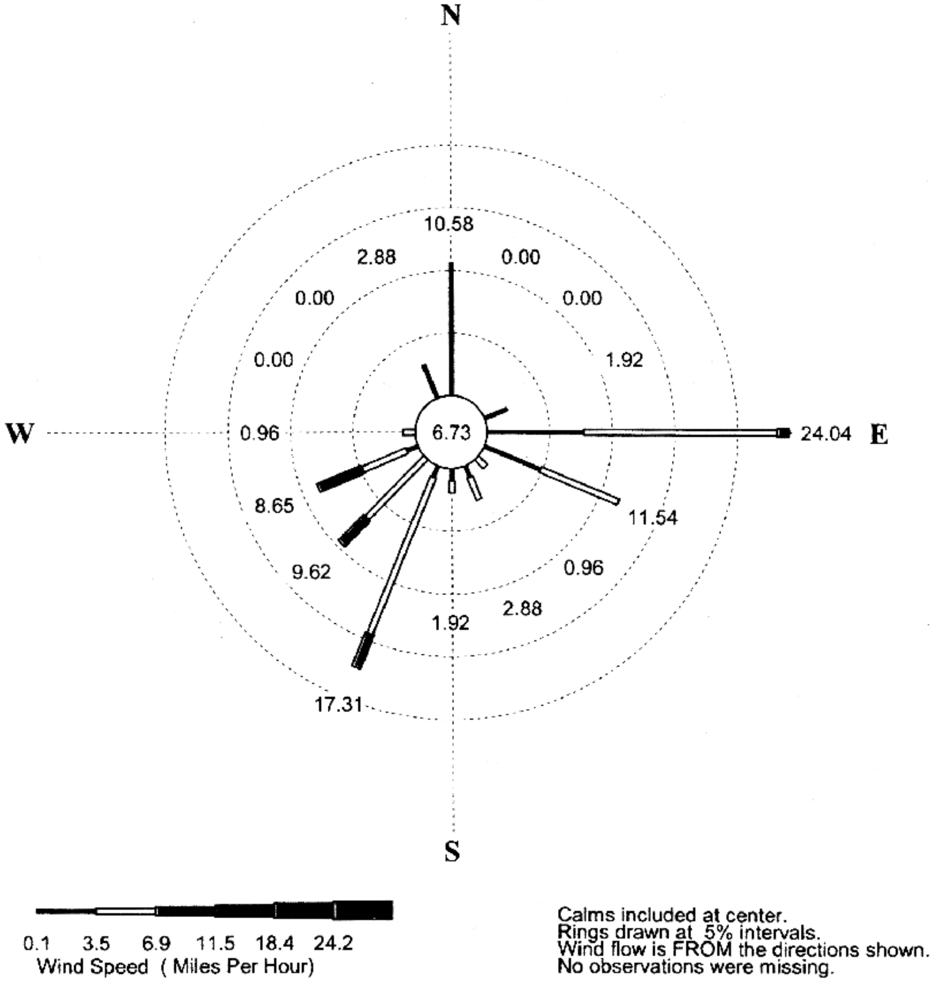


Figure K.2. Chromatogram of calibration standards (level 3): octa-, nona-PBDEs, PBDE 209 and heptabrominated dibenzofuran together with $^{13}C_{12}$-PBDE 209 as an internal standard mixed together. This chromatogram was used to identify impurities in PBDE 209 standard. Once again, ion m/z 79 $[Br]^-$ was monitored.

APPENDIX L
Meteorological Data for the Automotive Shredding Facility Sampling Episode

Wind Rose Data
for PBDE Monitoring Site 2
September 13-14, 2004 from 1400 to 1400
15 minute averages



Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
N	10.58	0.00	0.00	0.00	0.00	0.00
NNE	0.00	0.00	0.00	0.00	0.00	0.00
NE	0.00	0.00	0.00	0.00	0.00	0.00
ENE	1.92	0.00	0.00	0.00	0.00	0.00
E	7.69	15.38	0.96	0.00	0.00	0.00
ESE	4.81	6.73	0.00	0.00	0.00	0.00
SE	0.00	0.96	0.00	0.00	0.00	0.00
SSE	0.96	1.92	0.00	0.00	0.00	0.00

TOTAL OBS = 104 MISSING OBS = 0

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
S	0.96	0.96	0.00	0.00	0.00	0.00
SSW	0.96	13.46	2.88	0.00	0.00	0.00
SW	0.00	6.73	2.88	0.00	0.00	0.00
WSW	0.96	3.85	3.85	0.00	0.00	0.00
W	0.00	0.96	0.00	0.00	0.00	0.00
WNW	0.00	0.00	0.00	0.00	0.00	0.00
NW	0.00	0.00	0.00	0.00	0.00	0.00
NNW	2.88	0.00	0.00	0.00	0.00	0.00

CALM OBS = 7 PERCENT CALM = 6.73

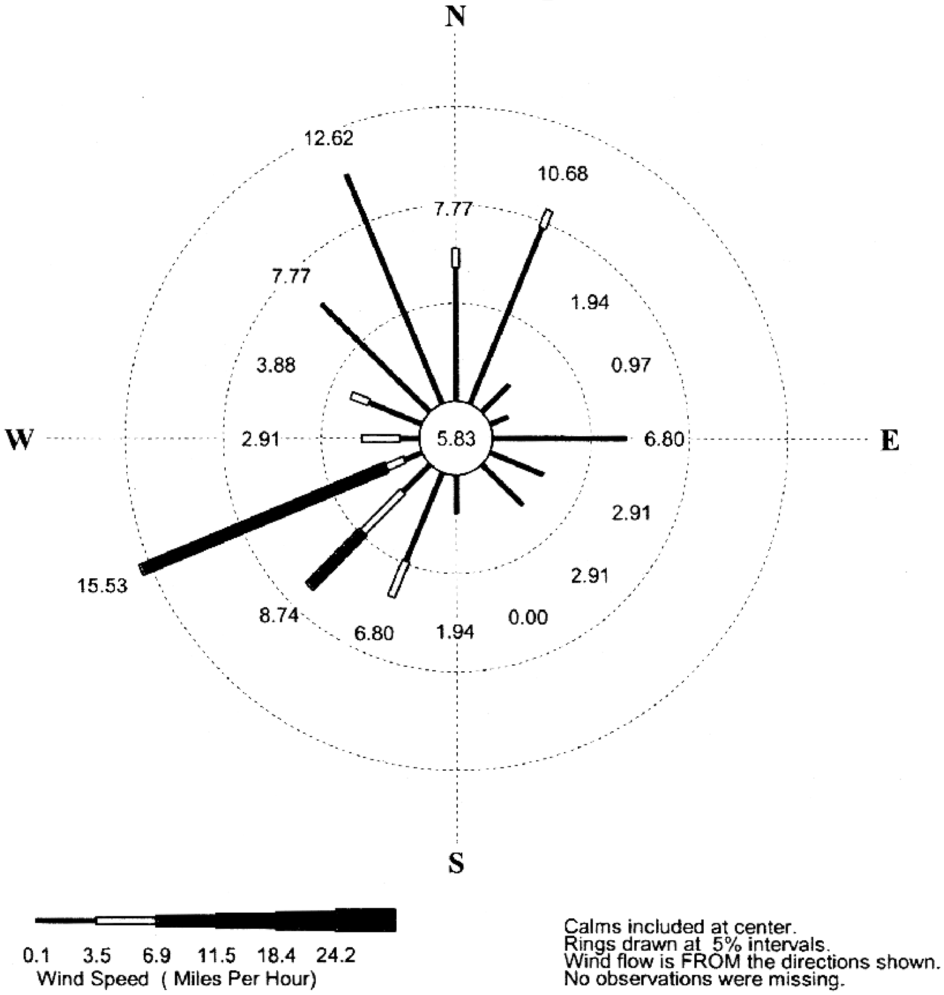
Table L.1. Raw meteorological data for the Sept. 13 to Sept. 14, 2004 sampling event at the automotive shredding and metal recycling facility.

Date	Time (minutes)	Wind speed (MPH)	Wind Direction (degrees)	Temperature (C)	Relative Humidity (%)
9/13/2004	14:00	9.6	247.1	20.2	70.4
9/13/2004	14:15	9.1	246.1	20.1	71.2
9/13/2004	14:30	7.7	255.1	20.2	70.6
9/13/2004	14:45	6.3	260.4	20.2	70
9/13/2004	15:00	5.9	237.2	19.8	72.1
9/13/2004	15:15	8.2	226.3	20	71.7
9/13/2004	15:30	7	222.8	20.2	71
9/13/2004	15:45	8.8	205	20	72.4
9/13/2004	16:00	7.9	209.8	20.1	71
9/13/2004	16:15	8.7	228.3	20.2	69.2
9/13/2004	16:30	7.5	239.8	19.8	67.7
9/13/2004	16:45	5.6	250.8	19.8	67.9
9/13/2004	17:00	5.5	245	19.6	68.9
9/13/2004	17:15	5.4	217.2	19.3	70.5
9/13/2004	17:30	4.7	167.9	18.9	71.6
9/13/2004	17:45	5.1	161.3	18.9	71.7
9/13/2004	18:00	6	142.8	18.9	72.9
9/13/2004	18:15	4	112.1	18.7	74.3
9/13/2004	18:30	5.5	95	18.4	75.7
9/13/2004	18:45	4.7	102.7	18.4	77.2
9/13/2004	19:00	7.5	93.9	18.1	78.1
9/13/2004	19:15	5.5	100.7	18	78.1
9/13/2004	19:30	4.8	107.1	17.8	78.5
9/13/2004	19:45	4.1	112.1	17.8	78.9
9/13/2004	20:00	3.8	109.2	17.8	79.5
9/13/2004	20:15	4	119.2	17.8	79.8
9/13/2004	20:30	4	109.7	17.7	79.8
9/13/2004	20:45	4.1	100.5	17.6	79.4
9/13/2004	21:00	6.7	95.2	17.6	78.9
9/13/2004	21:15	6.2	95	17.5	78.9
9/13/2004	21:30	6.4	92.6	17.5	80.6
9/13/2004	21:45	6.7	96.3	17.3	81
9/13/2004	22:00	5.4	96.9	17.2	81.3
9/13/2004	22:15	5.8	97.3	17.2	81.9
9/13/2004	22:30	5.5	91.1	17.1	82.5
9/13/2004	22:45	4.9	92.6	17.2	83
9/13/2004	23:00	5.6	94.5	17.3	83.1
9/13/2004	23:15	5.1	93.3	17.2	82.5
9/13/2004	23:30	4.7	92.1	17.3	82.9
9/13/2004	23:45	4.5	91.5	17.2	83.3
9/13/2004	24:00	2.9	104.4	16.9	84.6
9/14/2004	0:15	2.8	98.9	16.8	84.4
9/14/2004	0:30	2.9	99.1	16.8	84
9/14/2004	0:45	3.3	96.8	16.7	84.1
9/14/2004	1:00	3.7	95.8	16.8	82.8
9/14/2004	1:15	2.9	115.8	16.8	83.2

Table L.1. (continued)

9/14/2004	1:30	2.4	113.9	16.7	83.7
9/14/2004	1:45	2.5	93.3	16.8	82.6
9/14/2004	2:00	2.1	10.7	16.6	81.7
9/14/2004	2:15	2.5	2.8	16.7	80.9
9/14/2004	2:30	2.7	340.1	16.5	81.3
9/14/2004	2:45	1.5	342.2	16.4	81.5
9/14/2004	3:00	1.2	355.1	16.4	81.7
9/14/2004	3:15	2	331.4	16.3	82.8
9/14/2004	3:30	1.4	351.2	16.1	85.4
9/14/2004	3:45	1.2	3.5	16.2	85.6
9/14/2004	4:00	1.1	3.1	16.2	85.7
9/14/2004	4:15	1.1	355	16.2	85.7
9/14/2004	4:30	1.5	352.6	16.2	85.8
9/14/2004	4:45	1.3	357.3	16.2	85.8
9/14/2004	5:00	1.8	1.8	16.3	85.1
9/14/2004	5:15	1.5	355.1	16.3	85.1
9/14/2004	5:30	1.2	59.8	16.2	87.3
9/14/2004	5:45	1.7	95	16.2	88.5
9/14/2004	6:00	1.6	102.7	16.4	87.1
9/14/2004	6:15	1.9	96.3	16.6	86.4
9/14/2004	6:30	2	94.7	16.6	85
9/14/2004	6:45	1.6	74.7	16.8	84.5
9/14/2004	7:00	2	82.7	17.1	82.9
9/14/2004	7:15	2	121.6	17.3	82.8
9/14/2004	7:30	1.9	152.8	17.4	82.1
9/14/2004	7:45	2.1	179.6	17.6	80.9
9/14/2004	8:00	2.7	196.1	17.7	79.8
9/14/2004	8:15	3.8	199.2	18.2	79.2
9/14/2004	8:30	4.5	206.9	18.9	73.7
9/14/2004	8:45	3.4	237	19.8	64.6
9/14/2004	9:00	4.2	236	20.1	63.8
9/14/2004	9:15	4.2	250.2	20.5	61.2
9/14/2004	9:30	6	212.2	19.8	69
9/14/2004	9:45	5.9	215.8	20.4	66.8
9/14/2004	10:00	5.6	213.9	20.7	66.2
9/14/2004	10:15	4.4	201.4	20.9	64.6
9/14/2004	10:30	4.5	199.9	21.1	66.5
9/14/2004	10:45	5.1	202.7	21.4	65.1
9/14/2004	11:00	6.1	203.2	21.6	62.1
9/14/2004	11:15	5.5	208.6	21.9	57.1
9/14/2004	11:30	5.2	207.9	22.5	51.2
9/14/2004	11:45	5.4	207.6	23.3	44.3
9/14/2004	12:00	4.5	212.3	24.1	39.7
9/14/2004	12:15	6.6	219.4	24.9	35.8
9/14/2004	12:30	6.7	207.7	24.9	38.1
9/14/2004	12:45	7.2	192.8	23.9	45.8
9/14/2004	13:00	6.8	187.5	24.5	42.4
9/14/2004	13:15	6.3	207.5	24.5	44.3
9/14/2004	13:30	6.7	213	25.3	41.6
9/14/2004	13:45	6.1	223.7	25.5	41.4
9/14/2004	14:00	6.7	215.4	25.3	40.5

Wind Rose Data
for PBDE Monitoring Site 2
September 21-22, 2004 from 1200 to 1200
15 minute averages



Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
N	6.80	0.97	0.00	0.00	0.00	0.00
NNE	9.71	0.97	0.00	0.00	0.00	0.00
NE	1.94	0.00	0.00	0.00	0.00	0.00
ENE	0.97	0.00	0.00	0.00	0.00	0.00
E	6.80	0.00	0.00	0.00	0.00	0.00
ESE	2.91	0.00	0.00	0.00	0.00	0.00
SE	2.91	0.00	0.00	0.00	0.00	0.00
SSE	0.00	0.00	0.00	0.00	0.00	0.00

TOTAL OBS = 103 MISSING OBS = 0

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
S	1.94	0.00	0.00	0.00	0.00	0.00
SSW	4.85	1.94	0.00	0.00	0.00	0.00
SW	1.94	2.91	3.88	0.00	0.00	0.00
WSW	0.97	0.97	13.59	0.00	0.00	0.00
W	0.97	1.94	0.00	0.00	0.00	0.00
WNW	2.91	0.97	0.00	0.00	0.00	0.00
NW	7.77	0.00	0.00	0.00	0.00	0.00
NNW	12.62	0.00	0.00	0.00	0.00	0.00

CALM OBS = 6 PERCENT CALM = 5.83

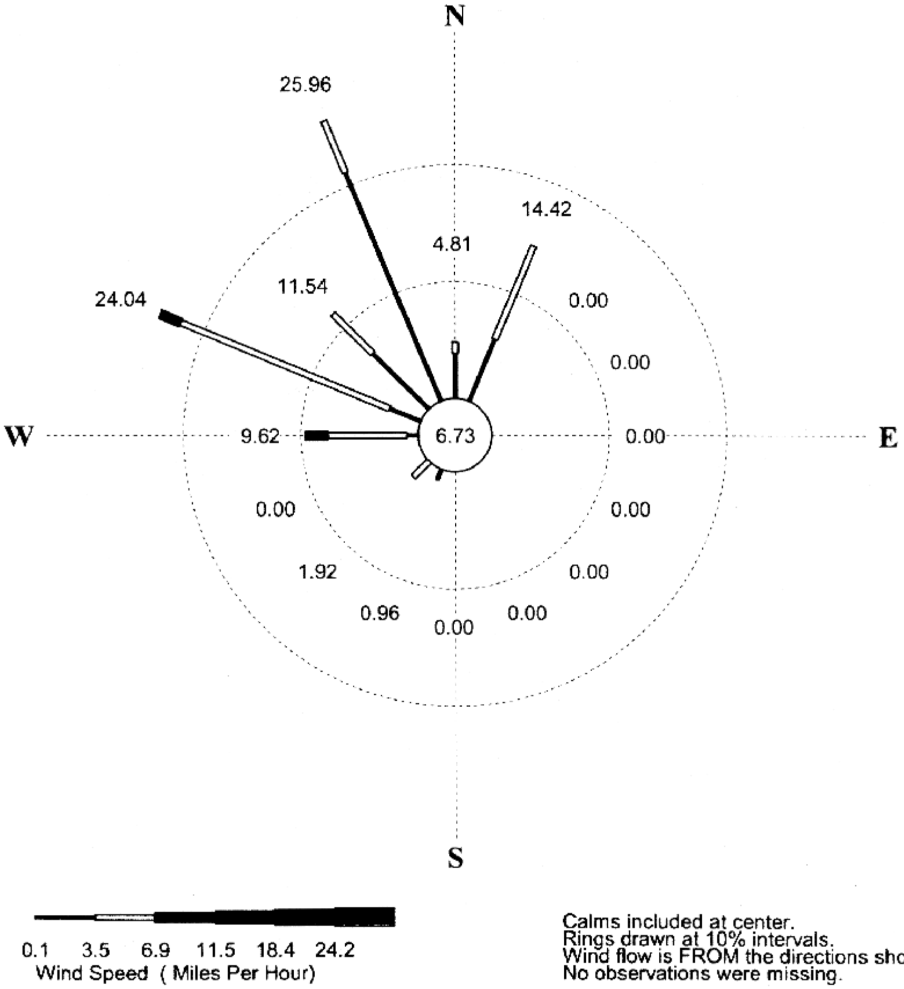
Table L.2. Raw meteorological data for the Sept. 21 to Sept. 22, 2004 sampling event at the automotive shredding and metal recycling facility.

Date	Time (minutes)	Wind speed (MPH)	Wind Direction (degrees)	Temperature (C)	Relative Humidity (%)
9/21/2004	12:00	6.6	226	22.8	33.2
9/21/2004	12:15	7.3	223.4	23.1	31.2
9/21/2004	12:30	6.6	229.6	23.7	28.1
9/21/2004	12:45	8	216.3	23.5	29.8
9/21/2004	13:00	7.8	216.3	23.6	29.4
9/21/2004	13:15	7	229.4	24.4	26.8
9/21/2004	13:30	7.7	238.3	24.9	24.6
9/21/2004	13:45	7.6	244.1	24.8	26.4
9/21/2004	14:00	8.4	249.1	24.8	26.4
9/21/2004	14:15	7.9	249.4	24.5	27.6
9/21/2004	14:30	8.5	254.2	24.5	27.1
9/21/2004	14:45	8.9	246	24.6	27.3
9/21/2004	15:00	8.7	247.9	24.5	25.3
9/21/2004	15:15	8.4	249.5	24.6	23.2
9/21/2004	15:30	9.6	248.1	23.9	23.6
9/21/2004	15:45	9.6	250.2	23.3	27
9/21/2004	16:00	7.2	243.5	23.2	30.9
9/21/2004	16:15	7.1	250	22.9	32.7
9/21/2004	16:30	6.9	253.2	23	31.6
9/21/2004	16:45	7.3	244.3	22.9	30
9/21/2004	17:00	7.2	243.5	22.6	30.3
9/21/2004	17:15	6.2	268.6	22.3	31.6
9/21/2004	17:30	3	307.9	22.4	32.8
9/21/2004	17:45	3.7	353.9	21.9	38.3
9/21/2004	18:00	4.1	14.2	21	43.6
9/21/2004	18:15	3.3	5.6	20.5	46.6
9/21/2004	18:30	2.8	355.8	19.9	51.7
9/21/2004	18:45	3.5	340	19.4	53.3
9/21/2004	19:00	3.3	341.2	19	55.2
9/21/2004	19:15	2.7	341.7	18.8	56.5
9/21/2004	19:30	3.1	331	18.6	56.8
9/21/2004	19:45	1.8	291.5	18.7	56.5
9/21/2004	20:00	2.3	301.5	18.8	54.1
9/21/2004	20:15	2.1	343.1	18.7	56
9/21/2004	20:30	1.7	340.5	18.5	56.7
9/21/2004	20:45	1.8	351.7	18.1	60.9
9/21/2004	21:00	1.4	342.5	18	62
9/21/2004	21:15	1.7	49.9	17.6	67.3
9/21/2004	21:30	2.7	19.5	17.1	71.1
9/21/2004	21:45	2.7	20.2	16.9	72
9/21/2004	22:00	3.5	13.3	16.8	72.3
9/21/2004	22:15	2.3	13.7	16.7	73.3
9/21/2004	22:30	2.9	19.2	16.7	73.1
9/21/2004	22:45	2.8	15.6	16.5	75.9
9/21/2004	23:00	2.4	13	16.4	77.4
9/21/2004	23:15	1.6	336.2	16.2	77.6

Table L.2. (Continued)

9/21/2004	23:30	1.3	324.8	16.1	77.8
9/21/2004	23:45	1.1	354.2	16.1	79.2
9/21/2004	24:00	1.3	82.7	16.4	78.9
9/22/2004	0:15	2.1	89.6	16.5	74.1
9/22/2004	0:30	2	99.1	16.3	71.8
9/22/2004	0:45	2.2	102.5	16.3	71.4
9/22/2004	1:00	2.5	128.2	16.2	72.9
9/22/2004	1:15	2.8	128.8	16.3	69.3
9/22/2004	1:30	2.4	101.3	16.1	67.9
9/22/2004	1:45	2.3	119.7	16.1	68.9
9/22/2004	2:00	2.6	137.2	15.9	70
9/22/2004	2:15	2.4	101.1	15.9	68.7
9/22/2004	2:30	2.3	98.6	15.8	68.2
9/22/2004	2:45	1.8	85.6	15.7	69.3
9/22/2004	3:00	2.4	92.1	16.1	68.9
9/22/2004	3:15	1.9	61.3	16.1	69.8
9/22/2004	3:30	1.8	14.5	15.7	68.7
9/22/2004	3:45	1.4	354.3	15.6	68.1
9/22/2004	4:00	1.7	310.3	15.5	67.6
9/22/2004	4:15	1.2	27.9	15.6	68.5
9/22/2004	4:30	1.3	44.4	15.6	67.4
9/22/2004	4:45	1.6	344.7	15.1	68.4
9/22/2004	5:00	2.2	345.1	15.2	66.1
9/22/2004	5:15	2	329	15	66.2
9/22/2004	5:30	1.9	330.4	15	65.3
9/22/2004	5:45	1.8	308.1	14.9	64.4
9/22/2004	6:00	1.8	305.6	15	63.8
9/22/2004	6:15	2.3	330.5	15.1	63
9/22/2004	6:30	2.8	4.1	15.1	63.6
9/22/2004	6:45	2.8	12.2	15.5	60.2
9/22/2004	7:00	2.7	355.1	15.7	57.4
9/22/2004	7:15	2.7	324.4	15.9	58.3
9/22/2004	7:30	2.9	317.5	16.4	63
9/22/2004	7:45	2.6	324.5	17	61.5
9/22/2004	8:00	1.8	299.8	17.5	61.5
9/22/2004	8:15	2.1	238.6	17.7	66.3
9/22/2004	8:30	2.3	219.2	18	66.3
9/22/2004	8:45	3.2	201.4	17.9	67.5
9/22/2004	9:00	2.3	226	18.4	62.6
9/22/2004	9:15	2.7	195	18.7	60.5
9/22/2004	9:30	2	190.2	19	58.7
9/22/2004	9:45	3.3	198.5	19.2	58.2
9/22/2004	10:00	3.4	204.4	19.5	57.1
9/22/2004	10:15	4.1	207.1	19.6	57.3
9/22/2004	10:30	2.4	189.6	20.4	49.9
9/22/2004	10:45	3.2	206.4	21	45.5
9/22/2004	11:00	4.6	213	21.6	45.5
9/22/2004	11:15	4.4	275.7	22.7	45.4
9/22/2004	11:30	4.4	290.2	23.5	40.1
9/22/2004	11:45	4.8	235.5	23.3	40.2
9/22/2004	12:00	3.5	280.1	24.3	29.7

Wind Rose Data
for PBDE Monitoring Site 2
September 22-23, 2004 from 1300 to 1300
15 minute averages



Calms included at center.
Rings drawn at 10% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
N	3.85	0.96	0.00	0.00	0.00	0.00
NNE	5.77	8.65	0.00	0.00	0.00	0.00
NE	0.00	0.00	0.00	0.00	0.00	0.00
ENE	0.00	0.00	0.00	0.00	0.00	0.00
E	0.00	0.00	0.00	0.00	0.00	0.00
ESE	0.00	0.00	0.00	0.00	0.00	0.00
SE	0.00	0.00	0.00	0.00	0.00	0.00
SSE	0.00	0.00	0.00	0.00	0.00	0.00

TOTAL OBS = 104 MISSING OBS = 0

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
S	0.00	0.00	0.00	0.00	0.00	0.00
SSW	0.96	0.00	0.00	0.00	0.00	0.00
SW	0.00	1.92	0.00	0.00	0.00	0.00
WSW	0.00	0.00	0.00	0.00	0.00	0.00
W	0.96	6.73	1.92	0.00	0.00	0.00
WNW	2.88	19.23	1.92	0.00	0.00	0.00
NW	6.73	4.81	0.00	0.00	0.00	0.00
NNW	21.15	4.81	0.00	0.00	0.00	0.00

CALM OBS = 7 PERCENT CALM = 6.73

Table L.3. Raw meteorological data for the Sept. 22 to Sept. 23, 2004 sampling event at the automotive shredding and metal recycling facility.

Date	Time (minutes)	Wind speed (MPH)	Wind Direction (degrees)	Temperature (C)	Relative Humidity (%)
9/22/2004	13:00	5.8	296	24.8	34.2
9/22/2004	13:15	5.7	292.8	25.1	31.4
9/22/2004	13:30	6.1	286	25.5	30.8
9/22/2004	13:45	7.1	303.3	25.5	30.6
9/22/2004	14:00	7.5	303.2	25.4	35.6
9/22/2004	14:15	6.4	299.9	25.1	42.8
9/22/2004	14:30	5.5	270.4	25.3	39.7
9/22/2004	14:45	5.6	267.1	25	38.9
9/22/2004	15:00	5.8	307.9	24.8	42.5
9/22/2004	15:15	5.8	289.9	24.5	37.8
9/22/2004	15:30	6.8	274.7	24.7	32.2
9/22/2004	15:45	7.2	277.2	24.7	29.4
9/22/2004	16:00	7.4	273.6	24.5	29.7
9/22/2004	16:15	6.4	266.5	24.2	30.3
9/22/2004	16:30	4.9	283.1	24.2	30.3
9/22/2004	16:45	4.3	271.8	23.8	32
9/22/2004	17:00	5.4	276.6	23.6	32.2
9/22/2004	17:15	4.8	286.1	23.3	32.9
9/22/2004	17:30	5.3	287.7	23.1	32.2
9/22/2004	17:45	5.9	292.9	22.6	33.4
9/22/2004	18:00	6.7	303.5	21.9	36.9
9/22/2004	18:15	4.6	332.8	21.4	39.7
9/22/2004	18:30	4.4	301.1	21.1	41.4
9/22/2004	18:45	3.9	329.7	20.7	44.6
9/22/2004	19:00	5.3	318.3	20.1	48.1
9/22/2004	19:15	3.5	358.8	19.5	55.8
9/22/2004	19:30	3.4	341.3	19.4	55.1
9/22/2004	19:45	3.9	335.5	19.5	48.7
9/22/2004	20:00	4.3	17.2	18.9	55.2
9/22/2004	20:15	3.8	6.5	18.2	62.3
9/22/2004	20:30	3.7	17.1	17.9	65.4
9/22/2004	20:45	4	12.5	17.7	68.7
9/22/2004	21:00	3.4	19.2	17.6	69.9
9/22/2004	21:15	3.6	19	17.3	72.8
9/22/2004	21:30	4.2	16.5	17.1	76.3
9/22/2004	21:45	2.6	15.4	17.1	75.5
9/22/2004	22:00	2.9	17.1	17.1	75.9
9/22/2004	22:15	2.9	16	17.1	76.2
9/22/2004	22:30	3.6	14.3	17.1	74.5
9/22/2004	22:45	4.1	15.1	16.9	76.5
9/22/2004	23:00	4.3	17.4	16.7	78.9
9/22/2004	23:15	4.7	18.5	16.4	80.5
9/22/2004	23:30	3.5	19.3	16.3	81.8
9/22/2004	23:45	2.3	11.8	16.5	80.6
9/22/2004	24:00:00	2	348.1	16.5	80
9/23/2004	0:15	1.8	316.6	16.3	80.4

Table L.3. (Continued)

9/23/2004	0:30	1.4	324.8	16.3	79.9
9/23/2004	0:45	1.6	305.7	16.4	80.3
9/23/2004	1:00	1.8	325.5	16.3	79.7
9/23/2004	1:15	1.8	335.3	16.2	79.4
9/23/2004	1:30	2.3	324.5	16	80.7
9/23/2004	1:45	1.8	328.3	16	81.2
9/23/2004	2:00	2.1	327.3	15.9	81.7
9/23/2004	2:15	1.7	328.6	15.9	82.3
9/23/2004	2:30	1.6	346.1	15.9	82
9/23/2004	2:45	1.7	333.4	15.9	81.8
9/23/2004	3:00	2.5	343.6	15.7	81.6
9/23/2004	3:15	2.4	333.5	15.5	82.1
9/23/2004	3:30	2.5	351.4	15.6	81.1
9/23/2004	3:45	2.5	344.7	15.6	80.8
9/23/2004	4:00	2.3	333.8	15.4	82.3
9/23/2004	4:15	2.3	337.4	15.3	84
9/23/2004	4:30	2.7	334.2	15.2	88.1
9/23/2004	4:45	2.8	330.8	15	89.8
9/23/2004	5:00	2.4	351.1	15	88.7
9/23/2004	5:15	2.3	358.2	15	87.7
9/23/2004	5:30	2.1	346.5	14.9	87
9/23/2004	5:45	2.7	333.2	14.9	85.9
9/23/2004	6:00	3.1	328.9	14.7	86.9
9/23/2004	6:15	3.3	330.1	14.7	87.9
9/23/2004	6:30	3.4	322.5	14.9	89.4
9/23/2004	6:45	2.9	329.5	15.4	89.7
9/23/2004	7:00	2.6	330	15.9	88.4
9/23/2004	7:15	3.8	328.8	16.3	84.2
9/23/2004	7:30	4.1	326.1	16.7	80.1
9/23/2004	7:45	4.8	327.7	16.9	75.6
9/23/2004	8:00	3.4	330.8	17.5	75.7
9/23/2004	8:15	4.2	320.4	17.8	69.6
9/23/2004	8:30	3.7	295.7	18.2	71.1
9/23/2004	8:45	3.3	295	18.7	68.4
9/23/2004	9:00	2.4	272.5	19.5	64.8
9/23/2004	9:15	3.3	287.9	19.6	64
9/23/2004	9:30	3.4	307.1	20	61
9/23/2004	9:45	3	299.3	20.6	57.4
9/23/2004	10:00	4.3	224.4	20.4	59.3
9/23/2004	10:15	3.5	207.3	20.4	56.9
9/23/2004	10:30	4.1	227.2	21.3	54.6
9/23/2004	10:45	5	292.1	22.3	49.6
9/23/2004	11:00	4.8	284.9	22.6	45.8
9/23/2004	11:15	5.1	288.2	23	40.6
9/23/2004	11:30	4.4	282.9	23.8	31.6
9/23/2004	11:45	3.9	278	24.6	29.4
9/23/2004	12:00	4.7	295.5	25	32.8
9/23/2004	12:15	6.3	306.2	25.1	33.1
9/23/2004	12:30	6.1	293.6	25.4	33.1
9/23/2004	12:45	6.2	293.9	25.9	33.6
9/23/2004	13:00	6.5	298	26.2	34.1

APPENDIX M

Blank, Limit of Detection and Extraction Efficiency Results from the Automotive Shredding Facility Sampling Episode.

Table M.1. Concentration (in terms of pg/m^3 equivalent concentrations for an 809 m^3 of air sample) of PBDEs in the blank sample matrices. The mean ± SD is presented for the three replicates samples.

Congener	Filter substrate	XAD-2 substrate
Tri-		
PBDE 17	ND	ND
PBDE 25	ND	ND
PBDE 28	ND	ND
PBDE 30	ND	ND
PBDE 32	ND	ND
PBDE 33	ND	ND
PBDE 35	ND	ND
PBDE 37	ND	ND
Tetra-		
PBDE 47	0.15 ± 0.02	0.16 ± 0.02
PBDE 49	ND	ND
PBDE 66	ND	ND
PBDE 71	ND	ND
PBDE 75	ND	ND
PBDE 77	ND	ND
Penta-		
PBDE 85	ND	ND
PBDE 99	0.16 ± 0.03	0.09 ± 0.02
PBDE 100	0.04 ± 0.00	0.03 ± 0.01
PBDE 116	ND	ND
PBDE 118	ND	ND
PBDE 119	ND	ND
PBDE 126	ND	ND
Hexa-		
PBDE 138	ND	ND
PBDE 153	ND	ND
PBDE 154	ND	ND
PBDE 155	ND	ND
PBDE 166	ND	ND
Hepta-		
PBDE 181	ND	ND
PBDE 183	ND	ND
PBDE 190	ND	ND
Octa-		
PBDE 196	ND	ND
PBDE 197	ND	ND
PBDE 203	ND	ND
Nona-		
PBDE 206	ND	ND
PBDE 207	ND	ND
PBDE 208	ND	ND
Deca-		
PBDE 209	1.85 ± 0.61	0.92 ± 0.21

Table M.2. The limit of detection for PBDE analysis (as expressed in terms of pg/m^3) for an 809 m^3 air sample. The means ± SD of three replicates are presented. Limit of detection could not be determined for PBDE 196, 197, 203, 206, 207, 208 due to interferences in these analyses.

Congener	Limit of Detection
Tri-	
PBDE 17	0.073 ± 0.022
PBDE 25	0.081 ± 0.022
PBDE 28	0.073 ± 0.026
PBDE 30	0.049 ± 0.018
PBDE 32	0.072 ± 0.023
PBDE 33	0.084 ± 0.018
PBDE 35	0.080 ± 0.023
PBDE 37	0.082 ± 0.025
Tetra-	
PBDE 47	0.075 ± 0.027
PBDE 49	0.084 ± 0.029
PBDE 66	0.096 ± 0.042
PBDE 71	0.076 ± 0.024
PBDE 75	0.069 ± 0.017
PBDE 77	0.077 ± 0.028
Penta-	
PBDE 85	0.103 ± 0.029
PBDE 99	0.080 ± 0.030
PBDE 100	0.066 ± 0.021
PBDE 116	0.095 ± 0.030
PBDE 118	0.109 ± 0.040
PBDE 119	0.069 ± 0.025
PBDE 126	0.150 ± 0.072
Hexa-	
PBDE 138	0.115 ± 0.049
PBDE 153	0.092 ± 0.032
PBDE 154	0.075 ± 0.024
PBDE 155	0.065 ± 0.009
PBDE 166	0.188 ± 0.051
Hepta-	
PBDE 181	0.286 ± 0.108
PBDE 183	0.157 ± 0.054
PBDE 190	0.377 ± 0.104
Deca-	
PBDE 209	0.534 ± 0.072

Table M.3. Extraction efficiency of PBDEs from filters used in outdoor air sampling. "ND" indicates that the analyte was not detected. PBDE 203 and 208 were not spiked onto the substrate.

Compound	Enriched Amount (ng)	Amount Measured (ng)	Background (ng)	Total Mass (ng)	Recovery (%)
PBDE 1	15.00	8.68	ND	8.68	57.8
	15.00	9.79	ND	9.79	65.3
	15.00	9.02	ND	9.02	60.1
	Mean ± SD	9.16 ± 0.57		9.16 ± 0.57	61.1 ± 3.8
PBDE 15	14.01	11.1	ND	11.1	79.5
	14.01	9.07	ND	9.07	64.7
	14.01	10.3	ND	10.3	73.7
	Mean ± SD	10.2 ± 1.04		10.2 ± 1.04	72.6 ± 7.5
PBDE 30	15.00	10.2	ND	10.2	67.9
	15.00	13.1	ND	13.1	87.3
	15.00	12.5	ND	12.5	83.1
	Mean ± SD	11.9 ± 1.5		11.9 ± 1.5	79.4 ± 10.2
PBDE 47	15.00	10.5	0.12	10.4	69.3
	15.00	11.1	0.12	11.0	73.1
	15.00	11.2	0.12	11.1	74.1
	Mean ± SD	10.9 ± 0.4		10.8 ± 0.4	72.2 ± 2.5
PBDE 99	15.00	12.9	0.13	12.7	84.8
	15.00	14.3	0.13	14.2	94.7
	15.00	12.3	0.13	12.1	80.9
	Mean ± SD	13.2 ± 1.1		13.0 ± 1.1	86.8 ± 7.1
PBDE 100	15.00	12.2	0.03	12.1	80.8
	15.00	13.2	0.03	13.1	87.8
	15.00	12.0	0.03	11.9	79.4
	Mean ± SD	12.4± 0.7		12.4 ± 0.7	82.7 ± 4.5
PBDE 153	15.00	13.1	ND	13.1	87.5
	15.00	14.6	ND	14.6	97.1
	15.00	12.8	ND	12.8	85.1
	Mean ± SD	13.5 ± 1.0		13.5 ± 1.0	89.9 ± 6.4
PBDE 154	15.00	13.6	ND	13.6	90.7
	15.00	14.9	ND	14.9	99.1
	15.00	12.7	ND	12.7	84.8
	Mean ± SD	13.7 ± 1.1		13.7 ± 1.1	91.6 ± 7.2
PBDE 190	15.00	10.6	ND	10.6	70.8
	15.00	16.6	ND	16.6	111
	15.00	13.2	ND	13.2	88.1
	Mean ± SD	13.5 ± 3.0		13.5 ± 3.0	89.8 ± 20.0
PBDE 209	15.15	14.5	1.50	13.0	85.8
	15.15	12.3	1.50	10.8	71.0
	15.15	13.6	1.50	12.1	79.7
	Mean ± SD	13.4 ± 1.1		11.9 ± 1.1	78.8 ± 7.4

Table M.4. Extraction efficiency of PBDEs from XAD-2 adsorbent used in outdoor air sampling. "ND" indicates that the analyte was not detected. PBDE 203 and 208 were not spiked onto the substrate.

Compound	**Enriched Amount (ng)**	**Amount Measured (ng)**	**Background (ng)**	**Total Mass (ng)**	**Recovery (%)**
PBDE 1	15.00	14.2	ND	14.2	94.7
	15.00	14.3	ND	14.3	95.3
	15.00	12.7	ND	12.7	84.3
	Mean ± SD	13.7 ± 0.9		13.7 ± 0.9	91.4 ± 6.2
PBDE 15	14.01	15.5	ND	15.5	111
	14.01	16.9	ND	16.9	121
	14.01	15.8	ND	15.8	112
	Mean ± SD	16.1 ± 0.8		16.1 ± 0.8	115 ± 5.5
PBDE 30	15.00	14.3	ND	14.3	95.6
	15.00	16.2	ND	16.2	108
	15.00	14.2	ND	14.2	94.6
	Mean ± SD	14.9 ± 1.1		14.9 ± 1.1	99.5 ± 7.6
PBDE 47	15.00	11.3	0.13	11.1	74.1
	15.00	12.1	0.13	12.0	80.1
	15.00	14.2	0.13	14.1	94.0
	Mean ± SD	12.5 ± 1.5		12.4 ± 1.5	82.8 ± 10.2
PBDE 99	15.00	14.7	0.07	14.7	97.8
	15.00	16.0	0.07	15.9	106
	15.00	13.9	0.07	13.9	92.5
	Mean ± SD	14.9 ± 1.0		14.8 ± 1.0	98.8 ± 6.9
PBDE 100	15.00	12.9	0.03	12.9	85.8
	15.00	14.7	0.03	14.7	97.7
	15.00	12.8	0.03	12.8	85.2
	Mean ± SD	13.5 ± 1.1		13.4 ± 1.1	89.6 ± 7.04
PBDE 153	15.00	15.1	ND	15.1	101
	15.00	15.8	ND	15.8	105
	15.00	14.2	ND	14.2	94.8
	Mean ± SD	15.0 ± 0.8		15.0 ± 0.8	100 ± 5.4
PBDE 154	15.00	15.1	ND	15.1	101
	15.00	16.6	ND	16.6	110
	15.00	15.0	ND	15.0	99.6
	Mean ± SD	15.5 ± 0.9		15.5 ± 0.9	104 ± 6.0
PBDE 190	15.00	16.0	ND	16.0	107
	15.00	15.7	ND	15.7	105
	15.00	16.7	ND	16.7	111
	Mean ± SD	16.1 ± 0.5		16.1 ± 0.5	108 ± 3.2
PBDE 209	15.15	14.0	0.75	13.2	87.2
	15.15	14.4	0.75	13.7	90.3
	15.15	13.0	0.75	12.3	81.0
	Mean ± SD	13.8 ± 0.7		13.1 ± 0.7	86.2 ±4.7