



STUART A. BATTERMAN, MS, PHD
PROFESSOR OF ENVIRONMENTAL HEALTH SCIENCES
DEPARTMENT OF ENVIRONMENTAL HEALTH SCIENCES
THE UNIVERSITY OF MICHIGAN
SCHOOL OF PUBLIC HEALTH
1420 WASHINGTON HEIGHTS
ROOM M6075 SPH-2 2029
ANN ARBOR, MICHIGAN 48109-2029, USA

A1. Title and Approval Sheet

Title of Plan

Quality Assurance Project Plan for “Emissions of Brominated Flame Retardants (BFRs) from Industrial and Commercial Sources in the Great Lakes Region” (and associated SOPs)

Name of Organization Implementing Project

University of Michigan, School of Public Health, Environmental Health Studies

Effective Date of Plan

June 14, 2006

Names, Titles, Signatures, Approval Dates of Approving Officials

Project Officer _____

PI electronic for *S. Batterman*

A2. Table of Contents

A1. TITLE AND APPROVAL SHEET	1
A2. TABLE OF CONTENTS	2
A3. DISTRIBUTION LIST	4
A4. PROJECT / TASK ORGANIZATION	4
A5. PROBLEM DEFINITION / BACKGROUND.....	4
A6. PROJECT / TASK DESCRIPTION.....	5
OBJECTIVES.....	5
STUDY SITES.....	5
BUILDING AUDIT	6
A7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA	7
A8. SPECIAL TRAINING / CERTIFICATION.....	9
A9. DOCUMENTATION AND RECORDS	9
SECTION B. DATA GENERATION AND ACQUISITION	10
B1. SAMPLING PROCESS DESIGN	10
WALKTHROUGH SAMPLING	10
AIR SAMPLING	10
AIR EXCHANGE RATES AND VOC SAMPLING	10
DUST SAMPLING.....	11
SAMPLING LOCATIONS AND FREQUENCIES	11
B2. SAMPLING METHODS	11
BFR AIR SAMPLING	11
AIR EXCHANGE RATES (AER) AND VOC SAMPLING	11
DUST SAMPLING.....	12
B3. SAMPLE HANDLING AND CUSTODY.....	12
BFR SAMPLING	12
B4. ANALYTICAL METHODS	12
B5. QUALITY CONTROL REQUIREMENTS.....	16
PRECISION	16
ACCURACY.....	16
COMPARABILITY	16
COMPLETENESS.....	16
BLANKS.....	17
DETECTABILITY	17
B6. INSTRUMENT / EQUIPMENT TESTING, INSPECTION AND MAINTENANCE	17
B7. INSTRUMENT / EQUIPMENT CALIBRATION AND FREQUENCY	17
B8. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES	18
B9. NON-DIRECT MEASUREMENTS.....	18
B10. DATA MANAGEMENT.....	18
SECTION C. ASSESSMENT AND OVERSIGHT	18
C1. ASSESSMENT AND RESPONSE ACTIONS.....	18
C2. REPORTS TO MANAGEMENT	19

SECTION D. DATA VALIDATION AND USABILITY 19
D1. DATA REVIEW, VERIFICATION AND VALIDATION 19
D2. VERIFICATION AND VALIDATION METHODS 19
D3. RECONCILIATION WITH USER REQUIREMENTS 19
REFERENCES 19

ATTACHMENTS

- E1. SOP 1 – rev 10.23.03 - Indoor passive VOC sampling**
- E2. SOP 2 – rev 10.23.03 - Laboratory VOC analysis**
- E3. SOP 3 – rev 05.15.05 - Protocols for use of PFT diffusion cells for air exchange and air flow determination**
- E4. SOP 4 – rev 01.31.06 - PBDE sampling**
- E5. SOP 5 – rev 01.26.06 - TSP and PM- 2.5 Sampling**
- E6. SOP 6 – rev 10.23.03 - Instrumental Calibration for VOCs**
- E7. SOP 7 – rev 05.05.04 - Gravimetric Filter Analysis**
- E8. SOP 8 – rev 10.23.03 - Sorbent Tube Packing, Conditionig and Flow Checking**

A3. Distribution List

Jon Dettling
Great Lakes Commission
2805 South Industrial Hwy., Suite 100
Ann Arbor, MI 48104-6791
dettling@glc.org
Phone: 734-971-9135

Stuart Batterman, Sergei Chernyak, Chris Godwin, Simone Charles
University of Michigan
Environmental Health Sciences, School of Public Health
109 Observatory Street
Ann Arbor, MI 48109
StuartB@umich.edu, Sergeic@umich.edu, ccgodwin@umich.edu, simonec@umich.edu
734/763-2417

A4. Project / Task Organization

Dr. Batterman is the principal investigator on this project. He will oversee all aspects of the project including data review, sample handling and analysis adherence to quality assurance and control (QA/QC), evaluation of necessity of corrective action, and interpretation of the generated data.

Research personnel for this project include Dr. Sergei Chernyak, an analytical chemist, who supervises laboratory personnel, specially, Erika Gwynn, M.S., and Chunrong Jia, M.S. Field activities will be supervised and conducted by Chris Godwin, Ph.D., field coordinator, and Simone Charles, PhD. with the assistance of M.S./Ph.D., students in the Environmental Health/Industrial Hygiene program at UM, including Michael Roenow, Josh Bennett, and Wang Wei. All individuals will have detailed laboratory and field training, as appropriate, in the measurement types to be utilized.

A5. Problem Definition / Background

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants and consequently incorporated into plastics, textiles and other materials. They are lipophilic and hence bioaccumulate. They also degrade slowly. Worldwide, elevated levels are reported in air, water, sediment, biota and people (Hale et al. 2003; Hites 2004). The emission sources and transport pathways of BFRs are, however, not well understood. Their presence in the environment has been attributed to several sources (Wilford et al. 2004; Alcock et al. 2003; Hales et al. 2002; Sjodin et al. 2001; Rice et al. 2002; Dodder et al. 2002; Jaward et al. 2004; Hale et al. 2001; Knoth et al. 2004; Fabrellas et al. 2004). The available, but limited, measurements of environmental BFR concentrations indicate that BFR indoor concentrations exceed outdoor concentrations primarily due to limited environmental degradation and dispersal occurring indoors. Jones-Otazo et al. (2005) found that ingestion and/or inhalation of household dust was the largest contributor of BFR exposure from toddlers to adulthood and represents the main exposure pathway for all life stages (except nursing infants whose exposure was primarily through human milk). They estimated a median Σ PBDE dust concentration of 1.6 $\mu\text{g/g}$. It is unknown what portion of PBDEs in indoor environments (dust, airborne in gas or particulate phases) are exchanged to the outdoor environment, and ultimately deposited into the Great Lakes.

Considering the dominance of the indoor environment (industrial and urban centers) as a PBDE reservoir (Alcock et al. 2003), the aims of this study are to:

- (1) Quantify the distribution and composition of BFRs in a set of commercial and industrial buildings, and
- (2) Quantify the source strength or emission factors for BFRs for these buildings from which estimates of emission rates and pathways from these urban sources into ambient (outdoor) air will be derived.

It is recognized that sample size utilized in this study is small, and thus it may be viewed as a pilot study that provides semi-quantitative results. However, we anticipate that the results will complement and reinforce the recent literature regarding levels of BFRs in urban area.

The study is designed to be relevant to the initiatives of the Great Lakes Commission, specifically the Emissions Inventory Development priority as its expected outcome includes improvements in toxic source and emissions inventories for brominated flame retardants (BFRs). Study results will help to target persistent toxics for pollution prevention and reduction efforts, and will also feed into other GLAD program priorities, including Source Identification and Characterization, and Atmospheric and Multi-media Modeling. This work will also assist screening and modeling efforts aimed at anticipating exposures and risks from emerging contaminants in the Great Lakes basin.

A6. Project / Task Description

Objectives

The objective of this work is to characterize both vapor and particulate phase BFR emissions from typical indoor environments. We propose to:

- (1) Measure incoming and exiting BFR concentrations in 12 industrial and 12 commercial buildings.
- (2) Determine air exchange rates using perfluorocarbon tracer (PFT) gas techniques, including estimation of air flows (requiring estimates of building volumes).
- (3) Conduct a building walkthrough audit to assess the general indoor air quality and presence of, or conditions potentially associated with, BFRs.
- (4) Obtain and analyze dust samples as an indicator of potential BFR sources.
- (5) Quantify BFR emission rates from buildings based on concentration, building, and air flow/exchange information.

Study sites

This work will analyze the following sites:

- (1) 12 commercial buildings
- (2) 12 industrial buildings
- (3) Ambient air samples at each of the sites above

Note that under separate (US EPA) support we are using similar protocols to examine BFRs in residences. Also, note that the study size is limited by funding constraints. We recognize that due to these constraints, we cannot obtain results that necessarily can be considered representative since the universe of indoor environments is very diverse, encompassing buildings and building contents that differ in age, design, construction, materials, and many other factors. We will endeavor to sample a range of buildings that reflect variation in a number of factors, however, it should be recognized that

the use of additional study sites would increase the representativeness of the study and the statistical power to associate sources with concentrations and emissions.

Building audit

A building walkthrough audit will be conducted at the beginning of the project by field staff to assess the general indoor air quality and presence of, or conditions potentially associated with, BFRs in each of the study sites.

Air Sampling

Both particulate and gas phase BFRs in air will be determined. We will utilize medium flow samplers to draw air through a pre-cleaned quartz filter followed by a pre-cleaned BFR-free polyurethane foam (PUF) cartridge. The details of the analytical methods and the contaminants of concern are detailed in section B below.

BFR Analysis

Sample preparation typically will be performed on a set of samples, consisting of test samples, a field blank, a method blank, and a matrix spike. Samples will be Soxhlet extracted and the extracts analyzed by GC/MS. The analysis will detect multiple BFR congeners as specified in Table 2. Note that Table 2 is a subset of compounds that can be detected. Since mass spectra and chromatograms will be preserved, we will have the ability (if necessary or helpful and with additional funding) to examine and quantify other compounds of interest.

Air Exchange Rates

Air exchange rates (AERs) will be measured over the BFR sampling period for each building using the constant injection tracer technique. Perfluorocarbon tracer gases will be injected at a constant rate in buildings. Tracer concentrations, measured over the BFR monitoring period at the same location, along with building /room volume and the tracer emission rate, will be used to derive AERs. These tracers (along with many other volatile organic compounds) will be measured using passive sampling, thermal desorption, gas chromatography-mass spectroscopy (GC-MS) following our well-developed protocols (Peng and Batterman 2000; Batterman et al. 2002a; 2002b; 2003; 2005).

Emission Rate

The basic approach to estimate BFR emissions essentially utilizes a building as a ‘natural’ test chamber in which we will measure indoor BFR concentrations, C_{in} (ng m^{-3}). The BFR emission rate, S (ng hr^{-1}) is derived as:

$$S = (C_{in} - C_{amb}) Q$$

where C_{amb} = incoming (ambient) BFR concentration (ng m^{-3}) (likely to negligibly affect emission rate; Wilford et al. 2004, Butt et al. 2004), and Q = volumetric flow rate, Q ($\text{m}^3 \text{hr}^{-1}$). The volumetric flow rate is derived from the air exchange rate, AER (hr^{-1}) and a measured or estimated building volume, V (m^3):

$$Q = V \text{ AER}$$

A7. Quality Objectives and Criteria for Measurement Data

Table 1. Measurement Quality Objectives for samples. See next page for QC flags, notes, and other information.

Requirement	Acceptance Criteria	QC Flag
Reporting Units	ng m ⁻³ or ng g ⁻¹	N/A
Instrument detection limit	Once per project per analyte; extrapolate from initial calibration curve (see note 1)	IDL
Method detection Limit	Once per project (see note 1)	MDL
Calibration	Set of standards of 5 different concentrations prior to analysis of samples and blanks, after instrument performance check (see note 1)	Rerun batch
Frequency	Performed every 12 months.	
Routine detectability frequency criteria	All samples (see note 1) > MDL	MDL
Blanks:		
Field blanks frequency criteria	Collection tubes 10% of total samples ≤ MDL (see note 1)	FPB
Laboratory blanks frequency criteria	Materials (solvents, reagents, etc.) from reference sample matrix 1 per analytical batch unless problems, then use replicates. ≤ MDL (see note 1)	FPB
Performance stds frequency % recovery	A standard run as check sample One per run batch 100% ± 20%	FPC
Reference Samples frequency % recovery	Check sample 1 per every 3 sample batches 100% ± 20%	FPC; Repeat, work halted until acceptable
Procedural Spikes frequency % recovery	Analyte cocktail spiked into solvent Beginning of project; if fail check sample 100% ± 30%	FPS; Repeat, work halted until acceptable
Internal stds frequency criteria	PCB-204, PCB-30, PCB- 52L (¹³ C-2,2',5,5'-tetraCB), PCB-138L (¹³ C-2,2',3,4,4',5'-HxCB) Every sample, blank and std Elution time of laboratory internal standard within 0.2 min window in given run Recovery of laboratory internal standard within 25% in given run.	FIS
Surrogate Recovery criteria % recovery	PBDE-139L (¹³ C-2,2',3,4,4',6-HxBDE) M/Z must be correct Recovery must be within 70 to 110% of theoretical	FSR
Completeness	Goal is 100% valid data; ≥ 90% is acceptable (see note 1)	INV
Duplicates		
Field Duplicate frequency criteria	Duplicate analysis of a composite 1 per every 5 sample sets representing ≥ 20% of samples < 25% RPD	FDL
Lab Duplicates frequency criteria	Duplicate analysis of a composite 1 per every 5 sample sets representing ≥ 20% of samples < 20% RPD (see note 1)	FDL

Abbreviations:

IDL	Instrument Detection Limit
MDL	Method Detection Limit
FPB	Failed Procedural Blank
FPC	Failed Performance Check
FPS	Failed Procedural Spike
FIS	Failed Internal Standard
FSR	Failed Surrogate Recovery
INV	Invalid
FDL	Failed Duplicate

Additional QA flags not included in Table 1 include:

LAC	<u>Laboratory accident</u> destroyed sample or rendered it unsuitable for analysis.
INT	Not analyzed due to <u>Interference</u> .
RIN	<u>Re-injection</u> of the sample extract produced the reported value.
REX	<u>Re-prepared</u> sample was used to generate the reported value.
FBK	<u>Found in procedural blank</u> at greater than acceptable criteria and reported value may be an overestimate.
UND	<u>Undetected</u> ; no instrument response
CAN	<u>Cancelled</u> ; value was not reported because analysis not performed.
REJ	<u>Rejected</u> ; reported value was rejected for an unspecified reason by the laboratory based on professional judgment. Value was not utilized in the calculation of any results where a mean was being determined.

Notes 1. Applies on a congener-specific basis.

Detection limits.

The calculation of detection limits are described in the SOPs. Briefly, they are calculated as the standard deviation of 7 low concentration laboratory-prepared samples multiplied by the t-statistic for 95% confidence for this sample size, e.g., $t_{0.05,7,0.05/2} = 2.84$.

Air sampling system calibration.

The air sampling calibration procedures are described in the SOPs. Briefly, flows are calculated as the average of the pre- and post-sampling flow measurements, using NIST-traceable methods.

Reference sample.

PBDE analyses will utilize a standard reference material, specifically National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2583 and SRM 2585 dust, which are well characterized materials designed for this purpose.

Labeled Surrogate Compounds

Both labeled and unlabeled surrogate BFRs will be used to confirm acceptable recovery.

A8. Special Training / Certification

Dr. Batterman and his personnel have extensive experience in trace level analysis of volatile and semivolatile organic compounds (VOCs). His laboratory personnel include an analytical chemist, a field coordinator, a Ph. D. candidate as well as other staff. These personnel have previously conducted numerous indoor air quality studies and have developed a variety of protocols and instruments. They have developed and widely utilized both passive and active sampling techniques. All personnel mentioned in Section A4 will have detailed hands-on laboratory and field training, as appropriate, in the measurement types to be utilized. This training includes detailed review of SOPs, side-by-side instruction in the laboratory, side-by-side training in the field, and reviews of knowledge and performance by the PI.

A9. Documentation and Records

Project documentation will include:

- (1) Lab notebooks (including method, file name, sample, tube number information)
- (2) Instrument (raw) data files (chromatograms)
- (3) Final processed data (in spreadsheet files) where concentrations are calculated, and
- (4) QA files containing all precision, accuracy and blank data.
- (5) Written protocols (SOPs, standard operating protocol) for each measurement and analysis type.

Attachments to this QAPP provide SOPs and standard data forms, where applicable, for the major measurement types, specifically:

- (1) SOP 1 – rev 10.23.03 - Indoor passive VOC sampling
- (2) SOP 2 – rev 10.23.03 - Laboratory VOC analysis
- (3) SOP 3 – rev 05.15.05 - Protocols for use of PFT diffusion cells for air exchange and air flow determination
- (4) SOP 4 – rev 01.31.06 - PBDE sampling
- (5) SOP 5 – rev 01.26.06 - TSP and PM-2.5 sampling
- (6) SOP 6 – rev 10.23.03 - Instrument Calibration for VOCs
- (7) SOP 7 – rev 05.05.04 - Gravimetric Filter Analysis
- (8) SOP 8 – rev 10.23.03 - Sorbent Tube Packing, Conditioning and Flow Checking

These SOPs plus this QAPP (including the latest revision) are on a web site accessible to the project team. An electronic inventory of samples will also be maintained. These files will be available for review on site. In addition, compliant with Part IV of the Requirements and Instructions for this grant program, we will submit this Quality Assurance Project Plan (QAPP, part of Quality System Documentation) for approval by the earlier of (i) the 30th day prior to use or collection of environmental data and (ii) the 90th day after the project start date. Defined identification criteria and QA/QC criteria and requirements will be used in evaluating the analytical data.

SECTION B. DATA GENERATION AND ACQUISITION

The following provides an overview of sampling process design and methods. The SOPs provide complete detail on these measurements types, as well as data forms.

B1. Sampling Process Design

Walkthrough sampling

The walkthrough will be conducted using survey instruments similar to those previously developed and used in several studies (e.g., Batterman et al., 2005). The walkthrough survey will allow assessment of the general indoor air quality and presence of, or conditions potentially associated with, PBDE and other BFRs. The survey will document building characteristics (e.g., age, type, size, number/types of windows and doors, heating/cooling systems, air filters), indoor environment (e.g., moisture damage, temperature, humidity, exhaust fans, stove type, use and storage of solvents/chemicals), potential indoor air contaminants (e.g., combustion products, environmental tobacco smoke); nearby outdoor sources (e.g., proximity to highways, industry); and presence of PDBE potential sources (e.g., foam in furniture, draperies, audio/video equipment, vacuum dust). Vacuum dust will be sampled from each building. This sample will provide a composite measure of particulate phase BFRs that complement the airborne measurements.

Air Sampling

Both particulate and gas phase BFRs will be determined. Medium flow samplers (10 L min^{-1}) to draw air through a pre-cleaned quartz-fiber filter followed by a pre-cleaned BFR-free polyurethane foam (PUF) cartridge will be used. The samplers will operate for 5-7 days ($72.0\text{-}100.8 \text{ m}^3$ of air). Spikes will be prepared in the laboratory after sample collection from the field. Blanks will be treated like the experimental samples.

For the pilot study, at 4 sites, two side-by-side sampling systems will be used to estimate the distribution of PDBEs on fine and coarse (<2.5 and $>2.5 \mu\text{m}$ dia) particulate matter. One sampling system will use a size-selective inlet to capture only $<2.5\mu\text{m}$ particulate matter. The other will use a shrouded, downward facing open-face filter. Very small particulate matter has been shown to have faster penetration rates through buildings, while larger particulate matter tends to be attenuated. In addition, larger particles are more effectively removed by the building's air filters, if present and operating.

Air Exchange Rates and VOC Sampling

Air exchange rates (AERs) must be known to estimate emission rates. Effective AERs will be measured over the sampling periods for each building using tracer gases. Diffusion tube emitters, which would emit a unique tracer gas at a constant known rate, will be placed in different locations of each building. Emission rates will be determined in the laboratory by a linear regression of weight change over time (before and after deployment). Tracer gas and VOC concentrations will be measured over the BFR monitoring period at the same location. Thermal desorption sorbent tube sampling and passive samplers will be used. The operating time, flow rates, and amount of air sampled will be recorded on a standard data sheet at the beginning and end of the sampling session. Together with a measured or estimated building/room volume and the tracer emission rate, the effective air exchange rate (AER) will be calculated. This method will provide measurements over a long and potentially representative time period. Tracer gases as well as other VOC concentrations will simultaneously be obtained. Blanks will be treated like the experimental samples.

Dust Sampling

Settled dust samples will be collected from specific corners of 2 to 3 rooms at a specific time point during the BFR monitoring period, and at the same location for each sampling. Samples will be taken from corners in “inaccessible” areas, that is, areas in which dust may accumulate but what would rarely cause exposure and away from traffic routes but accessible to sampling. As far as possible, the type of surface sampled at each location will be consistent. A pre-determined sampling area will be used at all locations for each sampling event. The timing of sampling in relation to cleaning activities in the residences will be noted. Composite samples will be obtained using a small handheld vacuum equipped with a hose, filter and HEPA filter. Dust collection efficiency will be determined.

Sampling locations and frequencies

Fifteen (15) buildings will be sampled. Ambient (outdoor) air samples will also be taken in 5 southeast Michigan locations. Buildings will primarily be residences, given the amount of foam, textiles, and plastics used (and hence BFR reservoirs). Sampling will be across a selection of old and new homes in different communities to measure spatial variability.

Pilot study

Prior to starting the main study, we will undertake a pilot study to ensure that quality goals are met, including (a) precision; (b) blanks cleanliness; (c) surrogate recovery, standard recovery. The pilot study will utilize collocated samplers (side-by-side) and replicates. This will include at least two indoor environments (e.g., homes), and one outdoor location. These pilot samples will also serve to make adjustments to the SOPs, if necessary, and to evaluate the distribution of PDBEs on fine and coarse (<2.5 and >2.5 μm dia) particulate matter, as described below.

B2. Sampling Methods

BFR Air Sampling

Both particulate and gas phase BFRs in air will be determined. We will utilize medium flow samplers to draw air through a pre-cleaned quartz filter followed by a pre-cleaned BFR-free polyurethane foam (PUF) cartridges. Components that may contact the sample are glass and/or Teflon, and are thoroughly cleaned prior to each use (see SOP). Samplers will be deployed for 5-7 days. Air flows will be checked before and after sampling using a DryCal flow meter. After sampling, the filter and PUF cartridge will be wrapped with aluminum foil, placed into a shipping container, labeled and shipped to the laboratory. The operating time, flow rates, and amount of air sampled, sampling dates and times will be recorded on a standard data sheet at the beginning and end of the sampling session. A unique ID will be assigned to the sample.

Air Exchange Rates (AER) and VOC Sampling

It should be noted that the sampling and analysis methodology for AER/PFT/VOC purposes is completely separate from the BFR/SVOC sampling analysis. The following applies only to the VOC analysis. Prior to use, thermal desorption tubes used for PFT sampling and analysis will be conditioned in a 24-tube conditioning oven (Scientific Instrument Services, Ringoes, NJ) at 325°C for 6 hours. The tubes and injection needles will be flushed with a carrier gas (e.g., high-purity helium or nitrogen) in order to prevent oxygen, which is destructive to the sorbent materials within the tubes (Tenax GR adsorbent), from entering the tubes, as well as to aid in flushing-out impurities from the tube and needles. After conditioning, stainless-steel caps with Teflon seals will be screwed onto both ends of the tubes. The tubes will then be wrapped in previously baked aluminum foil and stored in

glass jars in a 4°C refrigerator until use. A fresh carbon filled packet will be placed in each jar to adsorb any inadvertent VOCs and prevent contamination. Procedures for collecting samples, sampling equipment, and sampling materials are given in B1 above. A unique ID will be assigned to the sample. A minimum of 2 duplicate samplers will be deployed for 5-7 days, after which samplers will be retrieved, capped, wrapped in clean foil, stored in glass jars, and returned to the laboratory. Prior to analysis, sample collection tubes will be refrigerated at 4 °C. Maximum holding times to sample extraction and/or analysis is approximately 1-6 weeks at 4°C (Peng and Batterman 2000). However, samples are typically analyzed within 1 week. Tube contents will be thermally desorbed and analyzed by GC-MS (see SOP attached, and Peng and Batterman 2000).

Dust Sampling

A handheld vacuum cleaner with a hose and filter will be used to collect composite dust sample within a 1 m² area in a corner of specific rooms in the residences. Dust sample collection will be at a specific time point during the BFR sampling period. A pre-weighed filter (to a 0.1 mg precision) (equilibrated at 33% relative humidity) will be inserted in between the filter basket and vacuum's HEPA filter will be used to collect fine particle dust from each sampling area. After each vacuuming and sample collection, the filter containing the samples will be folded, wrapped in foil, placed into labeled polyethylene zip-lock bags, and shipped to the laboratory. After equilibration at 33% relative humidity, the filter will then be weighed to determine the weight of dust collected (to a 0.1 mg precision). Between sample collections, the vacuum will be cleaned with hot water and a methanol rinse. A measure of each dust sample as well as reference materials (SRM 2583 and 2585) will be extracted by pressurized fluid extraction with dichloromethane followed by a clean-up procedure through silica sep-pak cartridges using hexane. PCB congeners 30, 204, 52L and 138L will be added to each sample as internal standards. Samples will be analyzed by GC-MS using negative chemical ionization with select ion monitoring. Prior to analysis the samples will be stored at 4°C (see Stapleton et al. 2004).

B3. Sample Handling and Custody

Tracer gas / VOC sampling

After sampling, the sampling tubes will be capped with stainless steel caps with Teflon seals. The capped tubes will be wrapped in pre-baked aluminum foil, placed in polyethylene bags and then into glass jars containing a carbon packet, and shipped to the laboratory. Thereafter, the tubes will be stored in a refrigerator at 4°C until analysis within a week although storage times can be as high as 6 weeks (Peng and Batterman 2000). Blanks will be handled as experimental samples.

BFR Sampling

After sampling, the filter and PUF cartridge (containing the samples) and the flasks containing dust samples will be wrapped in aluminum foil, placed into a shipping container, labeled and shipped to the laboratory. Samples will be stored in a 4°C refrigerator until analysis. Samples will be analyzed within 1 week in most cases. Blanks will be handled as experimental samples.

B4. Analytical Methods

Tracer Gas/VOC Analysis

Tracer gas and VOC analysis will involve using an automated short-path thermal desorption/cyrofocusing system that sits directly on the injector/septum area of the gas chromatograph coupled to a mass spectrometer (GC-MS) following well-developed protocols. The GC-MS contains a split temperature injector and is equipped with a 60 m x 0.25 mm id column with a 1.4 µm film

thickness (DB-VRX, J & W Scientific, Palo Alto, CA, USA). Ultra-high purity (99.999%) helium, cleaned using a heated catalytic gas purifier and a fresh trap, will be used.

BFR Analysis

After sample collection, the filters, PUFs, and dust samples will be separately Soxhlet extracted for 16 hours. The extract will be subjected to an acid/base clean-up procedure followed by clean-up on micro columns of silica gel, alumina and carbon. The set of sample extracts will be analyzed by GC/MS using selected ion monitoring analysis and a 30-m DB-5 fused silica capillary column.

GC-MS Analysis

The sample extracts (i.e., air, particulate, dust) will be injected into the GC-MS, and the resulting ion chromatograms acquired electronically. All chromatograms will be examined visually for quality of baseline resolution and accuracy of the integration by laboratory personnel. Peak areas will be used to quantify analyte concentrations in sample extracts by ChemStation software via a macro program compared to peak areas of the analytical standards. The areas will be transferred electronically to a spreadsheet. The use of a pre-formatted spreadsheet reduces the potential for calculation errors in data handling.

For BFRs, we recognize that due to high injection and column oven temperatures and the long runs, several analytes (especially decaBDE congener 209) are susceptible to thermal degradation. We anticipate that the fraction of this congener that is degraded will be constant. Based on a review of current methods, we believe that the degradation fraction can be evaluated by contrasting results obtained using our normal approach for penta to hepta BDEs (30 m column and injection temperature of 280 °C), with an approach using a shorter column and lower temperatures (15 m column, 0.18 id x 0.07 µm, and injection temperature of 250 °C) that should result in very little degradation of congener 209. We have not yet tried this approach in our laboratory, but believe that it will yield reproducible results. If this approach works, we will perform this analysis in duplicate on laboratory-spiked and reference materials every 6 months, to confirm its validity.

Equipment for Study

Air samples for trace gas and VOC analysis collected using thermal desorption tubes will be analyzed using the Scientific Instrument Services (SIS) Model 200 automated short-path thermal desorption/cryofocusing system interfaced to a Hewlett-Packard 6890/5973 gas chromatograph/mass spectrometer running ChemStation. This equipment includes a liquid N₂ cooled cryofocus trap, sub-ambient oven capability, turbomolecular pump, and the NBS/EPA (NIST) mass spectral library. A second workstation is networked to this machine.

BFR and other semi-volatile analyses will be collected using quartz-fiber filter and glass cartridges containing PUF (BFR-free polyurethane foam) cartridges. Analysis will be performed using a second GC/MS system, consisting of an Agilent GC 5890/MSD 5973 equipped with electron impact and chemical ionization models, turbomolecular pump, auto-sampler, library, and workstation. A dedicated extraction laboratory houses a Bucki R-205 rotary evaporator, various extraction setups, large oven, and related facilities.

Dust samples will be collected using a handheld vacuum cleaner with a hose, filter and HEPA filter. Pre-cleaned glass flasks with cap corks will be used for sample transport and storage.

Data Processing and Quantification Methods

All chromatograms will be reviewed by one of Dr. Batterman's experienced research team. The ChemStation software automatically integrates all peaks of interest. The peak areas are extracted by a ChemStation macro program and transferred electronically to a PC spreadsheet operated through a

second workstation that is networked to the ChemStation. The mass of analyte in each extract will be converted to a concentration by dividing mass of analyte (ng) by the volume of air (m^3) or mass of dust (g) sampled.

Data Interpretation and Data Reporting

The data will be used to determine any changes in BFR concentration over time (seasonal differences) and space (spatial variability between sampling locations). The relationship between BFR concentrations and potential co-factors that can help explain results will be explored using correlation coefficients, scatter plots, regression models, and other statistical tests. The work is aimed at quantifying BFR emissions and partitioning from the largest BFR reservoir, materials in use. These rates are needed to predict future trends of BFRs, their significance and impact.

Table 2. Partial list of chemicals to be analyzed in dust and air samples, type of instrumental analysis used, estimated MDL expressed as ng m^{-3} or ng g^{-1} , and quantitation (Q) and confirmation (C) ions.

Analyte	Method of Analysis	MDL [†]		Q, C (m/z)
		ng m^{-3}	ng g^{-1}	
		Air	Dust	
PBDE #17	GC/MS using SIM	0.02	0.01	79, 81
PBDE #28	GC/MS using SIM	0.02	0.01	79, 81
PBDE #47	GC/MS using SIM	0.05	0.02	79, 81
PBDE #49	GC/MS using SIM	0.02	0.01	79, 81
PBDE #99	GC/MS using SIM	0.05	0.02	79, 81
PBDE #100	GC/MS using SIM	0.05	0.02	79, 81
PBDE #153	GC/MS using SIM	0.02	0.01	79, 81
PBDE #154	GC/MS using SIM	0.02	0.01	79, 81
PBDE #183	GC/MS using SIM	0.2	0.2	79, 81, 486, 494
PBDE #184	GC/MS using SIM	0.04	0.02	79, 81, 486, 494
PBDE #191	GC/MS using SIM	0.1	0.1	79, 81, 486, 494
PBDE #196	GC/MS using SIM	0.1	0.2	79, 81, 486, 494
PBDE #197	GC/MS using SIM	0.3	0.02	79, 81, 486, 494
PBDE #206	GC/MS using SIM	0.2	0.4	79, 81, 486, 494
PBDE #207	GC/MS using SIM	0.2	0.4	79, 81, 486, 494
PBDE #208	GC/MS using SIM	0.2	0.4	79, 81, 486, 494
PBDE #209	GC/MS using SIM	0.6	2.5	79, 81, 486, 494
PBDE-139L (¹³ C-2,2',3,4,4',6-HxBDE)	GC/MS using SIM	na	na	79, 81
TBBPA	GC/MS using SIM	0.1	0.1	79, 81
PCB- 52L (¹³ C-2,2',5,5'-tetraCB),	GC/MS using SIM	na	Na	291, 292
PCB-138L (¹³ C-2,2',3,4,4',5'-HxCB)	GC/MS using SIM	na	na	360, 362
HFB	GC/MS using Scan	24	na	186, 117
OFT	GC/MS using Scan	5.0	na	217, 236, 186

GC/MS refers to gas chromatography-mass spectroscopy. na – not applicable to dust samples.

[†] - MDL's for PBDE's calculated based on 10L sample; for HFB and OFT, calculated based on 2 L sample.

B5. Quality Control Requirements

Precision

Precision is a quantitative measure of the agreement between two or more measurements of the same parameter. It defines the relative uncertainty about a measurement. Precision will be determined through the use of duplicate samples. Duplicate (analytical) precision must be < 25% RPD (field duplicates) or < 20% RPD (laboratory duplicates). The measure of precision will be calculated as the absolute relative difference between two identical samples (given identical flow rates for a given time period).

$$\text{RPD} = \frac{|C - C_{\text{dup}}|}{[(C + C_{\text{dup}})/2]} * 100\%$$

where RPD = relative percent difference; C = measurement in the sample; and C_{dup} = measurement in a duplicate of that sample.

Accuracy

Accuracy is the degree of agreement between an observed value and an accepted reference or “true” value. It provides a measure of absolute uncertainty about a given measurement. Accuracy will be assessed using check samples, matrix spikes, laboratory control samples, duplicates, and blanks. Audit accuracy (i.e., the relative difference between the measurement result and the nominal concentration of the audit compound) must be within 30% for concentrations normally expected in contaminated ambient air (0.5 to 25 ppb). Check samples must be 100% ± 20% of the established value. Spike samples will be prepared by adding a given level of analyte to the solvent or reagent used for experimental samples analysis. The spike will be subjected to the same analytical procedure as the experimental sample. Using the spike sample data, the ability of the procedure to recover the analyte will be determined. If analyte recovery is poor (<70% or >130%), the analytical procedure will have to be modified. Percent recovery will be calculated as:

$$\%R = [C_{\text{meas}} / C_{\text{act}}] 100\%$$

where %R = percent analyte recovery; C_{meas} = concentration or mass of analyte measured in the spike sample; and C_{act} = concentration or mass of analyte added to the spike

Sample results will not be corrected for %R if %R is 100% ± 30%.

Comparability

Comparability is an expression of the confidence with which one data set can be compared with another. All analyses will be conducted by the same personnel within the same laboratory, methods, and instruments. This would aid to facilitate comparability between sample sets.

Completeness

Completeness is the percentage of acceptable data needed to validate the study. Completeness is calculated as:

$$\text{Completeness} = (N_{\text{samples}} / N_{\text{collected}}) 100$$

where N_{samples} = number of valid samples; and $N_{\text{collected}}$ = number of samples collected. We aim for a completeness of 100%. However, $\geq 90\%$ will be accepted.

Blanks

Laboratory and field blanks will be used to assess contamination from the matrix (solvent or reagent), sample containers and field equipment involved in sampling. Blanks will be analyzed using the analytical procedure used for the experimental samples. A blank is run with each sample set. Sample results will not be corrected for blank values. Analyte concentrations in the samples and blanks will be reported. The blank and associated samples will be flagged if the blank analyte concentration is greater than the MDL and the sampling tubes will be cleaned/ re-conditioned (e.g., tubes) or new solvents used.

Detectability

Experimental sample data that is $< \text{MDL}$ will be considered as zero concentration. The response for all samples will be examined. A sample response $< \text{MDL}$ will be flagged and set to the MDL. We will also calculate a detection frequency (i.e., the percent of samples $> \text{MDL}$) for each BFR congener.

Quality control samples

The BFR QC samples will include standard reference materials from NIST (SRM 2583 and SRM 2585) in addition to internal standards (PCB-204, PCB-30, PCB-52L, and PCB-138L). For VOC analysis, QC samples will include internal standards (10 ng) used to reference and standardize each compound of interest.

B6. Instrument / Equipment Testing, Inspection and Maintenance

The GC-MS is inspected prior to use for necessary pressures and temperatures. Any deviation from the set pressures and temperatures would require the termination of any runs and a complete evaluation of the instrument. Routine maintenance of the instrument is conducted following the instrument protocols. Maintenance also includes changing the instrument liner every 3 months and changing the injection inlet septa every 150 injections.

B7. Instrument / Equipment Calibration and Frequency

The GC-MS is auto-tuned prior to sample runs. In addition, after the instrument performance check standard criteria have been met, the instrument is calibrated at 5 concentrations spanning the monitoring range of interest. Each concentration level will have 3 replicates and 3 matrix blanks. From these, a calibration curve will be prepared. This will determine the instrument's sensitivity and the linearity of the response for the analytes of interest. Internal standards (e.g., fluorobenzene and p-bromofluorobenzene) are used to validate retention time and responses. The calibration curves will be used to determine the relative response factor (RRF), mean RRF, percent relative standard deviation (%RSD), relative retention times (RRT), mean RRT, mean area response (Y), mean retention times. Criteria that must be fulfilled are:

%RSD	must be $< 30\%$ with at most 2 exceptions up to a limit of 40%
RRT	must be within 0.06 RRT units of the mean RRT

After a major instrument upset (e.g., a power outage) or if the instrument is not used for an extended period (e.g. > 2 weeks) we will verify the calibration using QA samples.

Due to problems noted earlier regarding PBDE congener 209, this congener will not be subject to the criteria above, rather, separate tests using two columns will be used as described above.

B8. Inspection/Acceptance of Supplies and Consumables

Solvents will be unpacked on arrival and placed in solvent storage by the lab technician. Other reagents will be kept in the chemical storage in the laboratory. Reagent quality will be monitored by the appearance and acceptability of lab procedural blanks.

The preparation and use of standards will be documented, including date/method/condition for preparation, and date and purpose of use (see Instrument Calibration and Laboratory VOC Analysis SOPs and EPA Method 1614 – Section 7.7)

B9. Non-direct Measurements

Non-direct measurements are not anticipated for this project.

B10. Data Management

Assuming fully mixed and steady-state conditions, the air exchange rate, AER (hr⁻¹), will be calculated as:

$$\text{AER} = F / CV$$

where F = PFT emission rate (mg hr⁻¹), C = average PFT concentration (mg m⁻³), and V = building or zone volume (m³)

Other data (e.g., sample type, tube numbers, flow rates, sample location) will be recorded in the laboratory notebook and ultimately archived. All electronic files will be regularly backed up on storage devices that will be maintained in several places for redundancy. SOPs and data forms are appended to this document.

SECTION C. ASSESSMENT AND OVERSIGHT

C1. Assessment and Response Actions

All data validation procedures and corrective actions are listed in Table 1. Reviews of laboratory activities will be conducted periodically by Dr. Batterman and laboratory staff through weekly meetings to verify that analyses are performed in accordance with the procedures established in this QAPP. All corrective actions resulting from these reviews will be recorded in laboratory notebooks, and indicated with appropriate QC codes.

Analytical corrective actions may include:

- (1) If samples do not meet the data quality objectives, they will be rerun to rule out artifacts of instrumental analysis. If the samples are still out of compliance, these samples will be flagged.
- (2) If blank analyte concentrations do not meet data quality objectives, matrices will be checked for purity. If the data are of questionable quality following these control actions, samples associated with these blanks will be flagged appropriately. The sampling tubes will be cleaned/ re-conditioned (e.g., tubes) or new solvents used.

(3) If spike recovery is too low or high, analytical procedures will be modified.

The QA plan and standard operating procedures (SOPs) will help ensure that the data quality meets sponsor requirements as well as independent peer-review by experts in the field.

C2. Reports to Management

Dr. Batterman will supply progress reports quarterly. Reports will summarize progress to date, results of any performance or internal audits, interim data quality assessments and any notable lapses in quality assurance and plans for addressing these problems. He will supply a final project report to the EPA Project Officer at the conclusion of the study incorporating all data, data analysis and data interpretation.

SECTION D. DATA VALIDATION AND USABILITY

D1. Data Review, Verification and Validation

Data that meets the measurement quality objectives outlined in Table 1 will be deemed valid and used in the data analysis and interpretation.

Blanks will be run with each sample set. If sample data are consistent with previous data, and reagent blanks are acceptable (i.e., concentrations < MDL), the data will be accepted as valid. Blanks with analyte concentrations \geq MDL will be considered unacceptable and the reagents will be checked for purity prior to conducting further analyses. The associated sample sets will be compared to previous sample sets for self-consistency. If the sample data or reagent purity is questionable, e.g., criteria specified in Table 1 are not met (e.g., low IS recovery, chromatographic problems, etc.) samples will be flagged as shown in Table 1 and, if possible, another sampling done. The procedural, field or matrix blanks will not be subtracted from the sample concentrations in any case, but will be reported. If spike recovery is too low or high, analytical procedures will be modified.

D2. Verification and Validation Methods

Dr. Batterman will review all generated data associated with the project and ensure that appropriate systems and procedures were used. Verification of systems and procedures would be conducted through the use of spikes and performance standards, for example, which would cumulatively be used to validate the generated data.

D3. Reconciliation with User Requirements

The project objectives were designed to provide sufficient analysis of uncertainty such that a reasonable conclusion could be reached based on, but not limited by, current knowledge in the air quality field. Limitations on the use of and extent of explanation will be made clear in the interpretation of the project results.

References

Alcock, R.E., A.J. Sweetman, K. Prevedouros, and K.C. Jones. 2003. Understanding levels and trends of BDE-47 in the UK and North America: an assessment of principal reservoirs and source inputs. *Environ. Inter.*, 29: 691-698.

- Batterman, S., G. Hatzivasilis, and C. Jia. 2005. Concentrations and emissions of gasoline and other vapors from residential vehicle garages. *Atmospheric Environment*, in press.
- Batterman, S., C. Godwin, A. Franzblau, C. Jia, and S. Ellendula. 2003. VOC exposures among teachers and students in schools and at home. Presented at: ISEA, 13th Conference: September 21-25.
- Batterman, S., T. Metts, and P. Kalliokoski. 2002b. Diffusive uptake in passive and active adsorbent sampling using thermal desorption tubes. *Journal of Environmental Monitoring*, 4 (6): 870-878.
- Batterman, S., T. Metts, P. Kalliokoski, and E. Barnett. 2002a. Low-flow active and passive sampling of VOCs using thermal desorption tubes: Theory and application at an offset printing facility. *Journal of Environmental Monitoring*, 4 (3): 361-370.
- Butt, C.M., M.L. Diamond, J. Truong, M.G. Ikonou, and A.F.H. ter Schure. 2004. Spatial distribution of polybrominated diphenyl ethers in southern Ontario as measured in indoor and outdoor window organic films. *Environmental Science and Technology*, 38: 724-731.
- Dodder, N.G., B. Strandberg, and R. Hites. 2002. Concentrations and spatial variations of polybrominated diphenyl ethers and several organochlorine compounds in fishes from the Northeastern United States. *Environmental Science and Technology*, 36: 146-151.
- Environmental Protection Agency (EPA). 2004. Brominated diphenyl ethers in water, soil, sediment, and tissue by HRGC/HRMS. Retrieved February 07, 2006, from <http://www.arb.ca.gov/aaqm/qmosopas/dioxins/methods/1614-draft.pdf>
- Fabrellas, B., D. Larrazabal, M.A. Martinz, E. Eljarrat, and D. Barcelo. 2004. Presence of polybrominated diphenyl ethers in Spanish sewage sludges: Important contribution of decaBDE. *Organohalogen Comp.*, 66: 3755-376.
- Hale, R.C., M. Alae, J.B. Manchester-Neesvig, H.M. Stapleton, and M.G. Ikonou. 2003. Polybrominated diphenyl ether flame retardants in the North American environment. *Environ Int.*, 29: 771-779.
- Hale, R.C., M.J. La Guardia, E. Harvey, and T.M. Mainor. 2002. The potential role of fire retardant-treated polyurethane foam as a source of brominated diphenyl ethers to the US environment. *Chemosphere*, 46: 729-735.
- Hale, R.C., M.J. La Guardia, E.P. Harvey, T.M. Mainor, W.H. Duff, and M.O. Gaylor. 2001. Polybrominated diphenyl ether flame retardants in Virginia Freshwater Fishes (USA). *Environmental Science and Technology*, 35: 4585-4591.
- Hites, R.A. 2004. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environmental Science and Technology*, 38:945-956.
- Jaward, F.M., N.J. Farrar, T. Harner, A.J. Sweetman, and K.C. Jones. 2004. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environmental Science and Technology*, 38: 34-41.
- Jones-Otazo, H., J. Clarke, M. Diamond, J. Archbold, G. Ferguson, T. Harner, G. Richardson, J. Ryan, and B. Wilford. 2005. Is House dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure of PBDEs. *Environ Sci Technol.*, 39: 5121-5130.
- Knoth, W., W. Mann, R. Meyer, and J. Nebhuth. 2004. Occurrence and fate of PBDE in sewage sludge from municipal waste water treatment plants. *Organohalogen Comp.*, 66: 3749-3754.

Peng, C.Y., and S. Batterman. 2000. Performance evaluation of a sorbent tube sampling method using short path thermal desorption for volatile organic compounds. *Journal of Environmental Monitoring*, 2 (4): 313-324.

Rice, C.P., S.M. Chernyak, L. Begnoche, R. Quintal, and J. Hickey. 2002. Comparison of PBDE composition and concentration in fish collected from the Detroit River, MI and Des Plaines River, IL. *Chemosphere*, 49: 731-737.

Stapleton, H., M. Schantz, and S. Wise. 2004. Polybrominated diphenyl ether measurements in household dust. In: Alae, M. et al (eds). Proceedings of the third international workshop on brominated flame retardants. University of Toronto, Ontario, Canada. Pp 49-52.

Sjodin, A., D.G. Jr. Patterson, and A. Bergman. 2001. Brominated flame retardants in serum from U.S. blood donors. *Environmental Science Technology*, 35: 3830-3833.

Wilford, B.H., T. Harner, J. Zhu, M. Shoeib, and K.C. Jones. 2004. Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: Implications for sources and exposure. *Environmental Science and Technology*, 38: 5312-5318.