ATC1: Techniques for Monitoring FRs in the Environment
Approaches and techniques for sampling indoor air and dust

Pim Leonards

Outline

• Background
• Air sampling methods
• Dust sampling methods
• Protocols
Indoor air pollution

Chemicals released from modern building & furnishing materials

Outdoor air pollutants

Mold & Bacteria

Chemicals from cleaning products

Combustion gases from fireplaces & woodburning stoves

Animal Hair & Dander

Carbon Monoxide fumes from attached garage

Chemical fumes from paints & solvents

Gases including radon seeping through foundation

Cigarette smoke contains some 4000 chemicals
Sources of indoor air pollution

Flame retardants
- Furniture
- Electronics
- Household products
- Plastics
- Carpets
- Ventilation systems
- Print shops
- Offices
BFRs ARE EVERYWHERE

Home and Office
Televisions
Cell phones
Fax machines
Audio and video equipment
Computers
Printers
Scanners
Photocopiers
Remote controls
Lamp sockets
Hairdryers
Fans
Upholstered sofas
Upholstered chairs
Polyurethane foam
Building materials (walls, cellars, roofs)

Transportation (car, train, airplane)
Instrument panel
Battery case and tray
Electrical connectors
Engine control
Computer system
Stereo
GPS system
Upholstery
Sun visor
Head rest
Insulation

INFLAME
How to sample air for flame retardants?
Air sampling techniques

• High volume air sampling
  – Particulate filter and vapour phase sorbent

• Low volume air sampling
  – Particulate filter and vapour phase sorbent

• Personal sampler
  – only one study for FRs, Allen et al., 2007

• Passive samplers
Active high volume air sampler

**Advantage**
- Large amount of air
- Air flow controlled
- Exact volume of air

**Disadvantage**
- Noise
- Large equipment
High volume sampler Univ. Birmingham

Graseby–Andersen sampler fitted with aTSP inlet modified to hold a glass-fiber filter (1μm, Whatman) and a pre-cleaned PUF plug (827 cm³ volume)

Mohamed Abdallah, Univ. of Birmingham
Low volume air sampling

Advantage
• Large amount of air but more time consuming than with high volume sampler
• Air flow controlled
• Exact volume of air

Disadvantage
• Some noise
• Equipment

Capex L2X pump operated at a flow rate of 6 L min⁻¹. Particulate phase collected on 47 mm filter (1 μm, Whatman). Two PUF plugs (4 cm d x 8 cm L) housed by a glass holder were used as a gas phase sorbent.

Mohamed Abdallah, Univ. of Birmingham
Indoor air sampling—low volume personal sampling pump

Filter  PUFs

1 cm
Indoor air sampling – 24 hrs

Ventilation sampling

INFLAME

itm. Department of Applied Environmental Science
Personal sampler

• Fitted with rechargeable battery operated pump
• Very light in weight
• Provision to attach a cyclone to monitor respirable dust
• Measure the breathable air and dust
Personal sampling vs. high volume sampling


• Fixed point sampling vs personal exposure monitor:
• Fixed samplers in bedroom and main living room
• Equipment used for both area and personal sampling were identical
• Both fitted with particulate filter and vapour phase sorbent
• Lower brominated BDEs 17 and 28 not significantly different between personal and area monitors
• Highly brominated congeners (47, 99, 100, 153, 154, 209) significantly higher by personal monitors
• Higher molecular weight compounds phase-dust associated probably due to “personal cloud” effect
Why passive air sampling?

- Easy to handle
- Cost effective
- Unobtrusiveness
- Noise-free
- Do not require electricity
- Time weighted average (TWA) concentrations
- Appropriate for exposure assessment of POPs
Drawbacks

- Relatively low sampling rates necessitating long sampling times
- PUF disk-based samplers effectively sample only the vapor phase
- PUF in combination with glass fiber filter for vapor phase and particulates
- To obtain quantitative data, the specific passive uptake rate for each contaminant should be determined and the sampling duration must remain within the linear stage of uptake

Mohamed Abdallah, Univ. of Birmingham
PUF disk samplers and flame retardants

- Applied successfully for monitoring concentrations of PBDEs and PCBs in indoor air\(^a\)
- Vapor : particle partitioning\(^b\)

Passive air sampling equipment vapour phase only

Mohamed Abdallah, Univ. of Birmingham
PUF Disk passive sampler uptake rates

\[ V_{eq} = \frac{M}{C_A} = k_A \ A_{PUF} \ \Delta t \]

- \( V_{eq} \) = equivalent air volumes sampled (cm\(^3\))
- \( M \) = mass of compound sequestered by the PUF disk (pg)
- \( C_A \) = concentration of the target analyte sampled (pg cm\(^{-3}\))
- \( k_A \) = air side mass transfer velocity (cm sec\(^{-1}\))
- \( A_{PUF} \) = exposed surface area of the PUF disk (cm\(^2\))
- \( \Delta t \) = sampling period (sec)

Mohamed Abdallah, Univ. of Birmingham
Comparison of ΣHBCDs Concentrations (pg m$^3$) Derived Using passive Samplers with those Derived via Active Samplers

<table>
<thead>
<tr>
<th>Location</th>
<th>Active sampler</th>
<th>Full-sheltered</th>
<th>Part-sheltered</th>
<th>Full-sheltered +filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Office 1</td>
<td>239</td>
<td>171</td>
<td>182</td>
<td>219</td>
</tr>
<tr>
<td>Office 2</td>
<td>283</td>
<td>199</td>
<td>217</td>
<td>269</td>
</tr>
<tr>
<td>Office 3</td>
<td>377</td>
<td>299</td>
<td>286</td>
<td>391</td>
</tr>
<tr>
<td>House 1</td>
<td>290</td>
<td>206</td>
<td>214</td>
<td>279</td>
</tr>
<tr>
<td>Pub 1</td>
<td>880</td>
<td>689</td>
<td>723</td>
<td>n.m.</td>
</tr>
<tr>
<td>Pub 2</td>
<td>924</td>
<td>771</td>
<td>759</td>
<td>n.m.</td>
</tr>
</tbody>
</table>

Abdallah MA, Harrad S. 2010. EST, 44, 3059-65
Passive air sampling vapour phase and particulates

PUF disk

Glass fiber filter (GFF), 1\(\mu\)m, 12.5 cm diameter

Filter holder

Fully sheltered + filter

Abdallah MA, Harrad S. 2010. EST, 44, 3059-65
What is particulate matter and house dust?
Particles

• Almost any shape or size
• Solid particles or liquid droplets
• Two major groups:
  – PM10 (“bigger particles): 2.5 – 10 μM
  – PM2.5 (smaller particles): <2.5 μM
Which particles do you think travel farther?

PM\textsubscript{10} (big) \textbf{OR} \ PM\textsubscript{2.5} (small)

How far do you think PM\textsubscript{10} particles can travel?

30 m \hspace{1cm} 40 km \hspace{1cm} 800 km

How far do you think PM\textsubscript{2.5} particles can travel?

30 m \hspace{1cm} 40 km \hspace{1cm} 800 km
<table>
<thead>
<tr>
<th>Where particulate matter comes from ...</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>What they are</strong></td>
</tr>
<tr>
<td>Coarse Particles (PM$_{10}$)</td>
</tr>
<tr>
<td>smoke, dirt and dust from factories, farming, and roads</td>
</tr>
<tr>
<td>• mold, spores, and pollen</td>
</tr>
<tr>
<td>Fine Particles (PM$_{2.5}$)</td>
</tr>
<tr>
<td>• toxic organic compounds</td>
</tr>
<tr>
<td>• heavy metals</td>
</tr>
<tr>
<td><strong>How they’re made</strong></td>
</tr>
<tr>
<td>Coarse Particles (PM$_{10}$)</td>
</tr>
<tr>
<td>crushing and grinding rocks and soil</td>
</tr>
<tr>
<td>then blown by wind</td>
</tr>
<tr>
<td>Fine Particles (PM$_{2.5}$)</td>
</tr>
<tr>
<td>• driving automobiles</td>
</tr>
<tr>
<td>• burning plants (brush fires and forest fires or yard waste)</td>
</tr>
<tr>
<td>• smelting (purifying) and processing metals</td>
</tr>
</tbody>
</table>
House dust

Small amounts
- Plant pollen
- Human and animal hairs
- Textile fibers
- Paper fibres
- Minerals from outdoor soil
- Human skin cells
- Many other materials
Particle distribution in house dust

- Dust particles range from 0.8-796 μm
- Household dust peaked at 20 μm, 40 μm and 200 μm
- Household dust 46% of particles were <90 μm and only 0.79% were

<table>
<thead>
<tr>
<th>Particle Size (micron)</th>
<th>ISO Fine Dust Volume (%)</th>
<th>ISO Fine Dust Volume Less Than (%)</th>
<th>Household Dust Volume (% n=12)</th>
<th>Household Dust Volume Less Than (%) n=12</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1.26</td>
<td>0.12</td>
<td>0.00</td>
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</tr>
<tr>
<td>0.4</td>
<td>4.00</td>
<td>1.38</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>0.8</td>
<td>2.07</td>
<td>5.38</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>1.0</td>
<td>9.93</td>
<td>7.45</td>
<td>0.74</td>
<td>0.05</td>
</tr>
<tr>
<td>2.0</td>
<td>19.61</td>
<td>17.38</td>
<td>1.75</td>
<td>0.79</td>
</tr>
<tr>
<td>4.5</td>
<td>16.33</td>
<td>36.99</td>
<td>2.72</td>
<td>2.54</td>
</tr>
<tr>
<td>8.9</td>
<td>10.95</td>
<td>53.32</td>
<td>5.14</td>
<td>5.25</td>
</tr>
<tr>
<td>15.9</td>
<td>4.43</td>
<td>64.27</td>
<td>3.41</td>
<td>10.39</td>
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<tr>
<td>20.0</td>
<td>15.86</td>
<td>68.7</td>
<td>14.42</td>
<td>13.79</td>
</tr>
<tr>
<td>39.9</td>
<td>14.81</td>
<td>84.56</td>
<td>18.07</td>
<td>28.21</td>
</tr>
<tr>
<td>89.3</td>
<td>0.63</td>
<td>99.37</td>
<td>11.74</td>
<td>46.28</td>
</tr>
<tr>
<td>158.9</td>
<td>0.00</td>
<td>100</td>
<td>5.11</td>
<td>58.02</td>
</tr>
<tr>
<td>200.0</td>
<td>0.00</td>
<td>100</td>
<td>16.25</td>
<td>63.13</td>
</tr>
<tr>
<td>399.1</td>
<td>0.00</td>
<td>100</td>
<td>12.93</td>
<td>79.38</td>
</tr>
<tr>
<td>796.2</td>
<td>0.00</td>
<td>100</td>
<td>6.27</td>
<td>92.31</td>
</tr>
<tr>
<td>1415.9</td>
<td>0.00</td>
<td>100</td>
<td>0.00</td>
<td>98.59</td>
</tr>
</tbody>
</table>

Southey et al., 2011
Count distribution in house dust

- Household dust 99.65% were <10.0 μm with 65% at 1.5 μm

Southey et al., 2011
Air borne particles after sweeping and vacuum cleaning

Clark et al., 1976, J. Hyg Comb. 77, 321
High volume air sampling for PM10

- Size selective inlet (requires correct flow)
- Collection of PM on filters
- Flow control (for correct size selection and known sampled volume)
Monitoring Instrument for AeRosols and Gases
Developed by ECN and Applikon Analytical

Air Pollution not only comprises gaseous components but also Particulate Matter (PM) in the form of tiny particles.

MARGA offers a unique approach in which PM, but also acidifying gasses are quantitatively sampled and separated by respectively a WRD (Wet Rotating Denuder) and SJAC (Steam Jet Aerosol Collector).

The collected samples are analyzed by integrated ion chromatographs.

A MARGA system is also available with two sample boxes, to determine size segregated composition or deposition velocities.
Condensation

Liquid pump to air pump

Steam generator

Demi water 25L

SJAC

PM2.5 cyclone

Outflow

Sample to injection loop

Air with aerosols
How to sample dust for flame retardant analysis?
Contaminants in dust

Screening chemicals in household dust

Dust sampling techniques

- Filter (low and high volume samplers)
- Vacuum cleaner
- Wipes (surface areas)
- Handwipes
Vacuum cleaner

Advantage

Solution: use forensic equipment outside vacuum cleaner or wipes

Disadvantage

• Source of FRs could be electronics and plastics from vacuum cleaner
• Small particles are not trapped with normal vacuum bags
Collection of dust outside vacuum cleaner

• Dust collection outside vacuum cleaner
• Replaceable filters – test multiple sites with a single collector
• Universal adaptor—fits most vacuum cleaner models
• Easy seal leak proof caps
• For allergens, molds, endotoxins, other biologics
• Cost effective
Dust sampling by ITM

Surfaces at least 1 m above the floor

itm. Department of Applied Environmental Science
Sample treatment of collected dust

- Sieving, different protocols are used:
  - <150 μm
  - <500 μm
  - 1 mm sieve
  - <2 mm German guideline VDI 4300-8 (VDI 2001)

Conclusion: method is not standardized!
Wipes

- Dust collecting by wiping surfaces
- Wipes are cleaned before use
- Sampling of a specific surface area
- More difficult to determine concentration of flame retardant per gram of dust: absolute amount per area is possible
- Screening tool for products (e.g. TVs, electronics)
Handwipes

Method of Watkins et al., EHP, 2011, 119 (9), 1247-1252

- Hand wipes 60 min after their last hand washing
- 3 × 3 inch sterile gauze pad in 3 mL isopropyl alcohol and then wiped the palm and back of the hand from wrist to fingertips
- Unit is amount per handwipe
- Blank wipe samples are important

Watkins et al., EHP, 2011, 119 (9), 1247-1252
Some factors affecting particle mass measurements

- Water absorption by the filter material
- Humidity on PM
- Loss of filter material
- Sampling, storage and transport (VOCs)
- Chemical reactions and gas absorption on the filter
- Balance drift....
Indoor air procedures
Steps included in protocols

1. Preparing sampling locations
2. Collecting of samples
3. Analysis
Steps includes in protocols (I)

1. Pre-sampling inspection
   - Conditions that may affect or interfere with the proposed testing: type of structure, floor layout, physical conditions, airflows
   - Potential sources of chemicals: product inventory

2. Preparation of buildings
   - Ventilation, heating, etc.
Steps includes in protocols (II)

3. Collection of samples
   - Sampling personnel familiar with protocol
   - Adequate number of locations
   - Period
     • schools and office buildings: during normally occupied periods to
       be representative of typical exposure
   - Duration of sampling
   - Flow rates, sampling area
   - Spatial variation
     • breathing zone, floor
   - Temporal variation
   - Sampling information

4. Analysis of samples
   - QA/QC

Hazrati and Harrad, EST, 40(24), 7584-7589
Information collected during sampling

• Building Inventory
  – Floor plan sketches
  – Sample locations
  – Chemical storage areas, garages, doorways, stairways, location of basement sumps, heating and air condition systems etc.
  – Airflow patterns
  – Outdoor plot sketches

• Product Inventory Form
  – Products (e.g. printers, computers, furniture)
1. In the plastic bag you will find: A twist tie and a sample 'sock' for dust collection. Please keep the bag closed until sampling and minimise touching the socks.

2. Use the 'sock' marked 'living room floor' (or ‘rug’; see below). Slide the opening of the 'sock' over the furniture attachment (small vacuum foot) of the vacuum cleaner.

3. Trap the 'sock' firmly into place. The 'sock' should always overlap onto the attachment.

4. Measure out a square of 1 m² in (or close to) the sitting area on carpeted floor. In case of bare smooth floor sample 4 m². Mark the corners of the measured square meter(s). Small pieces of furniture may be moved, but do not move large objects such as sofas, book cases etc.

5. Vacuum the square (1 m² in case of wall to wall carpet and 4 m² in case of bare smooth floors) evenly and thoroughly for exactly 2 minutes (or 4 minutes in case of smooth floor). The dust will collect inside the 'sock'. TURN THE FOOT UP AND THEN SWITCH OFF THE VACUUM CLEANER (to avoid dust falling out).

6. Carefully remove the 'sock'. Tie the top with the twist tie. Place the 'sock' into the plastic bag and close it tightly. Complete the information questionnaire, and return as advised.
Car sample collection Univ. of Birmingham

1. The package includes one nylon sock, 1 tie and 1 plastic sealable bag.

2. Place the nylon sock, over the tubing on the head of the vacuum cleaner.

3. Insert sock into tubing, making sure there is about 1cm of sock around the outside of the nozzle.

4. Vacuum for two minutes the seats (front and rear), parcel shelf and dashboard (the areas highlighted on the diagram).

5. Turn vacuum head up and switch off vacuum cleaner. Remove bag and seal with tie.

6. Place sock and questionnaire in plastic bag and seal.
Protocols

• New York department of Health Division of Environmental Health Assessment Center for Environmental Health indoor Air sampling & analysis guidance, February 1, 2005
• US EPA: Guidance for the sampling and analysis of lead in indoor residential dust for use in the integrated exposure uptake biokinetic (IEUBK) model OSWER 9285.7-81 DECEMBER 2008
• EN 12341,1998.: Air quality. Determination of the PM10 fraction of suspended particulate matter. Reference method and field test procedure to demonstrate reference equivalence of measurement methods
• Position of sampler and cartridge accordance to the international guideline EN ISO 16000-12., (2008)
Dust reference materials

NIST Standard Reference Material house dust
• SRM-2585: organic contaminants
• SRM 2583: elements
• SRM 2584: elements
Summary air and dust sampling

- Low volume, personal and passive samplers most suitable for flame retardant sampling indoors
- Separate vapour phase from particle bound FRs
- Sieving protocol for dust to be discussed with INFLAME consortium
Acknowledgements

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• Cynthia de Wit