ATC1: Techniques for Monitoring FRs in the Environment

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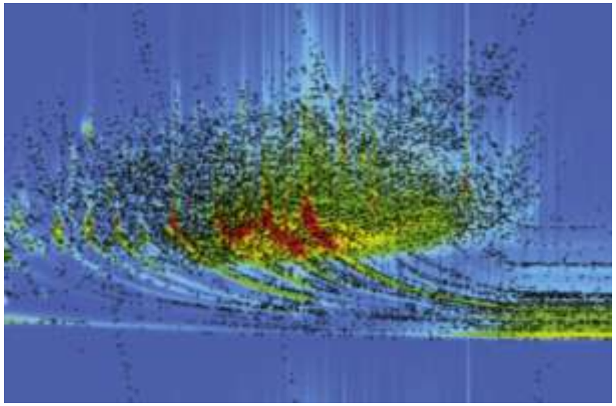
Approaches and techniques for sampling indoor air and dust

Pim Leonards



Hilton et al., 2010. J. Chrom A, 1217 (2010) 6851–6856

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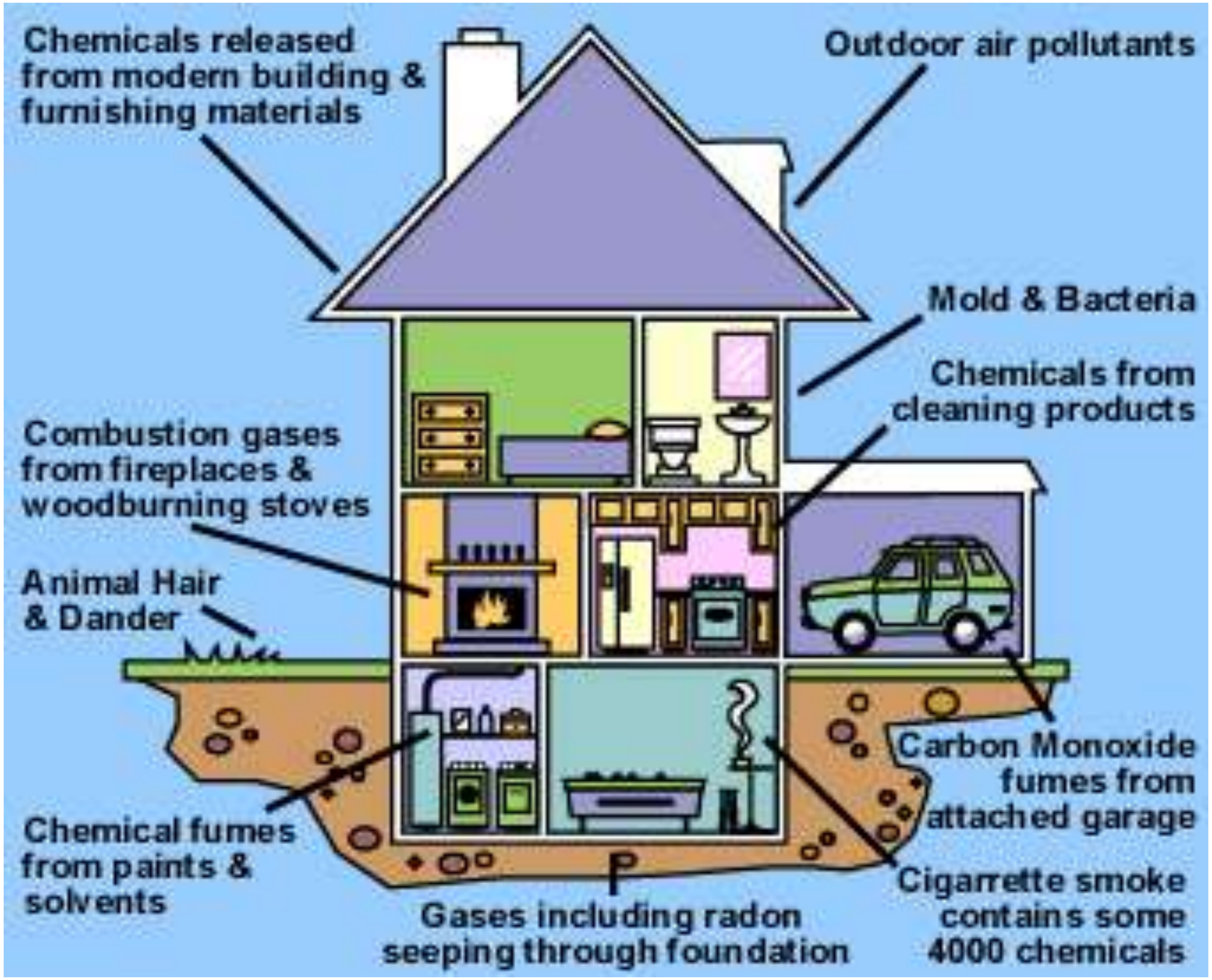
IVM Institute for Environmental Studies

Outline

- Background
- Air sampling methods
- Dust sampling methods
- Protocols

Indoor air pollution



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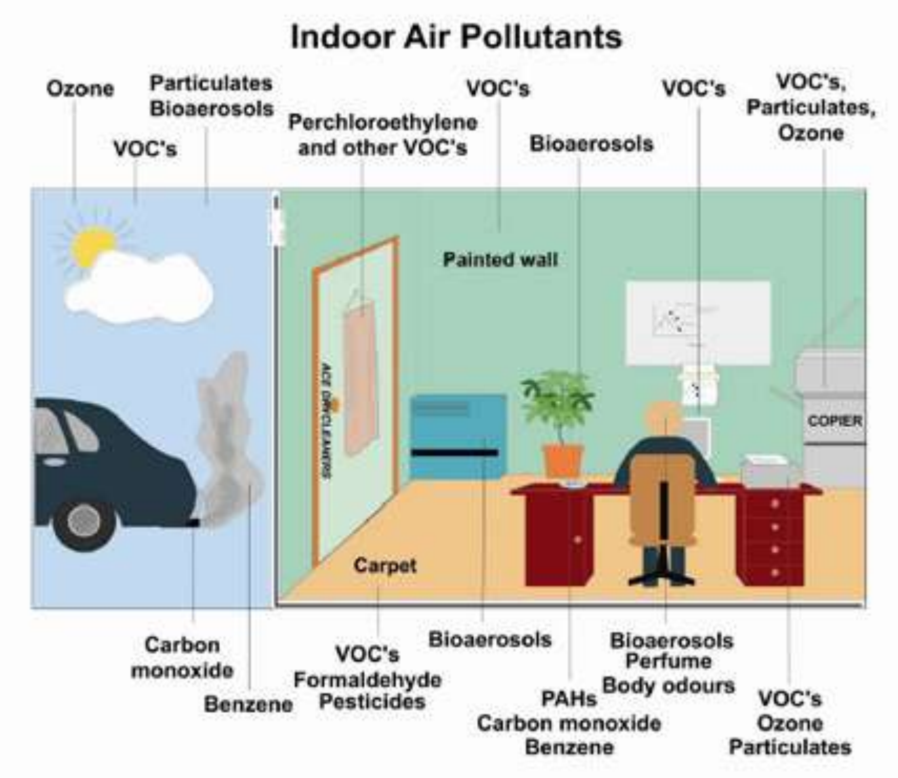
Sources of indoor air pollution

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)

Home and Office
Mattress
Curtains
Drapes
Carpet padding
Ovens and stoves
Stove hoods
Refrigerators
Dishwashers
Washing machines
Clothes dryer
Microwaves
Toasters
Coffee makers
Water heaters
Wires and cables
Circuit breakers
Electrical outlets

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

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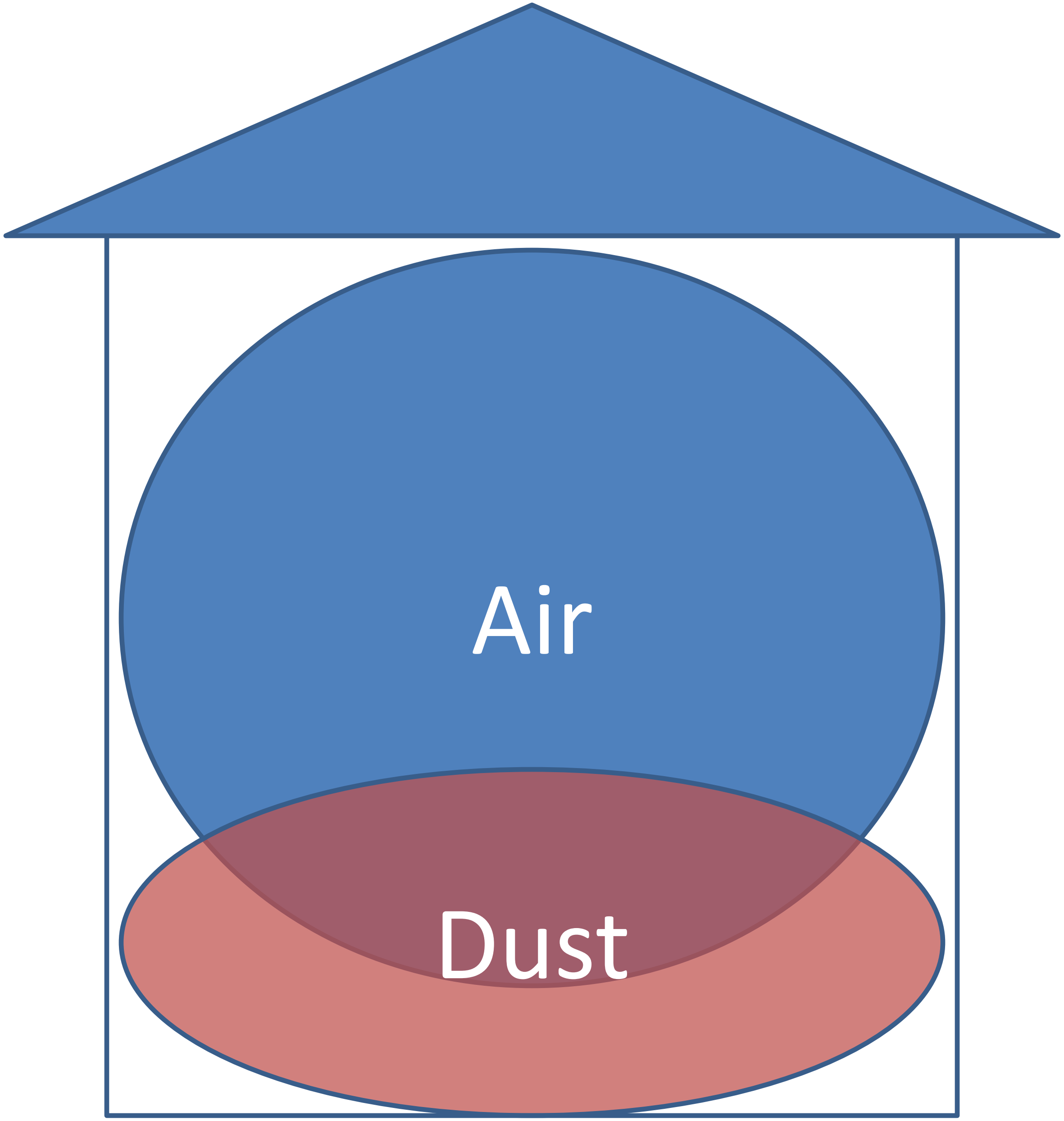
Air
Dust

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

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Active high volume air sampler

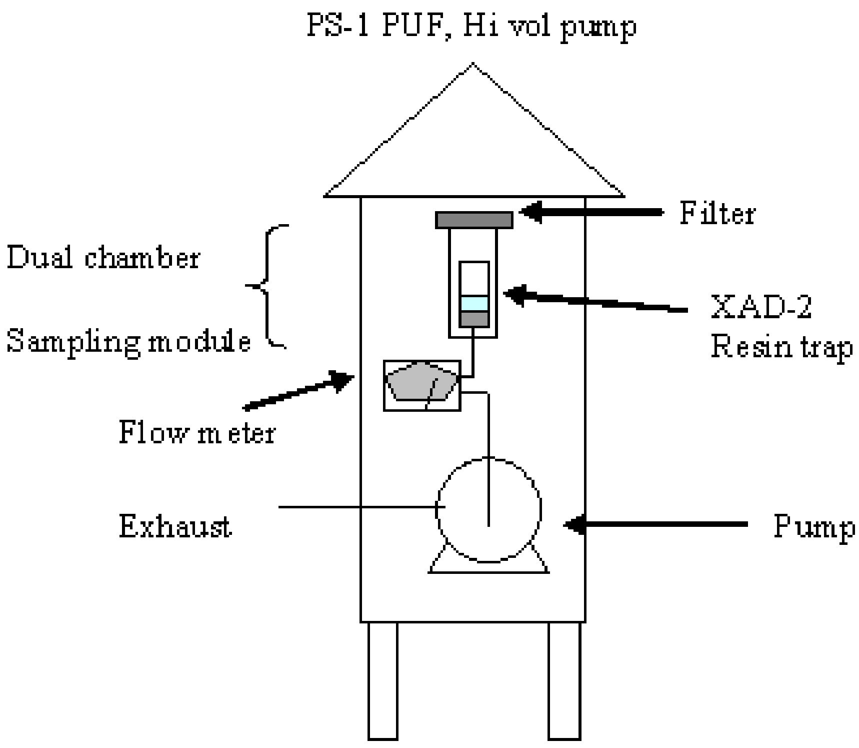
Advantage

•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 cm^3 volume)

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Low volume air sampling

Advantage

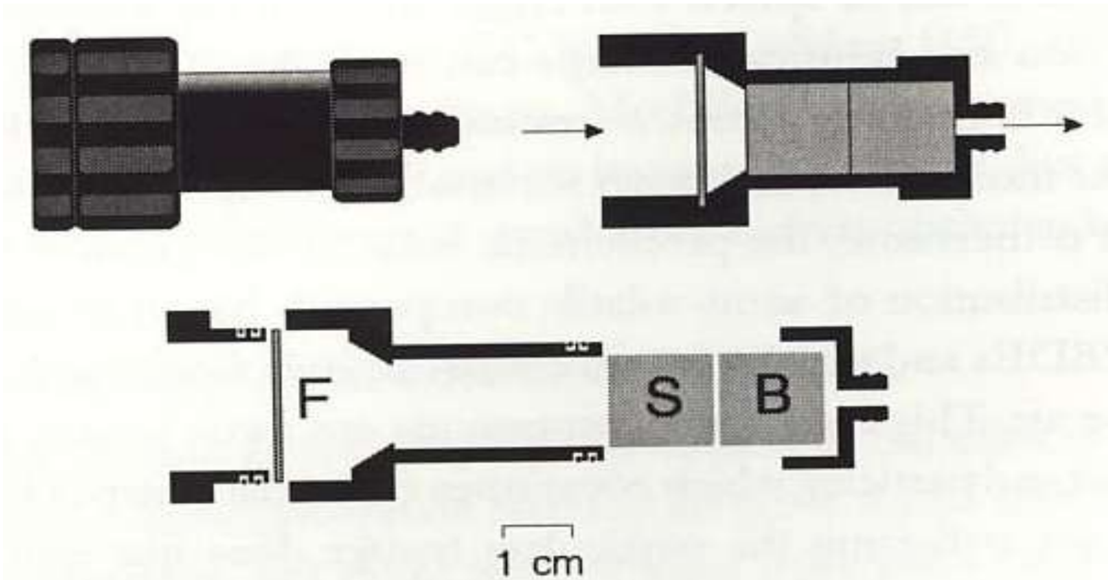
•Large amount of air but more time consuming than with high volume sampler
•Air flow controlled
•Exact volume of air

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.

Indoor air sampling– low volume personal sampling pump



Filter PUFs

Indoor air sampling – 24 hrs

Ventilation sampling

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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

Envirotech APM 800

Personal sampling vs. high volume sampling

Allen et al 2007. EST,2007, 41(13):4574–9

- 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

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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

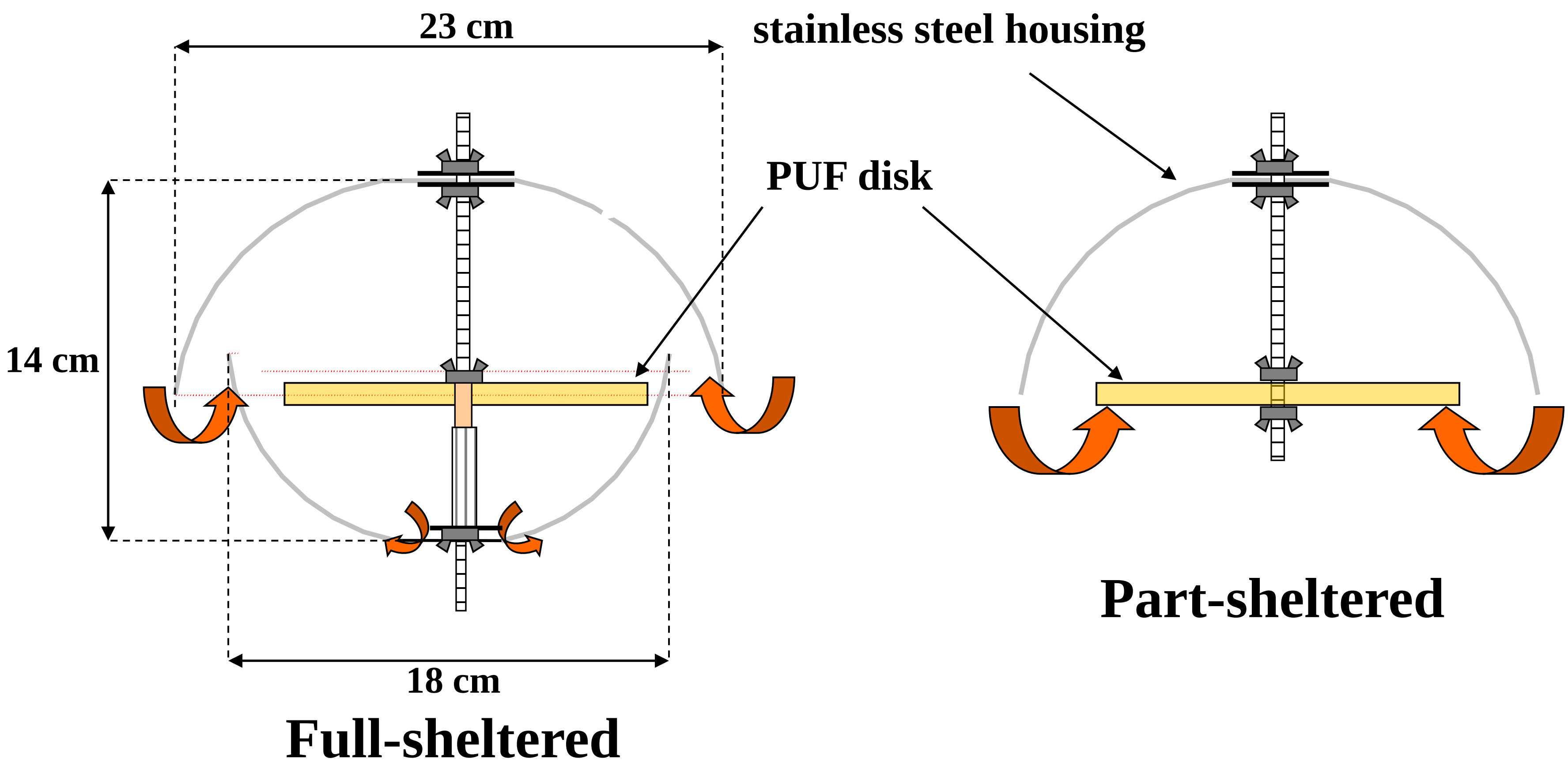
PUF disk samplers and flame retardants

- Applied successfully for monitoring concentrations of PBDEs and PCBs in indoor air[a]
- Vapor : particle partitioning[b]

[a] Harrad S. et al. *Environ. Sci. Technol.* 2006; 40: 4633.

[b] Hoh E. and Hites R. Environ. Sci. Technol .2005; 39:7794.

Passive air sampling equipment vapour phase only



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PUF Disk passive sampler uptake rates

$$\boxed{V_{eq} = \frac{M}{C_A} = k_A \, A_{PUF} \quad \Delta t}$$

- 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 (cm2)
- Δt = sampling period (sec)

Comparison of ΣHBCDs Concentrations (pg m^3)Derived Using passive Samplers with those Derived via Active Samplers

	Active sampler	Full-sheltered	Part-sheltered	Full-sheltered +filter
Office 1	239	171	182	219
Office 2	283	199	217	269
Office 3	377	299	286	391
House 1	290	206	214	279
Pub 1	880	689	723	n.m.
Pub 2	924	771	759	n.m

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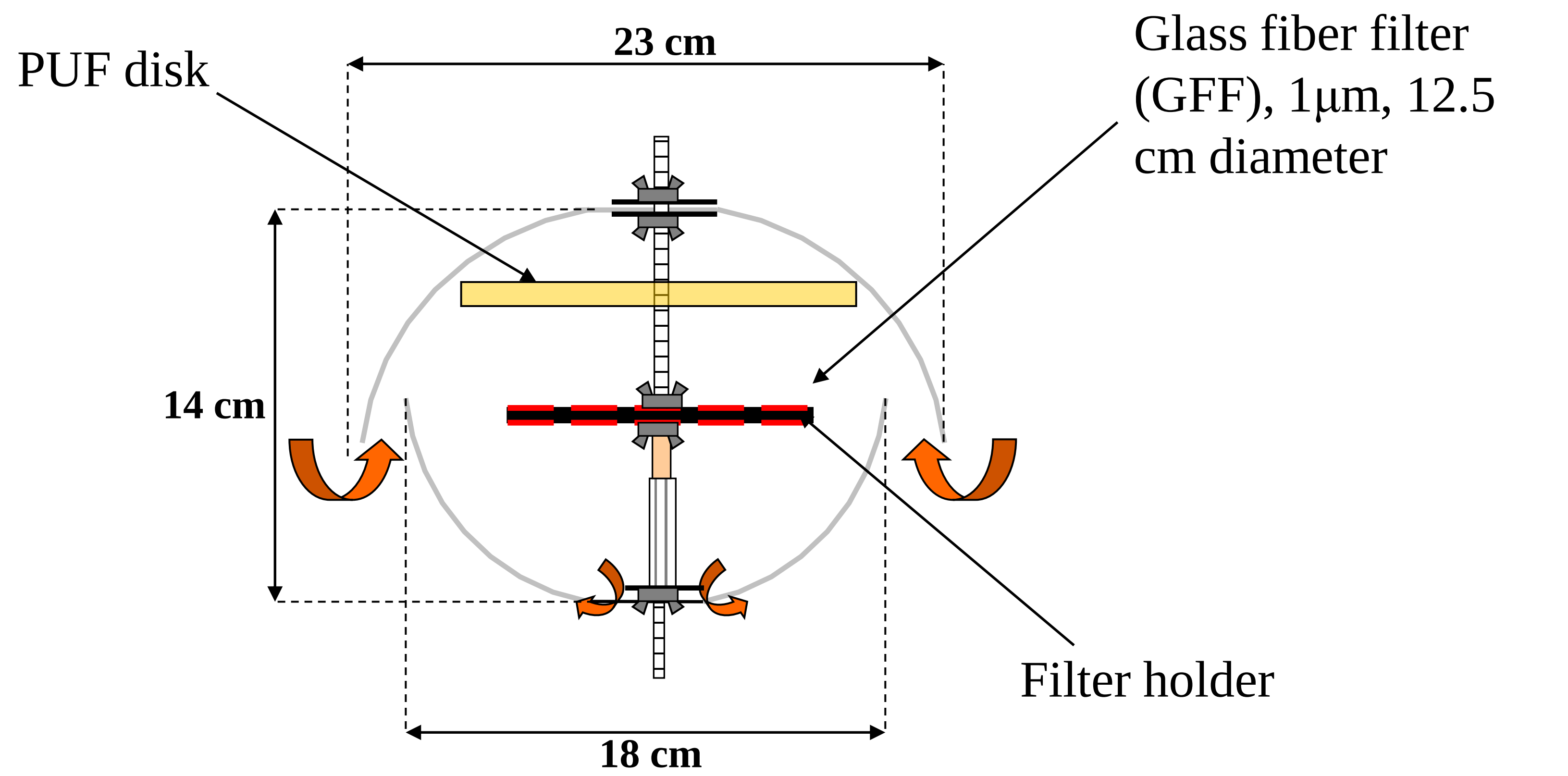
Abdallah MA, Harrad S. 2010. EST, 44, 3059-65

Passive air sampling vapour phase and particulates



Fully sheltered + filter

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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

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Which particles do you think travel farther?

PM_{10} (big) **OR** $PM_{2.5}$ (small)

How far do you think PM_{10} particles can travel?

30 m 40 km 800 km

How far do you think $PM_{2.5}$ particles can travel?

30 m 40 km 800 km

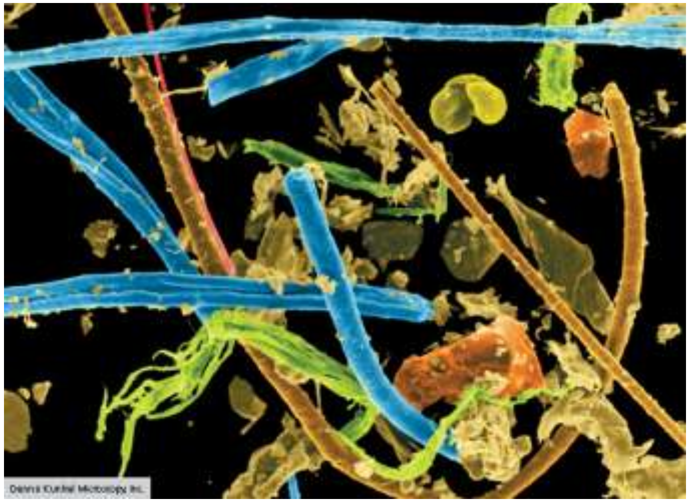
Where particulate matter comes from ...

	Coarse Particles (PM_{10})	Fine Particles ($PM_{2.5}$)
What they are	smoke, dirt and dust from factories, farming, and roads • mold, spores, and pollen	• toxic organic compounds • heavy metals
How they're made	crushing and grinding rocks and soil then blown by wind	• driving automobiles • burning plants (brush fires and forest fires or yard waste) • smelting (purifying) and processing metals

House dust

Small amounts

- Plant pollen
- Human and animal hairs
- Textile fibers
- Paper fibres
- Minerals from outdoor soil
- Human skin cells
- Many other materials



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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

Volume distribution

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

Southey et al., 2011

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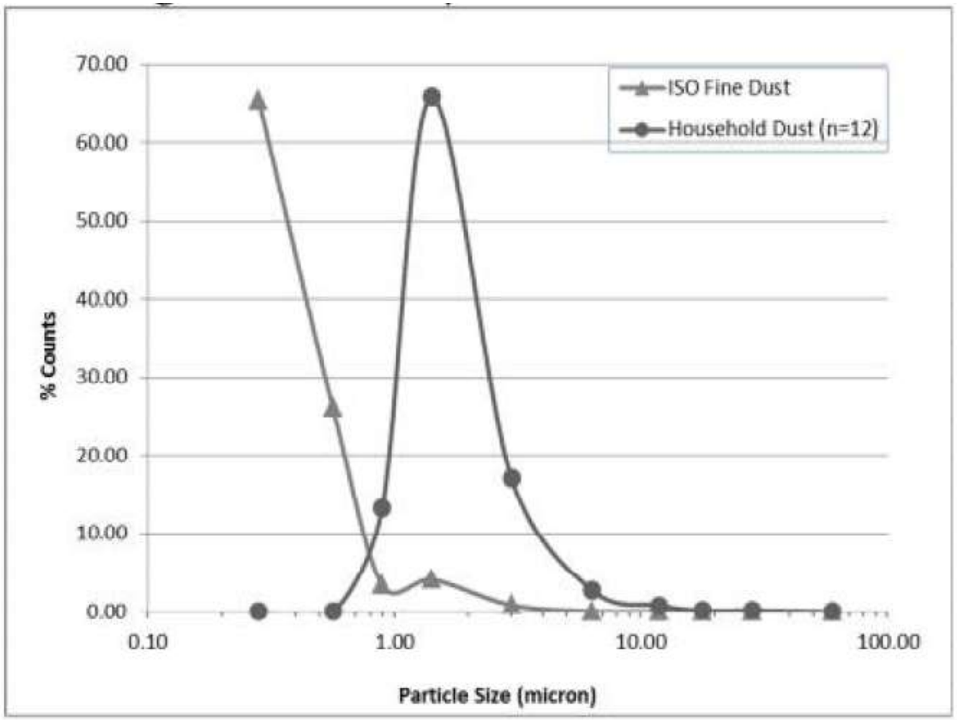
Count distribution in house dust

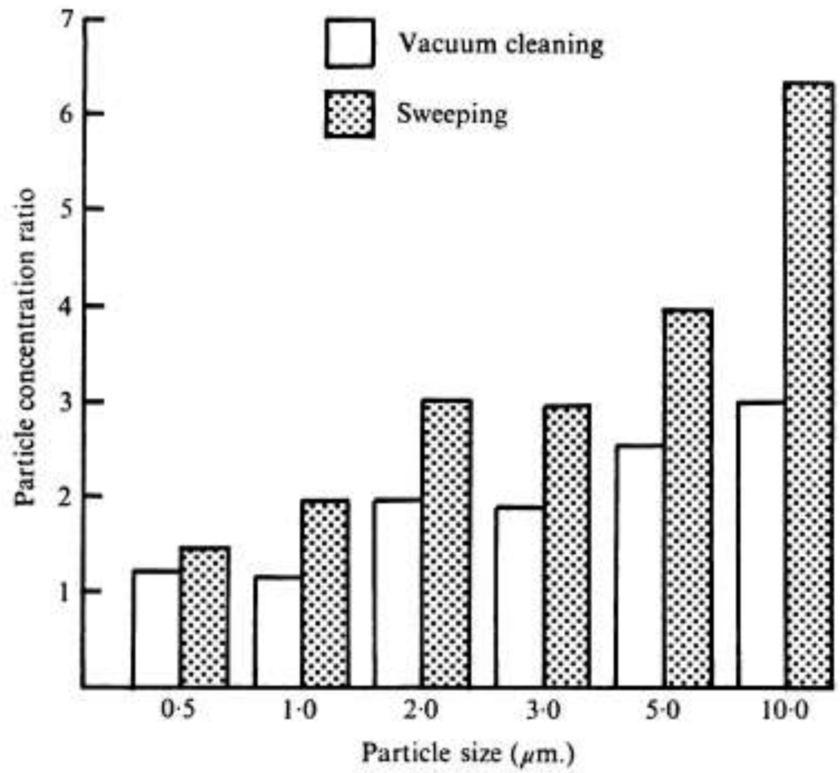
- Household dust 99.65% were <10.0 µm with 65% at 1.5 µm

Count distribution

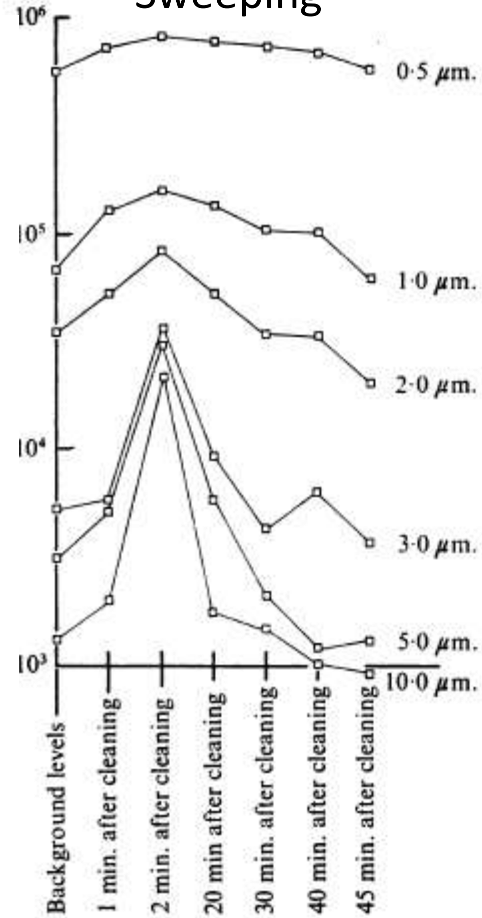


Southey et al., 2011

Air borne particles after sweeping and vacuum cleaning



Sweeping



Clark et al., 1976, J. Hyg Comb. 77, 321

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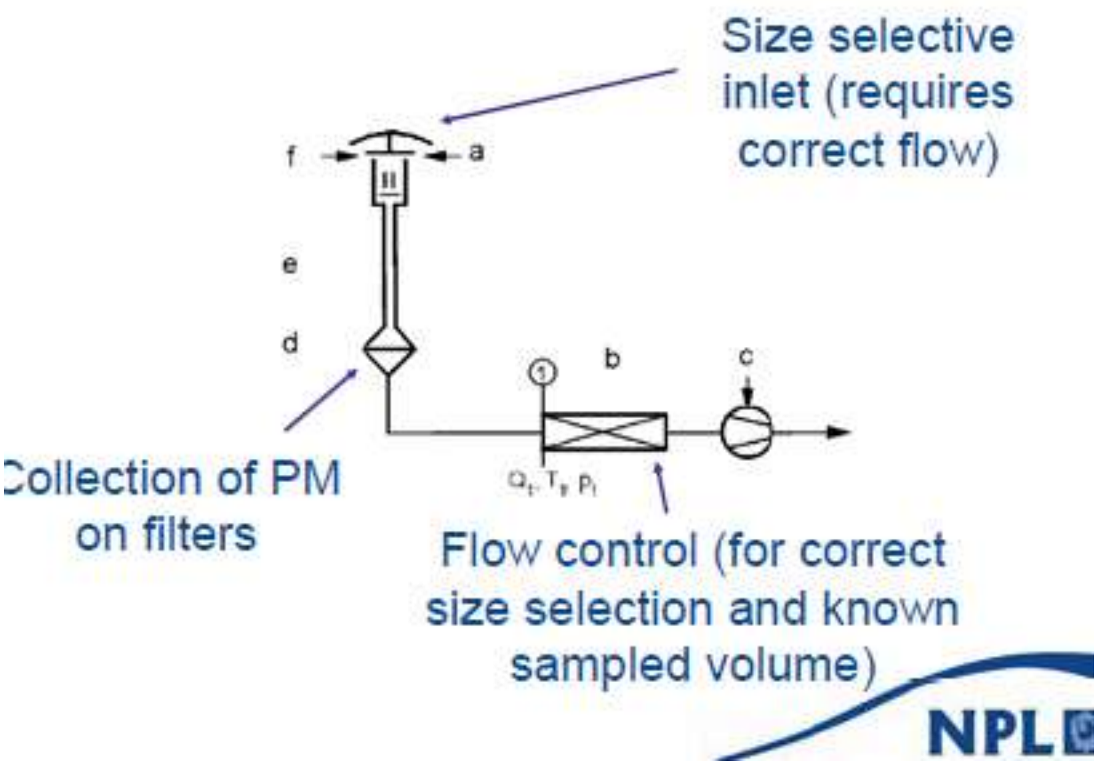
High volume air sampling for PM10



ECN MARGA

ECN

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.

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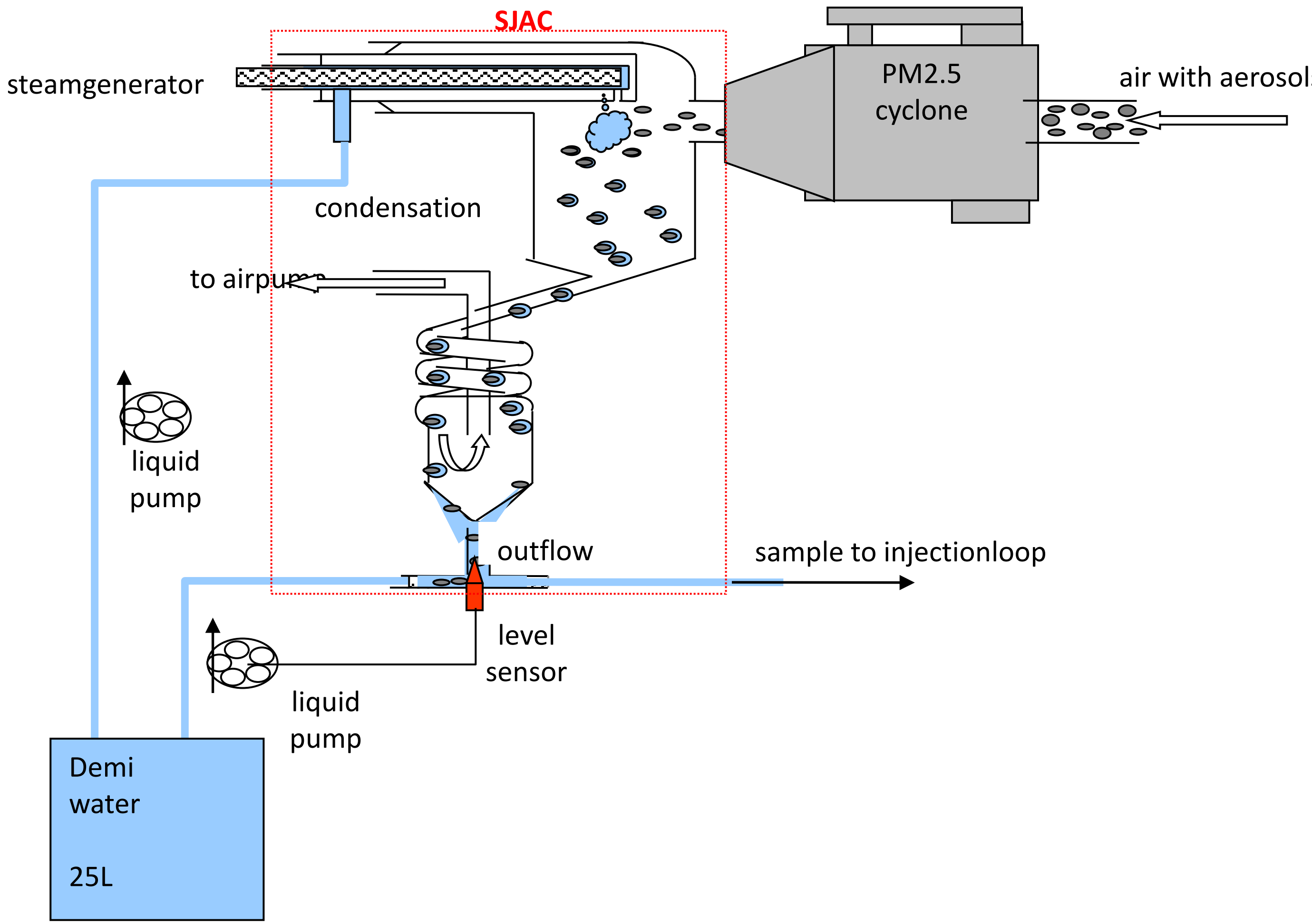
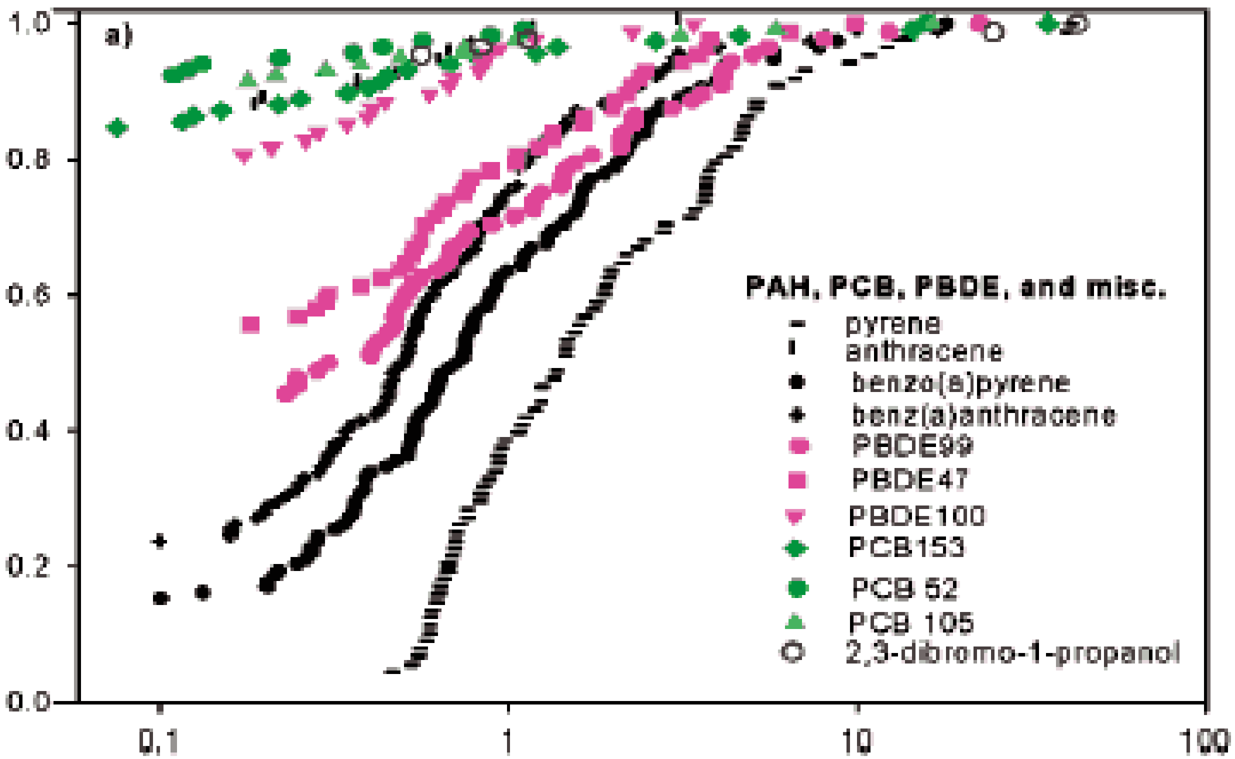

SJAC
steamgenerator
PM2.5
cyclone
air with aerosols
condensation
to airpump
liquid
pump
outflow
sample to injectionloop
level
sensor
liquid
pump
Demi
water
25L

How to sample dust for flame retardant analysis?

Contaminants in dust

Cumulative Frequency

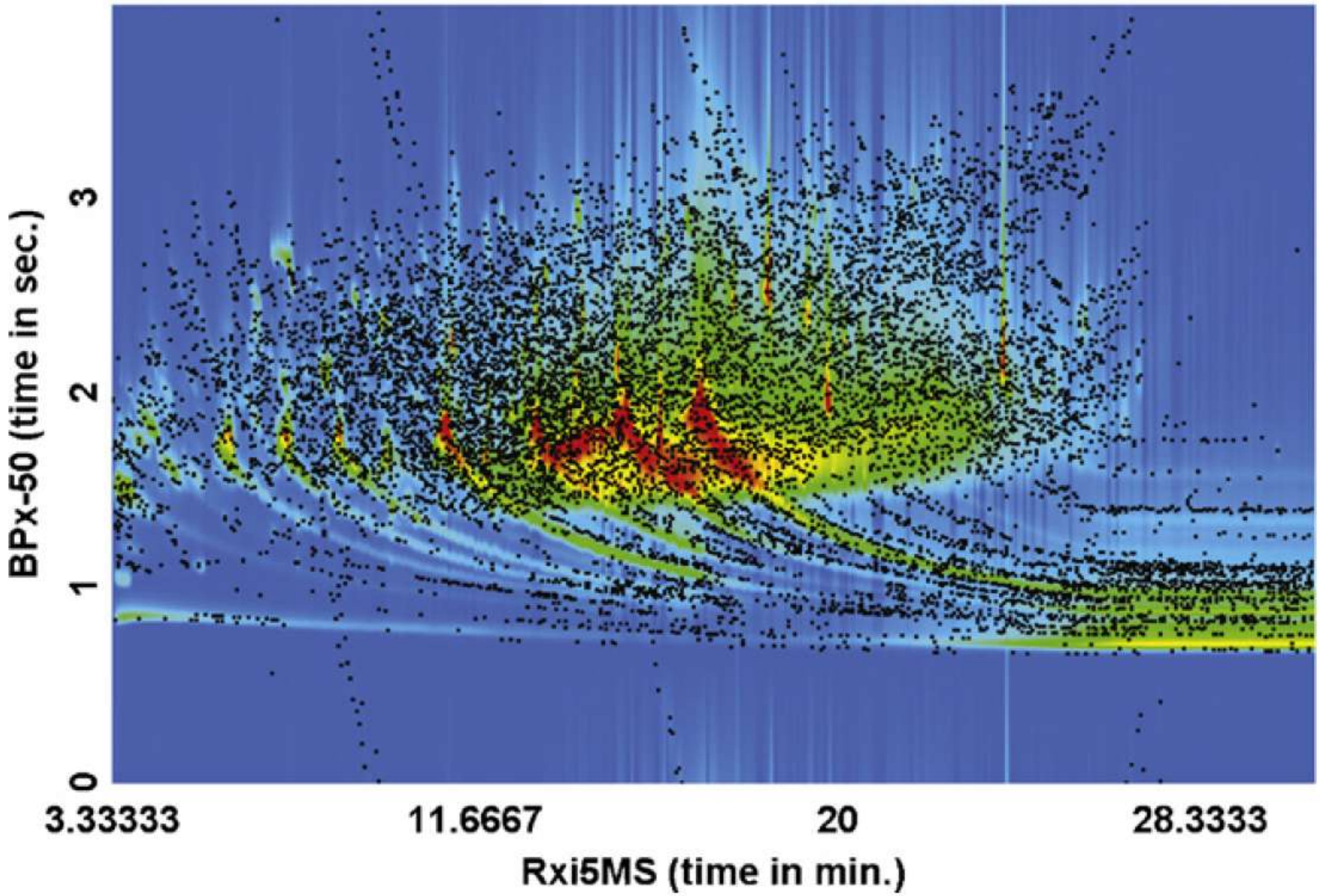


Concentration (µ g/g dust)

Rudel et al . EST, 2003.

Screening chemicals in household dust

GCxGC-ToFMS



Hilton et al., 2010. J. Chrom A, 1217 (2010) 6851–6856

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

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Collection of dust outside vacuum cleaner

DUSTREAM™ Collector

- 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

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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)

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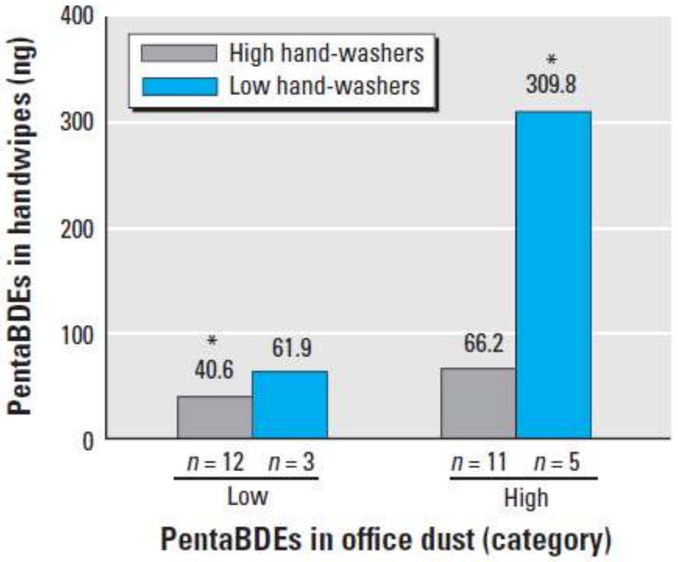
Handwipes

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

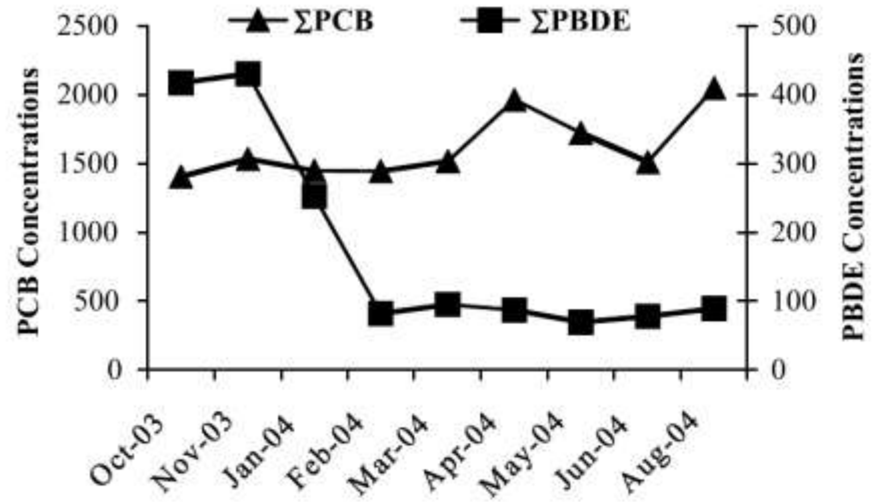
Steps includes in protocols (I)

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

Levels (pg/m^3) office



Hazrati and Harrad, EST, 40(24), 7584-7589

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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)

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Dust living room Univ. of Birmingham

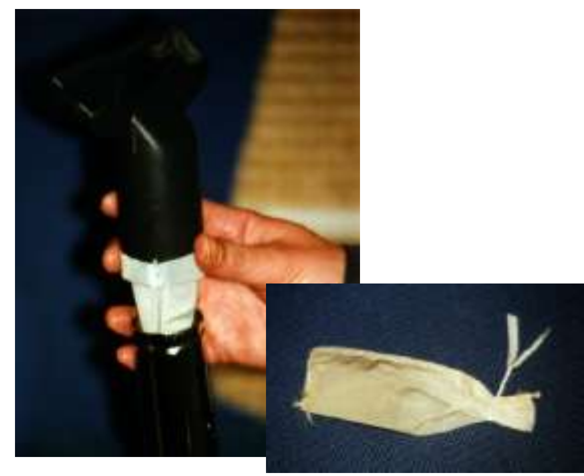
1.In the plastic bag you will find: A twist tie and a sample 'sock' for dust collection. <u>Please keep the bag closed until sampling and minimise touching the socks.</u>

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' <u>firmly</u> into place. The 'sock' should always overlap onto the attachment.

4.Measure out a square of **<u>1 m^2</u>** in (or close to) the **sitting area** on *carpeted floor*. In case of *bare smooth floor* sample **<u>4 m^2</u>**. 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 m^2** in case of **wall to wall carpet** and **<u>4 m^2</u>** 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).



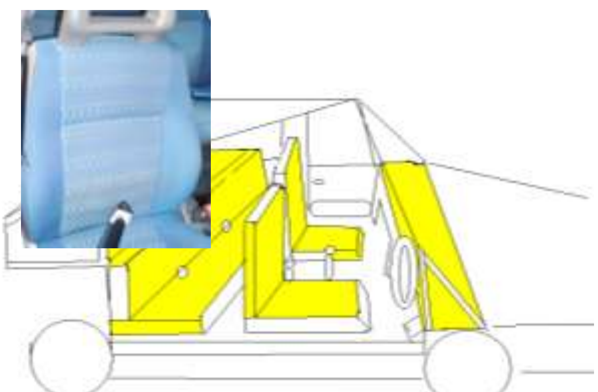
6.Carefully remove the 'sock'. Tie the top with the twist tie. Place the 'sock' into the plastic bag and close it tightly. Complete the information questionnaire, and return as advised.

Car sample collection Univ. of Birmingham

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

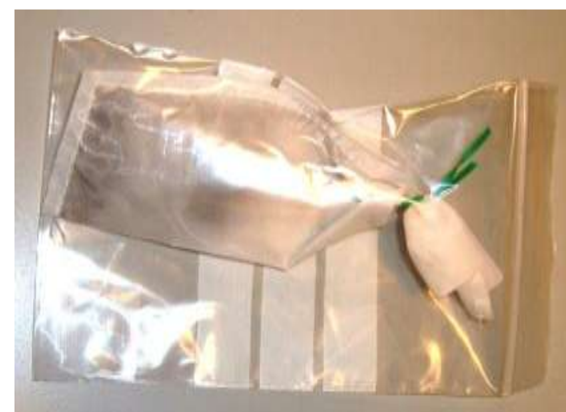
2. Place the nylon sock, over the tubing on the head of the vacuum cleaner.

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

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Acknowledgements

- Stuart Harrad
- Mohamed Abdallah
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