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Evaluation of settled floor dust for the presence of microbial metabolites and volatile anthropogenic chemicals in indoor environments by LC–MS/MS and GC–MS methods

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ABSTRACT

This study reports on detection of a large number of biological and anthropogenic pollutants using LC–MS/MS and GC–MS technologies in settled floor dust (SFD). The latter technique was applied to obtain a general picture on the presence of microbial as well as non-microbial volatile organic compounds, whereas the targeted LC–MS/MS analysis focused on identification of species specific secondary metabolites. In the absence of moisture monitoring data the relevance of finding of stachybotrylactam and other metabolites of tertiary colonizers are confined only to accidental direct exposure to SFD. To the best of our knowledge 30 of the 71 identified volatile organic compounds (VOCs) are newly reported in SFD matrix. Coordinated application of "AMDIS and Spectconnect" was found beneficial for the evaluation and identification of prime volatile pollutants in complex environmental samples. Principal component analysis (PCA) of peak areas of 18 microbial volatile organic compounds (MVOCs) resulted in identification of nonanal as potential MVOC marker. Two more volatiles toluene and 1-tetradecanol though had discriminative influence, are not regarded as MVOC markers, considering their probable alternate origin from paints and cosmetics, respectively.

1. Introduction

The advantages of various methods and matrices for the purpose of indoor evaluation are well documented in earlier reports [1–9]. The suitability of settled floor dust (SFD) for the above mentioned purpose can be best explained on the basis of mode of its formation. SFD is typically formed by the deposition of indoor aerosols, outdoor particles (due to ventilation) and also particles brought by foot trafficking. Moreover criticality and relevance of chosen SFD matrix for the mass spectrometric evaluation are also justified by the reports of Rosas et al. [1] for the detection of antibiotic multi resistance *E. coli* serotypes and reports of SFD surface adsorption of polycyclic aromatic hydrocarbons and other volatile and semi-volatile organic compounds [10,11]. Since the process of degradation indoors is typically slow, settled floor dust is also considered as a well preserved fossil evidence for indoor evaluation [12].

The new findings since reports of sick building syndrome (SBS), indoor pollutants are classified either as biogenic or anthropogenic pollutants. Biogenic pollutants include aerosols of viruses, bacteria, fungal spores and mycelial fragments containing toxic metabolites (e.g.: *Stachybotrys* containing Stachybotrylactam and Satra toxins), pollen, animal dander, dust mite residues and other particles of biological origin [13]. Anthropogenic pollutants are hazardous chemicals which arise as a consequence of their wide spread use in day to day consumer products (phthalate in PVC products). A variety of adverse health effects following human exposure to bioaerosols have been well documented [14]. Some of them are allergy, hypersensitivity, respiratory and toxicological problems, and infectious diseases [15]. Microbial role in indoor pollution and health implications are well known. For instance, fungi as well as bacteria (antigens, structural components, bioactives compounds as endotoxins) in humidifiers have been implicated in "humidifier fever", a disease with both toxic and allergic manifestations [16]. Bacteria in indoor air of houses or offices have also been reported to be associated with extrinsic allergic alveolitis among occupants [17].

Under non obvious moisture complications types and levels of fungal spores in the indoor samples are generally lower to those

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detected in the outdoor samples. Fungal flora of damp buildings comprises species addition to outdoor fungi that can utilize the nutrients present in building materials and adaptable to particular level of water activity. Based on water activity molds grown on building materials can be divided into primary, secondary and tertiary colonizers. Many of the toxigenic species *Stachybotrys*, *Chaetomium*, *Memnoniella*, *Aspergillus* and *Trichoderma* belong to the class of tertiary colonizers. Indoor isolates of *A. versicolor* from building materials are reported to produce sterigmatocystin, a class 2B carcinogen and biosynthetic precursor of aflatoxin B_1. Prevalence of airborne spores of *Stachybotrys chartarum* in houses with water incursion [18] and satratoxin G–albumin adducts (in vivo) upon human and animal exposures to *S. chartarum* [19] are some evidences for probable health threats due to mycotoxins in water damaged indoor environments. Animal exposure studies of low molecular weight compounds from fungi from the built environment have shown implications on health, such as inflammatory processes [20]. Microbial volatile organic compounds (MVOCs) are an addition to the list of biogenic indoor pollutants and have drawn attention as potential contributors for adverse health effects observed in residents of moisture damaged buildings [21]. In vitro studies of histamine release by bronchoalveolar cells exposed to MVOCs of *Trichoderma viride* [22], is a good example of the experimental evidences of MVOCs connections to clinical aspects.

Studies on house dust have shown for the presence of banned chemicals, and chemicals with endocrine disrupting, carcinogenic, neurotoxic potentials at levels that are considered to be of concern for human health [23,24]. Traditionally, consumption of food has been considered a primary route of exposure to contaminants mentioned above. However, it is becoming clear that exposure through ingestion and/or inhalation of indoor dust may be comparable to corresponding food consumption especially for younger children [24]. Independent studies monitoring for occupational exposure to volatile organic compounds (VOCs) toluene, o-xylene and n-butyl acetate and correlation of these substances to clinical symptoms upon long-term exposure such as deficits in concentration and memory, and an increase in the reaction time are proofs for ill effects of some of the VOCs in adults too [25,26].

State-of-the-art technology GC–MS may be useful for detecting hidden mold [27] and proved to be useful to differentiate between fungal strains [28]. Extremely low MVOC concentrations and the existence of many disturbing concomitants indoor complicate the analysis of microbial VOC in moldy houses leading to false positives [29]. Secondary metabolites being inconsistent in distribution throughout the fungal kingdom are unique as markers for speciation and chemotaxonomy purposes [30]. This was also reported true for fungal species found indoors [31,32]. Hence application of complementary technologies GC–MS and LC–MS/MS for evaluation of complex indoor matrix as SFD can be highly advantageous for comprehensive indoor evaluation and to monitor, e.g., ongoing remediation processes.

Enumeration studies based on microbial viability [1,2], detection of microbial volatiles [3–6] and non volatiles [7–9] in indoor matrices including settled dust are known. To our knowledge this is the first report of comparison of dust matrix from indoors used for different purposes using microbial volatiles and secondary metabolites. Dust samples from vastly differing indoor environments such as waste management and recycling units (WMU), houses with and without any water damage and mold infestation are screened for microbial effectors and subsidiary chemicals. Additionally, we wanted to test feasibility of source recognition/apportionment based on (M)VOC pattern among various indoor dust samples using principal component analysis (PCA) and hierarchical cluster analysis (HCA). Some of the methodological challenges in GC–MS such as sample volume, extraction time, and temperature for the optimal extraction of volatile substances in dust matrix are addressed. Appertain to data evaluation we demonstrated usability of AMDIS deconvoluted chromatograms in combination with Spectconnect [33] for additional verification of sampling and method performance. Practical relevance of the study can be best explained in relation to safety of toddlers in homes with crawling and hand to mouth behavior and workers of WMUs. The extraction temperature condition (max 90 °C) of our GC–MS method is similar considering the working temperature of common home appliances (e.g. surface of a electric bulb (110–160 °C)). This aforementioned fact makes volatile pattern generated under our experimental conditions realistic and comparable to real world scenario. This is the first comparative study of individual SFD samples derived from relatively differing indoor environments in their purposes using both LC–MS/MS and GC–MS methods.

2. Materials and methods

2.1. Study sites and sampling

2.1.1. Waste management facilities

Settled floor dust samples were collected using vacuum cleaner from different waste management units (WMU) in Germany dealing with municipal waste or paper recycling. Samples MWD 1–7 (Municipal waste dust, Group A) were collected from waste handling facilities treating municipal waste with "biological and mechanical" or "biological" methods. Samples PWD 1–8 (Paper waste dust, Group B) were from enclosures used for paper recycling activities such as sorting, storage, or mechanical pressing (Table 1).

2.2. Residential indoors

Settled floor dust samples were collected from houses inhabited by small group of people, generally less than 5. Samples AHD 1–5 (Affected house dust, Group D) were vacuum cleaner dust bag dust samples derived from single family houses located in Eastern and southern Finland. These houses had severe moisture damage/dampness problems that were confirmed by trained engineers upon building inspection. Residents of these buildings typically complained about building related symptoms. Samples CHD 1–2 (Control house dust, Group C) were samples, respectively, from United States of America (SRM 2583) and India (CHD-2). SRM 2583 is a certified reference material (CRM) for 5 elements viz., Arsenic, Cadmium, Chromium, Lead and Mercury. CHD-2 is a self collected house dust where no clinical symptoms of ill health or visible mold growth were observed or reported.

3. Methods for analysis of non volatile and volatile substances

Volatile organic compounds (microbial and anthropogenic) were evaluated using GC–MS technology. Non volatile microbial organic compounds were monitored using LC–MS/MS technology.

3.1. GC–MS screening for volatile and microbial volatile organic compounds

3.1.1. Analytical reagents and supplies

The alkane mixture C_5–C_{10} was mixed in-house. C_8–C_{20} and C_{21}–C_{40} straight chain alkanes of 40 mg L^{-1} concentration in hexane and toluene, respectively, were purchased from Fluka (Buchs, Switzerland). All pure GC–MS standards (substances in Table 2 and Supplementary Table 1 highlighted with "*") used in this study were purchased from Sigma–Aldrich, Vienna, Austria. To avoid artifact originating from GC-column bleeding, SPME fiber coating or from laboratory air, head space vials were left open for 24 h in laboratory

Table 1
Sample description. MW: municipal waste management units, PW: Paper waste recycling units, TA: treatment area, ST: storage, NA: not applicable.

Sample	Nature of sample	Sampling site	Mode of waste treatment at the sampling site	Ventilation of sampling site	Processing load/turn over of waste handling units (kilotons/year)
MWD-1	MW	TA	Biological and Mechanical	Mechanical	62
MWD-2	MW	TA	Biological and Mechanical	Mechanical	62
MWD-3	MW	TA	Biological and Mechanical	Mechanical	62
MWD-4	MW	TA	Biological and Mechanical	Mechanical	62
MWD-5	MW	TA	Biological and Mechanical	NA	62
MWD-6	MW	TA	Mechanical	Natural	400
MWD-7	MW	TA	Mechanical	Natural	200
PWD-1	PW	ST	Paper-Storage	Natural	7.3
PWD-2	PW	TA	Mechanical	Natural	100
PWD-3	PW	TA	Sorting-Mechanical & Manual	Natural	40
PWD-4	PW	TA	Sorting-Mechanical	Natural	20
PWD-5	PW	TA	Sorting-Mechanical	Natural	60
PWD-6	PW	TA	Sorting & Pressing-Mechanical	Natural	10
PWD-7	PW	TA	Sorting & Pressing-Mechanical	Natural	10
PWD-8	PW	TA	Sorting & Pressing-Mechanical	Natural	10

and subsequently analysed. Substances identified this way were excluded during final compilation of data.

3.1.2. GC–MS

Automated sample extraction, chromatographic separation and MS detection was done with an Agilent 6890 GC (Waldbronn, Germany) instrument, coupled to a 5975B MSD detector for recording the mass spectra. The following pair of GC–MS columns were used one at a time during the entire study:

(A) HP-5MS 30 m × 0.25 mm, 0.25 μm f.th. (Agilent, Waldbronn, Germany),
(B) Optima® Wax 30 m × 0.25 mm, 0.25 μm f.th. (Agilent, Waldbronn, Germany).

For both columns Helium (5.0, Messer, Austria, Gumpoldskirchen) was used as carrier gas at a constant flow rate of 1 mL/min. Oven program: HP-5MS: (apolar) 35 °C (hold 2 min), 5 °C/min to 230 °C, 40 °C/min to 260 °C (hold 5 min). Optima® Wax: 35 °C (hold 2 min), 5 °C/min to 250 °C (hold 10 min). The inlet was equipped with a headspace inlet glass liner, 1.5 mm i.d. (Supelco, Bellefonte, USA) and set to 250 °C in splitless mode during desorption (2 min) of analytes from the fiber. The transfer line to MS was at 270 °C. MSD parameters: electron impact ionisation (EI) at 70 eV, source temperature 230 °C, quadrupole temperature 150 °C, full scan mode, mass range 35–500 amu.

3.1.3. HS-SPME

Sampling was done by headspace volatiles extraction procedure fully automated by an auto sampler (MPS 2 XL, Gerstel, Mülheim a.d. Ruhr, Germany).

Fiber selection and extraction optimization were done on a 30 m HP-5MS column using real world settled dust ($n = 5$) and SRM 2583 (certified indoor reference dust) with an empirical sample amount of 0.05 g which was found to be well suited upon validation in due course of the study. The following SPME-fibers with different polarities were tested: polydimethylsiloxane (PDMS), 100 μm; polydimethylsiloxane/divinylbenzene (PDMS/DVB), 65 μm; carboxene/polydimethylsiloxane (CAR/PDMS), 85 μm; polyacrylate (PA), 85 μm and divinylbenzene/carboxene/polydimethylsiloxane (DVB/CAR/PDMS), 50/30 μm (Supelco, Bellefonte, USA). Selection of fiber was on the basis of number of conserved component upon extraction of representative sample of each group using above mentioned 5 fibers. All fibers tested and used were preconditioned according to the manufacturer's guidelines. Dust samples were weighed into 20 mL head space glass vials covered with Teflon capping and heated to 90 °C for 30′ to release dust bound volatiles. The conditioned fiber was then inserted 21 mm into the head space vial and incubated for 60′ unagitated at constant temperature of 90 °C for adsorption of volatiles. For desorption, the fiber was inserted for 2 min in the split less injector (250 °C, fiber penetration depth 57 mm).

The following SPME parameters were tested: equilibration time (0 and 30 min), extraction time (30 and 60 min), and equilibration and extraction temperature (30, 60 and 90 °C). For all subsequent experiments of parameter evaluation the best found SPME fiber CAR/PDMS, 85 μm was employed (fiber selection elaborated in Section 4).

3.1.4. Method evaluation: reproducibility, representative sampling and source recognition/apportionment studies

For all the above purposes systematic conserved component identification was done, using open source software http://spectconnect.mit.edu. The working principle, algorithm, data extraction procedures followed by Spectconnect are described elsewhere in detail [33]. This is the first report of application of Spectconnect for evaluation of both analytical method and comparability of samples without compound identification. Criterions for picking conserved components were kept stringent and are as follows: elution threshold of 0.5 min (high), support threshold occurrence in all samples (high) and similarity threshold with minimum spectral similarity of 90% (high). Statistical software Unscrambler® [34] and R package (R 2.12.0) [35] were used for multivariate statistics Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA), respectively. The data was leverage corrected and centered before subjecting to PCA and for the hierarchical clustering "Euclidean" distance and "Ward" linkage methods (between groups) were used. The effect of several well established clustering methods as single linkage, complete linkage and centroid methods were tested before finalizing with ward linkage. The results from PCA and HCA were used in concurrence for drawing final conclusion.

3.1.5. Volatile data evaluation: identification and confirmation of components

The data acquisition software MSD Chemstation G1701EA E.01.00.237 (Agilent, Waldbronn, Germany) was used to compare mass spectra of chromatographic peaks found in combined Nist and Wiley 2008 databases/spectral libraries. For peak picking all chromatograms were queried to an empty/blank msl library prior querying against combined Nist and Wiley 2008 spectral library. This method was found beneficial avoiding omission of peaks. Addition to this in-house sub libraries were built deriving mass spectra from Nist 05a and Wiley 7n for all those volatiles with AMDIS mass

Table 2
List of identified volatile organic compounds originating from settled floor dust samples from Groups A, B, C and D.

CAS No.	Name	*m/z* (precursor ion)	RT-HP5 (min)	RI-HP5 literature	RI-HP5 experimental	RT-Optima® Wax (min)	RI-Optima® Wax literature	RI-Optima® Wax experimental	References
123-73-9	2-Butenal, (E)-	70.08	6.29	644.0	657.3	9.95	1046.0	1046.4	
79-09-4	Propanoic acid	74.07	8.02	740.0	732.7	23.37	1528.0	1560.1	
71-36-3	1-Butanol	74.12	6.52	668.9*	669.3	13.05	1140.0	1162.6	[45,47]
110-62-3	Pentanal	86.13	7.22	698.0	704.3	8.35	983.0	981.0	[45,47]
107-92-6	Butanoic acid	88.10	10.81	831.0	827.4	25.57	1637.0	1654.7	
71-41-0	1-Pentanol	88.14	9.13	764.0	771.8	15.89	1261.0	1266.6	[47]
108-88-3	Toluene	92.13	9.10	771.2*	770.9	9.78	1037.9*	1040.0	
108-95-2	Phenol	94.11	16.01	983.9*	985.6	33.32	2023.4*	2026.0	[48]
109-08-0	2-Methylpyrazine	94.11	10.99	832.0	832.7	16.45	1312.0	1287.0	
6728-26-3	2-Hexenal, (E)-	98.14	11.81	859.7*	857.9	14.90	1228.8*	1230.1	
66-25-1	Hexanal	100.15	10.07	804.8*	804.6	10.97	1086.3*	1086.0	[45,47]
109-52-4	Valeric acid	102.13	13.15	921.0	899.0	28.10	1744.0	1770.0	[47]
503-74-2	Isovaleric acid	102.13	11.74	876.0	855.8	26.55	1674.0	1698.0	[47]
111-27-3	1-Hexanol	102.17	12.28	873.3*	872.3	18.61	1370.2*	1369.0	[47]
100-42-5	Styrene	104.14	13.09	880.0	897.3	15.73	1260.0	1260.6	[45]
100-41-4	Ethylbenzene	106.16	12.35	869.6*	874.4	12.12	1128.1*	1128.9	
106-42-3	p-Xylene	106.16	12.36	875.0*	874.6	12.31	1119.0	1135.9	
108-38-3	1,3-Dimethyl-benzene	106.16	12.35	864.4	874.6	12.31	1140.0	1136.0	
95-47-6	o-Xylene	106.16	12.36	879.0*	874.8	13.69	1189.2*	1185.7	
100-51-6	Benzyl alcohol	108.13	17.83	1042.0*	1041.3	30.86	1905.2*	1902.15	
4313-03-5′	2,4-Heptadienal, (E,E)-	110.15	17.03	1015.2*	1016.7	22.28	1515.8*	1514.7	
57266-86-1	2-Heptenal, (Z)-	112.16	15.22	958.0	961.5	17.83	1331.0	1339.1	
111-71-7	Heptanal	114.18	13.36	904.4*	905.4	13.79	1186.25*	1189.4	[45,47]
53535-33-4	1-Heptanol	116.20	15.58	974.0	972.6	21.24	1458.0	1472.2	
104-87-0	4-Methyl-benzaldehyde	120.14	19.45	1079.0	1091.0	25.44	1653.0	1649.0	
108-67-8	1,3,5-Trimethyl-benzene	120.19	16.48	1006.0	999.6	14.70	1221.0	1222.8	
526-73-8	1,2,3-Trimethyl-benzene	120.19	16.48	1019.9	999.7	18.00	1344.0	1345.5	[45]
611-14-3	o-Ethylmethylbenzene	120.19	15.95	975.0	983.7	15.36	1248.0	1247.2	
620-14-4	m-Ethylmethylbenzene	120.19	15.37	958.5	966.2	14.80	1231.0	1226.4	
622-96-8	p-Ethylmethylbenzene	120.19	15.50	960.0	970.0	14.15	1181.0	1202.5	
95-63-6	ψ-Cumene	120.19	16.46	989.0	999.2	15.36	1252.0	1247.2	
589-18-4	4-Methyl-benzenemethanol	122.16	20.96	1135.0	1141.2	32.58	1977.0	1989.0	
2363-89-5	2-Octenal	126.19	18.48	1060.0	1061.2	20.61	1436.0	1447.1	
124-13-0	Octanal	128.21	16.69	1005.6*	1006.3	16.70	1294.33*	1296.4	[45,47]
3391-86-4	1-Octen-3-ol	128.21	15.92	981.9*	982.7	21.00	1462.6*	1462.7	
104-76-7	2-Ethyl-1-hexanol	130.22	17.46	1031.4*	1030.0	22.03	1504.0*	1503.8	
111-87-5	1-Octanol	130.22	18.81	1073.1*	1071.2	23.73	1574.67*	1575.0	[47]
1195-32-0	Dehydro-p-cymene	132.20	19.54	1087.0	1093.7	20.25	1415.0	1433.0	
874-41-9	1-Ethyl-2,4-dimethyl-benzene	134.21	19.06	1078.0	1079.0	18.27	1348.0	1356.0	
99-87-6	p-Cimene	134.21	17.46	1040.0*	1029.9	16.08	1250.0	1273.3	[11]
138-86-3	α-Limonene	136.23	17.61	1041.9*	1034.3	13.92	1190.6*	1194.1	
5989-54-8	L-Limonene	136.23	17.61	1031.0	1034.3	13.92	1199.0	1194.1	[45]
80-56-8	α-Pinene	136.23	14.47	939.0	939.0	9.28	1026.0	1020.3	[46]
3777-69-3	2-Pentylfuran	138.20	16.26	994.0*	992.9	14.84	1222.8*	1228.2	[45,47]
18829-56-6	2-Nonenal, (E)-	140.22	21.59	1164.0	1162.3	23.26	1524.0	1555.5	
90-12-0	1-Methyl-naphthalene	142.19	25.77	1306.8	1310.6	30.46	1875.0	1882.4	
124-19-6	Nonanal	142.23	19.90	1107.0*	1105.4	19.52	1403.0*	1403.6	[47]
4180-23-8	Anethole	148.20	25.31	1283.0	1293.7	29.76	1818.0	1848.4	
25152-84-5	2,4-Decadienal, (E,E)-	152.23	22.90	1314.0	1207	29.56	1800.0	1838.6	
3913-81-3	2-Decenal, (E)-	154.24	24.53	1261.0	1265.5	25.78	1630.0	1664.3	
112-31-2	Decanal	156.26	22.90	1207.7*	1207.1	22.185	1510.33*	1510.3	
112-05-0	Nonanoic acid	158.23	24.70	1273.7*	1271.8	36.51	2233.5*	2196.0	

Table 2 (*Continued*)

CAS No.	Name	*m/z* (precursor ion)	RT-HP5 (min)	RI-HP5 literature	RI-HP5 experimental	RT-Optima® Wax (min)	RI-Optima® Wax literature	RI-Optima® Wax experimental	References
644-08-6	p-Phenyltoluene	168.23	30.58	1492.0	1498.9	35.11	2117.0	2117.1	
2463-77-6	2-Undecenal	168.27	27.28	1350.0	1368.2	28.26	1755.0	1777.0	
334-48-5	n-Decanoic acid	172.26	27.72	1380.0	1384.9	38.35	2258.0	2303.4	[47]
112-53-8	1-Dodecanol	186.33	30.82	1472.0	1509.0	32.57	1920.0	1988.4	
143-07-7	Dodecanoic acid	200.31	32.55	1565.0*	1582.8	41.97	2564.0*	2526.5	[48]
112-70-9	n-Tridecan-1-ol	200.36	32.46	1577.0*	1578.7	34.47	2076.0	2083.5	[48]
96-76-4	2,4-Bis(1,1-dimethylethyl)-phenol	206.32	30.82	1519.0	1509.1	38.71	2323.3*	2324.75	
120-51-4	Benzyl benzoate	212.24	36.98	1765.0	1783.9	44.27	2613.0	2658.6	
128-37-0	Butylated hydroxytoluene	220.35	30.80	1513.6*	1508.3	31.28	1920.6*	1923.1	
629-80-1	Palmitaldehyde	240.42	37.72	1811.0	1819.7	35.76	2124.0	2153.5	
36653-82-4	Cethyl alcohol	242.44	38.99	1876.0	1882.8	39.97	2363.0	2400.6	
57-10-3	Palmitic acid	256.42	40.63	2010.0	1966.7	49.04	2865.0	2903.0	[48]
502-69-2	Hexahydrofarnesyl acetone	268.47	38.18	1846.0*	1842.6	35.55	2134.0	2141.7	
1921-70-6	2,6,10,14-Tetramethyl-pentadecane	268.52	35.29	1703.0	1704.6	25.93	1669.0	1670.7	
110-27-0	Isopropyl myristate	270.45	37.78	1824.0	1822.7	33.77	2023.0	2048.3	
112-39-0	Hexadecanoic acid methyl ester	270.45	39.81	1926.7*	1924.3	37.15	2229.5*	2233.0	
112-92-5	1-Octadecanol	270.49	42.87	2081.0	2084.4	43.26	2569.0	2607.0	
84-69-5	Isobutyl-o-phthalate	278.34	38.66	1868.0	1866.2	42.78	2526.0	2578.1	
84-74-2	Dibutyl phthalate	278.34	40.51	1969.0	1960.3	45.18	2726.0	2705.3	

* Retention index (RI) values determined by us with pure reference standards. Listed in the order of increasing precursor ion mass.

spectral match factor ≥90. This was done to minimize data evaluation time in addition to convenient automation. Moreover, the in-house sub libraries dedicated for individual column specifications were supplemented with linear temperature programmed retention indices (LTPRI, Van Den Dool and Kratz index values) corresponding to the stationary phases of the GC used in the study. The added LTPRI values were either experimentally determined by us using authentic standards or literature values retrieved from NIST Chemistry Web Book (2009). In case a putatively identified substance was reported with more than one LTPRI, the value most frequently stated was taken into account. Automated data evaluation was done by AMDIS software (automated mass spectral deconvolution and identification system, version 2.64) [36]. The optimization of AMDIS parameters for deconvolution and identification were done as described earlier by Meyer et al. [37]. The following parameters were found optimal and used for deconvolution and identification during the study; width, 20; adjacent peak subtraction, 1; sensitivity, high; resolution, high; shape requirement, high. Mixture of alkane standards (C_5–C_{10}), (C_8–C_{20}) and (C_{21}–C_{40}) were analysed separately and LTPRI values were determined [38]. Data presented in Table 2 are designated as "identified" when LTPRI value of a volatile compound was within relative deviation of ±2% from literature or from experimentally determined value (using pure standard) in addition to mass spectral match factor greater or equal to 90 on both columns of inverse polarities in triplicates. In cases where detection was on one of the columns meeting the other three criterions for identification, compounds were designated "annotated" (Supplementary Table 1). The set criterions in this study are based on our previous investigation [39] of fungal and other complex matrices and other reports for impact of matrix composition on RI [40,41].

3.2. Liquid chromatography/tandem mass spectrometry – non volatile microbial metabolites

3.2.1. Analytical reagents and supplies

Methanol, acetonitrile (both LC gradient grade) were purchased from J.T. Baker (Deventer, The Netherlands), ammonium acetate (MS grade) and glacial acetic acid (p.a.) were obtained from Sigma–Aldrich (Vienna, Austria). Water was purified successively by reverse osmosis and a Milli-Q plus system from Millipore (Molsheim, France). Individual fungal and bacterial metabolites were from the same sources as mentioned in our earlier publication [7].

3.2.2. LC–MS/MS

Detection and quantification was done with a QTrap 4000 LC–MS/MS System (Applied Biosystems, Foster City, CA) equipped with a TurboIonSpray electrospray ionization (ESI) source and an 1100 Series HPLC System (Agilent, Waldbronn, Germany). Chromatographic separation was performed at 25 °C on a Gemini® C18-column, 150 mm × 4.6 mm i.d., 5 μm particle size, equipped with a C18 security guard cartridge, 4 mm × 3 mm i.d. (all from Phenomenex, Torrance, CA, USA). Elution was carried out in binary gradient mode. Both mobile phases contained 5 mM ammonium acetate and were composed of methanol/water/acetic acid 10:89:1 (v/v/v; eluent A) and 97:2:1 (v/v/v; eluent B), respectively. After an initial time of 2 min at 100% A, the proportion of B was increased linearly to 100% within 12 min, followed by a hold-time of 4 min at 100% B and 2.5 min column re-equilibration at 100% A. The flow rate was 1000 μL min^{-1}.

ESI-MS/MS was performed in the scheduled multiple reaction monitoring (sMRM) mode both in positive and in negative polarities in two separate chromatographic runs per sample by scanning two fragmentation reactions per analyte. The sMRM detection window of each analyte was set to the respective retention time ±24 s and the target scan time was set to 1 s. The settings of the ESI source

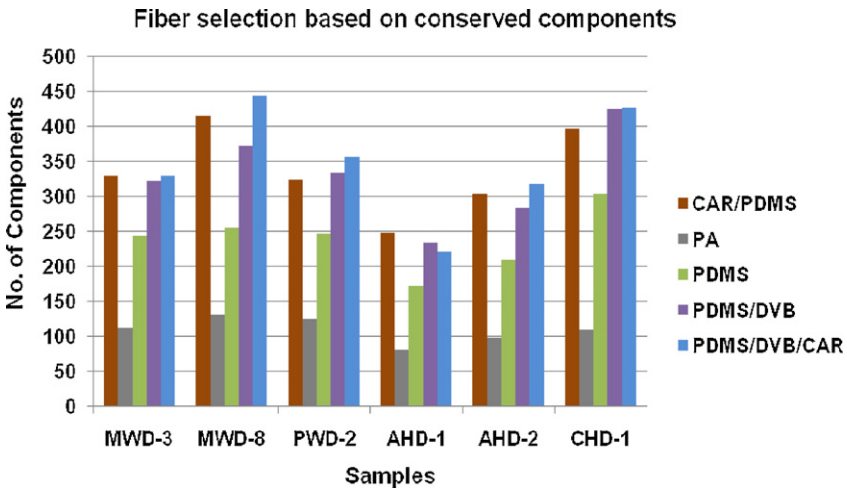

Fig. 1. Comparison of different fiber coatings and number of adsorbed components.

were as follows: source temperature 550 °C, curtain gas 10 psi (69 kPa of max. 99.5% nitrogen), ion source gas 1 (sheath gas) 50 psi (345 kPa of nitrogen), ion source gas 2 (drying gas) 50 psi (345 kPa of nitrogen), ion-spray voltage −4000 V and +4000 V, respectively, collision gas (nitrogen) high. Confirmation of positive analyte identification is obtained by the acquisition of two sMRMs per analyte, which yields 4.0 identification points according to commission decision 2002/657/EC [42]. In addition, the LC retention time and the intensity ratio of the two sMRM transitions have to agree with values of corresponding standards.

3.2.3. Secondary metabolite data evaluation

LC–MS/MS data evaluation was done using the Analyst® 1.5 (AB SCIEX 2008). Identification of positive target analytes in samples was confirmed by comparing retention time (RT) and ratios of qualifier to quantifier to authentic standards, measured before and after a particular sample batch of 30 samples.

4. Results and discussion

4.1. SPME and GC–MS

The sensitivity of the HS-SPME-GC–MS technique depends mainly on the distribution constant of analytes partitioned between sample and stationary phase of fiber (K_{fs}) [43]. To generate comprehensive profile of volatiles with variable volatility, selection of optimal fiber becomes a crucial factor in qualitative but mainly in quantitative analysis, where limits of detection are related to amount of adsorbed compound on phase covering the fiber. Among the tested fibers the most polar fiber coatings of polyacrylate (PA) as well as non polar polydimethylosiloxane (PDMS) were found not suitable for our profiling study. Fiber performances of CAR/PDMS, PDMS/DVB and PDMS/DVB/CAR were similar concerning the number of conserved components derived from Spectconnect (Figs. 1 and 2a–e). Hence annotation was considered as an additional criterion for the selection. Among the three semipolar fibers CAR.PDMS was found superior for the purpose with 30% more identification or annotation (Fig. 3). CAR.PDMS is often a fiber of choice in food industries for sensory aroma evaluation [44]. Better suitability of this fiber for profiling purpose is also reported for fungal volatile profiling [6]. Comparison of different extraction temperatures showed that use of 90 °C was suitable for evaluation of substances with wide range of volatilities. Choice of extraction temperature becomes critical, since use of higher temperatures though promoting detection of low volatile substance can be inappropriate as causing premature desorption of other more volatile analytes from the fiber coating which is not suitable for profiling studies like ours [43]. Other factors that need to be considered selecting extraction temperature are nature of matrix and stationary phase. Sample volume and pre-incubation time and temperature were also evaluated in order not to overlook low abundant or moderately volatile substances. Optimization for these parameters resulted in values of 0.05 g sample mass/vial and extraction at 90 °C for 30 min, respectively (Supplementary Tables 2 and 3). Increasing the sample volume did not show any significant increase in number of conserved components indicating either fiber saturation or limitation of the fiber in terms of its potential to adsorb different compounds. The reduction of empirical sample amount (0.025 g) reduced number of components by 25% possibly due to inadequate ion current/intensity of low abundant substances. In our method pre incubation and extraction temperatures are kept constant to minimize temperature ramping. We assume that this in addition to reducing ramping time is also beneficial achieving equilibrium of low and semi volatile compounds in the mixture. Application of a pair of columns with inverse polarities for identification was compared to earlier reports based on single column [6,11,45–47], found advantageous in case of stereo isomers o- and p-xylenes and constitutional isomers ψ-cumene, mesitylene, hemimellitene. The compounds which were barely resolved on apolar column were well resolved on polar Optima® Wax with RT and RI of 13.69 min and 12.31 min and 1186 and 1136, respectively, for o and p-xylenes. Similarly mesitylene, ψ-cumene, hemimellitene had RT of 14.7, 15.4 and 18.0 min and LTPRI 1223, 1247, 1346, respectively.

Total of 71 volatile organic compounds were detected (Table 2) on both columns of different polarity. 20 of the compounds have been reported as microbial volatile organic compounds produced by either individual or mixtures of microbes under laboratory conditions on different matrices [5,6,45,48–51]. Additionally 85 substances designated as “annotated” (Supplementary table 1) were detected on only one of the two columns HP5(89%)/Optima® Wax (11%) with exact LTPRI match or LTPRI within relative deviation of ±2% from literature or from a value determined by measuring a pure standard. Spectral match factor for both identified and annotated compounds were above or equal to 90. Assigning the origin of a compound might not be straight forward as many of the detected volatiles are produced by microbes and plants, as well as they were known to be integral part of many solvents that are commonly used indoors. The best observed examples for

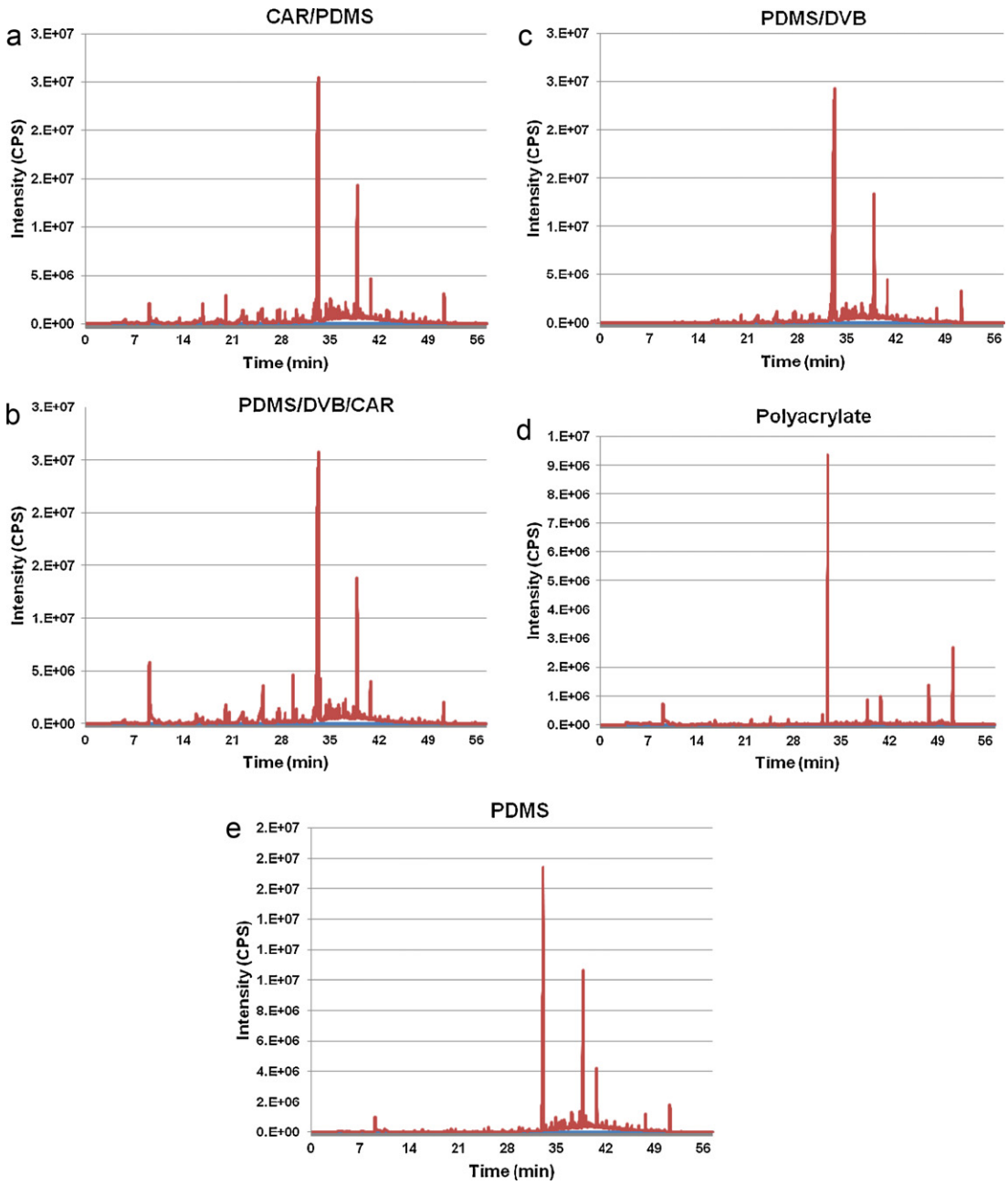

Fig. 2. Fiber selection-chromatographic profile of extracted volatile from sample AHD-1 on different fiber coatings.

this class of compounds were toluene, phenol, ethylbenzene, 1-butanol, limonene, styrene and α-pinene [51–53]. The compounds nonanal, toluene, butanoic acid, benzyl alcohol, phenol, 1-octanal, phthalic acid, and dibutyl phthalate were uniform in their occurrence across all four groups of samples. 1-Octanol and nonanal without any ambiguity could be related to microbial origin [51]. All other frequently found substances with exception of toluene and phenol could be traced back to either combustion by product of gasoline, adhesive or plasticizers [53]. Limonene is a constituent of many household consumer products such as deodorizers, polishes, fabric softeners, cigarettes and food beverages [52,54]. Limonene occurrence in samples derived exclusively from municipal waste management units and not in other can be an argument for its insignificant synthesis and release by microbes compared to non biological sources.

4.1.1. Statistical evaluation: GC–MS method performance and source identity recognition/apportionment based on volatile profile of samples

Multivariate statistics PCA and HCA were employed to identify probably existing differences and similarities in volatile profiles of different indoor environments. Our assumption for this was discrepancies in volatile profiles of different indoor environments also exist in dust samples (due to surface adsorption and particle accumulation), and arises as a result of dissimilar indoor purposes, climate and geographical location. For this purpose ISmatrix generated by Spectconnect was used. ISmatrix is a result output Microsoft Excel CSV file, consisting of complement peaks areas consistently detected in multiple chromatograms across sample groups or sample replicates. ISmatrix of the order 66*1993 representing conserved peak areas across 22 samples in replicates of

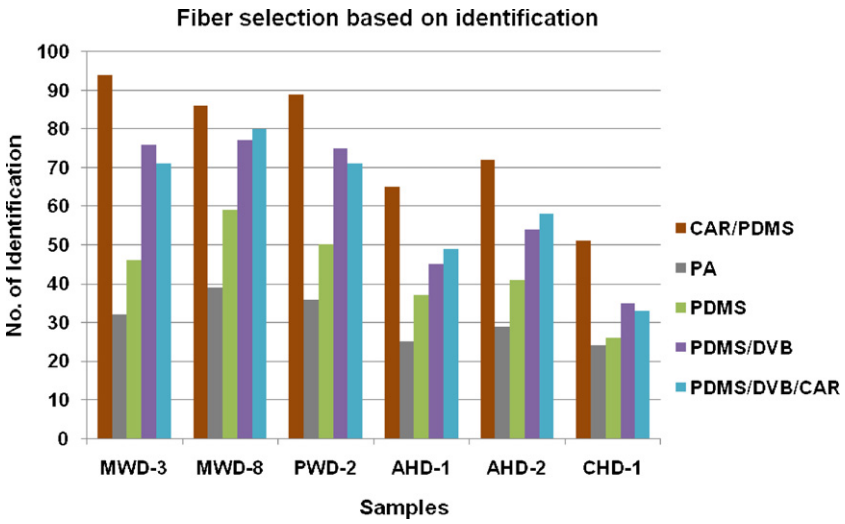

Fig. 3. Comparison of different fiber coatings and number of identified components.

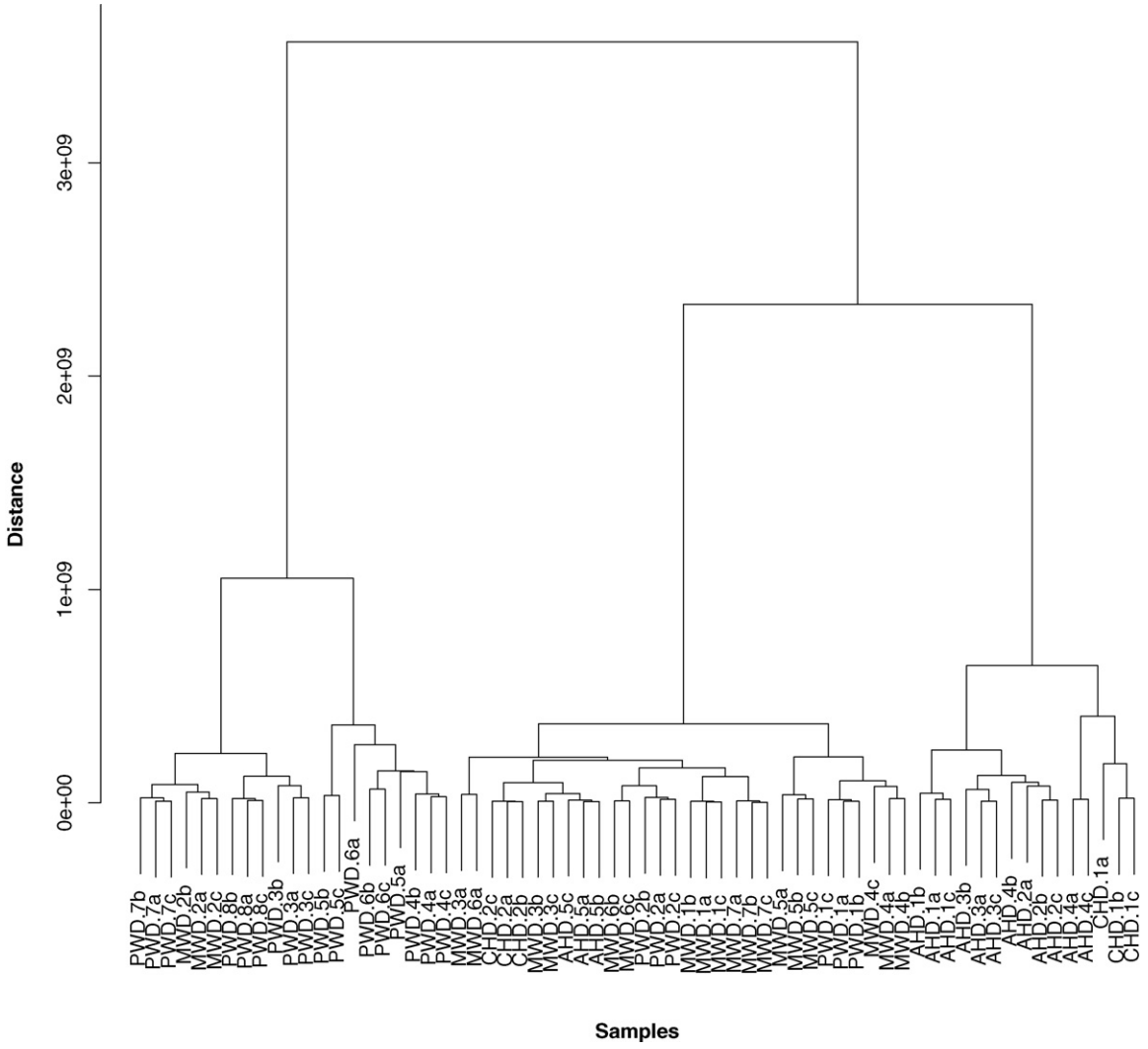

Fig. 4. Hierarchical clustering considering selected volatile components with loading score >0.1 with resultant matrix (66*7). Data clusters 1: PWD, Data clusters 2: AHD, CHD, MWD, PWD, Data clusters 3: AHD.

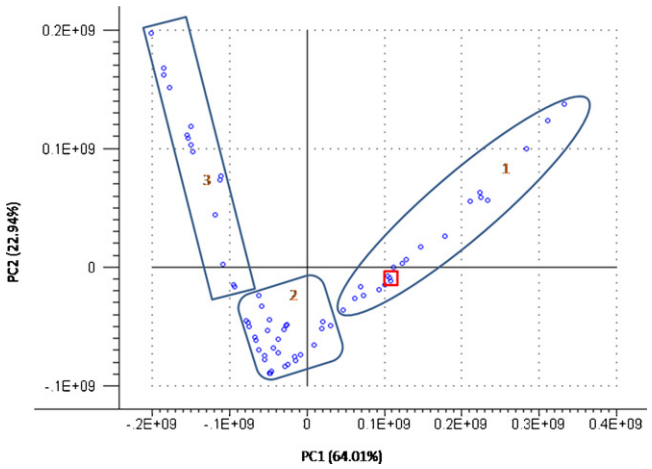

Fig. 5. PCA of selected volatile components with loading score >0.1 with resultant matrix (66*7). Data clusters 1: PWD, Data clusters 2: AHD, CHD, MWD, PWD, Data clusters 3: AHD.

three or at least conserved in triplicates of a single sample was used for hierarchical clustering to verify analytical aspects (sample homogeneity and component distribution) in addition to other mentioned purposes. Concerning homogeneity and component distribution 17 of the 22 samples showed good clustering among replicates. This resulted in two super-clusters with 2 sub clusters each (Supplementary Fig. S1). Replicates of individual house dust samples from distant geographical origins clustered along with the samples from municipal waste handling units forming one of the four major clusters consisting of 11 elements (Supplementary Fig. S1) with the exception one sample MWD-2. Four of the five Finnish house dust samples from moisture damaged houses (AHD 1–5) were equidistant and clustered together and were different to other groups in their volatile pattern. Contrary to anticipation samples from paper recycling units (exception of PWD 1–2) split into two sub clusters of four and three elements each, representing occurrence of probable intrinsic differences. This minor separation could be explained by the different waste handling methods and its influence on aerosols or deposited particles and ultimately leading to formation of dust with compositional irregularities. One or more sample replicates clustering sparsely or distant samples merging into a close knit cluster may not be amenable for an easy explanation (example Fig. 5, clustering of MWD-2 along with PWD samples highlighted with red square). Nevertheless clustering among the majority of sample replicates is good evidence for validity and applicability of our method and instrumental set up for indoor evaluation studies. The recommended procedure for PCA for differentiation of samples is to analyse all variables at the same time. But in cases where numbers of variable are higher than the number of cases this may not be feasible. The observation of loading scores from the matrix 66*1993 suggests that the majority of variables had typically low in the magnitude of <0.1 indicating insignificant influence on separation. Hence a cut off loading score of 0.1 was fixed for variable selection. The resulting new matrix (66*7) comprising both volatiles and reported microbial volatiles (two) accounted for 86.95% of the total variance in the data on PCA. The first principal component (PC1) explained

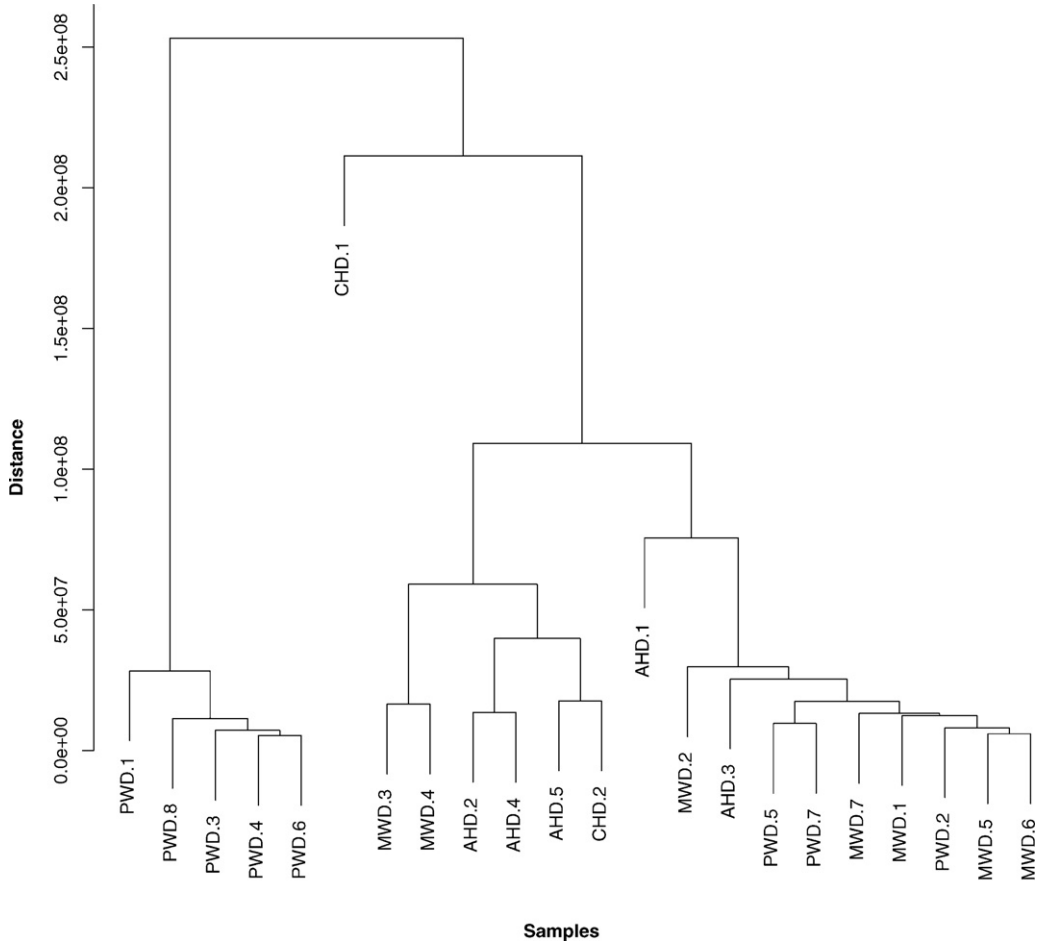

Fig. 6. Hierarchical clustering considering literature reported microbial volatile components with resultant matrix (22*18). Data cluster: 1: CHD1, Data cluster: 2: AHD, MWD, PWD, Data cluster: 3: AHD, MWD, CHD, Data cluster: 4: PWD.

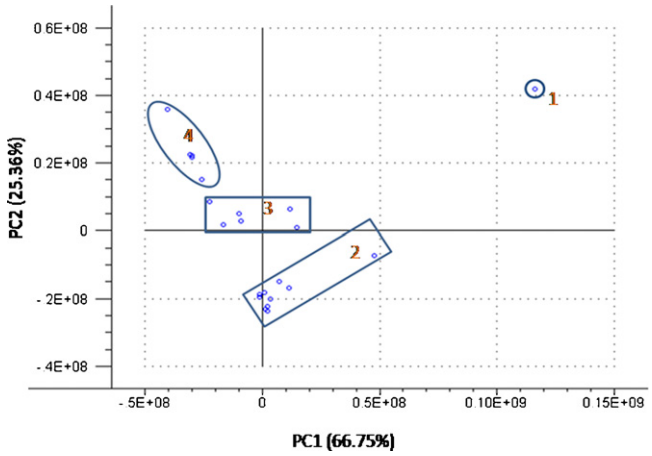

Fig. 7. PCA of selected microbial volatile components with loading score >0.1 with resultant matrix (22*18). Data cluster: 1: CHD1, Data cluster: 2: AHD, MWD, PWD, Data cluster: 3: AHD, MWD, CHD, Data cluster: 4: PWD.

64.01% of the variance separating samples and second principal component (PC2) with 22.94% of variance. The PC1 identified as linear combination of 2,6-diisopropylnaphtalene and 1-tetradecanol. The PC2 was mainly characterized by variables diethyl phthalate and minor influence by 1-butyl 2-isobutyl phthalate and Toluene. Scattered plot corresponding to this discrimination is illustrated in Fig. 5.The conclusion that can be drawn from the illustrated classification study is that 71% of affected house dust samples and 75% of waste management units dealing with paper were clearly separable on first principal component. Considering samples from a distinct cluster on negative PC1 and PC2 it can be concluded that overlap in volatile and semi volatile profiles are consistent with the statistical reports of the Parliament office of science and technology, England (statistics discussed at later part) for household contribution for municipal waste formation. Hierarchical clustering of the same matrix resulted in two major clusters each having two minor clusters (Figs. 4 and 5). Comparative evaluation of dendrograms showed grouping in Fig. 4 is similar to Supplementary Fig. S1, thus confirming the independent influence of chosen variables in separation for the group of samples. In parallel averaged replicates peak areas of identified MVOCs that are well documented in the scientific literature were considered for PCA. This was done to verify their probable role in separation of samples and differentiation of enclosures (22*18). The PCA of MVOCs indicated the extraction of two principal components representing total variance of 92.10% of the data set. PC1 represented 66.75% of variance and was strongly characterized by toluene, PC2 on the other hand accounted for 25.36% of variance due to nonanal. Due to ambiguity concerning the origin of toluene this compound may not be an ideal volatile marker for separation of samples and sources, based on microbial volatile profile. In this view nonanal underlying PC2 and explaining a variance of 25.36% could be an important microbial marker for separation of samples in the indoor environments. HCA of the same matrix (22*18) resulted in three super-clusters. Extreme right cluster (Fig. 6), where samples belonging to paper recycling units can be seen grouped together (PWD 1, 3, 4, 6, 8). This may explain similar purposes of indoor or occurrence of common abundant cellulose matrix promoting climate favorable for particular set microbes, in addition to influencing their physiology and volatile pattern. Similarly another main cluster consisting of house dust samples (AHD 2, 4, 5 and CHD 2) cluster at similar height which could be best reasoned as a consequence of comparable thermal and humidity comfort pattern practiced in homes leading to comparable/general micro climates in these indoor environments (Figs. 6 and 7).

4.2. Evidence for natural occurrence of microbial secondary metabolites in settled dust

The analysis of non volatile/secondary microbial metabolites in settled dust matrix was done using a validated method described earlier [7]. In cases of samples from waste management units containing paper and other matrices with absorptive consistency a larger sample to solvent ratio of 1:8 or 1:12 was used to ensure complete submersion of samples and optimum extraction. Dust samples were source of 38 different microbial metabolites to variable quantities. The concentrations of the investigated toxins in the positive samples are listed in Table 3. Their relative standard deviation between replicates was generally below 20% (e.g. 50% of samples), which we consider to be a reasonable value in view of the heterogeneity of the matrix (thus confirming the accuracy of the method). The microbial metabolite spectrum detected included following microbial taxa, *Penicillum* ($n=12$), *Aspergillus* ($n=5$), *Fusarium* ($n=7$), *Beauveria* ($n=1$),*Trichoderma* ($n=1$), *Claviceps* ($n=1$), *Alternaria* ($n=2$), *Stachybotrys* ($n=1$), *Metarrhizium* ($n=1$), *Chaetomium* ($n=1$) and Bacterial ($n=6$) [55]. A few of the metabolites could be attributed to more than one genus of indoor fungi and bacteria.

Samples from municipal and paper recycling waste management units were similar in terms of microbe-metabolite pattern and quantities. A post note released by the Parliament office of science and technology, England (http://www.parliament.uk/documents/post/postpn252.pdf) provides some insight concerning organic content of municipal waste and offers an additional indirect explanation for high prevalence of saprophytic/parasitic microbes in dust samples procured from municipal waste dealing units. The above mentioned report states that, the bulk of municipal waste generation is contributed by the households and consists of biodegradable material (41%, kitchen, garden, soil), biodegradable & recyclable material (18%, paper, cardboard), recyclable waste (17%, glass, plastic, metal) and other materials (20%, wood, non-combustibles, textiles). Municipal waste with complex organic content thus could be a potential matrix nurturing diverse set of fungi and bacteria. Each group of enclosures was unique having set of metabolites not found in the other sampling sites. The samples of WMUs dealing with municipal waste were distinct from samples of WMUs dealing with paper by the presence of griseofulvin, dechlorogriseofulvin, chlamydeosporal, malformin C, myriocin, patulin and puromycin. Presence of griseofulvin and its halogenated derivative, dechlorogirsofulvin in one and the same municipal waste management sample is confirmation for mutual occurrence addition to proving the greater relevance of our chosen indoor target metabolites in the course of method expansion [56,57]. Patulin, a mycotoxin on decomposing apples and a metabolite of species of *Pencillium* and *Aspergillus* is not frequently found in indoor dust makes its presence interesting. Presence of malformin C could indicate occurrence of the indoor mold. *Aspergillus niger* [58] known for causing skin diseases and ear infection [59]. Similarly samples from paper recycling units were different to those of municipal waste management units in their microbe-metabolite pattern due to the presence of deoxybrevinamide E and cytochalsin D. Cytochalasin D is a metabolite produced by filamentous saprophobic ascomycetes of the genus *Chaetomium* found in soil, air and plant debris [60]. Several species of *Chaetomium* are common in indoor environments such as *C. elatum*, *C. globosum*, *C. murorum* [61]. Similarities in the metabolite patterns of the two waste handling units might be a result of similarities in the fungal spectra present in such work places due to similar micro-climatic conditions, substrates and the hygiene principles applied.

As apprehended settled dust samples from inhabited houses showed lower metabolite diversity ($n=18$) compared to other groups. Metabolites enniatin B2 and alternariol were exclusively

Table 3
Non volatile/secondary microbial metabolites detected in settled floor dust samples from Groups A, B, C and D. Quantification values presented are average of replicates.

Metabolite	Precursor ion	Municipal waste (Gp A) management (μg/kg)	Household paper (Gp B) recycling (μg/kg)	Settled dust from (Gp C) house (μg/kg)	Settled dust from (Gp D) house (μg/kg)
3-Methylviridicatin	281.07$[M+H]^+$	5.8–10.0	8.5–9.0	–	–
Alamethicin F30	775.5 $[y7^d+H]^+$	4.0–35.0	14.0–15.0	–	–
Alternariol	257.0 $[M-H]^-$	–	–	39.7	34.6–41.0
AME	271.1 $[M-H]^-$	11.2–42.0	17.3–37.0	8.0	7.3–10.0
Apicidin	622.4 $[M-H]^-$	1.1–1.4	0.5–0.8	–	–
Beauvericin	801.5 $[M+NH_4]^+$806.5 $[M+Na]^+$	1.6–22.0	0.3–10.4	3.1	0.7–1.8
Chaetoglobosin A	695.0 $[M-H]^-$	193.0–258.0	83.0–242.0	–	–
Chanoclavine	257.1$[M+H]^+$	1.9–2.8	0.6–5.9	–	–
Chlamydosporol	245.2$[M+H]^+$	16.0–59.0	–	–	–
Chloramphenicol	320.9 $[M-H]^-$	39.5–108.3	2.7–22.6	–	3.6–4.6
Cyclopenin	295.1$[M+H]^+$	32.0–188.0	26.0–303.0	–	–
Cyclopeptine	281.07$[M+H]^+$	7.8–50.0	3.0–46.0		–
Cycloaspeptide A	642.3 $[M+H]^+$	9.6–29.0	10.8–11.7	155.4	–
Cytochalasin D	609.3 $[M+2H]^{2+}$	–	51.0–221.0	–	57.1
Dechlorogriseofulvin	319.1$[M+H]^+$	230.5	–	13.0	–
Deoxybrevianamid E	352.2$[M+H]^+$	–	221.3	–	–
Emodin	269.0 $[M-H]^-$	61.0–314.0	26.0–88.0	15.15	4.0–117.0
Enniatin A	699.4 $[M+NH_4]^+$	7.4–17.0	3.0–17.0	–	0.7–223.0
Enniatin A1	685.4 $[M+NH_4]^+$	2.0–30.0	1.3–14	–	1.4–185.0
Enniatin B	657.5 $[M+NH_4]^+$	2.2–23.0	0.2–8.1	–	0.9–10.3
Enniatin B1	671.4 $[M+NH_4]^+$	4.0–49.0	1.3–19.3	–	–
Enniatin B2	643.5 $[M+NH_4]^+$	–	–	1.9	0.6–2.0
Equisetin	372.2 $[M-H]^-$	21.2–422.4	12.5–185.3	–	19.0–20.0
Fumigaclavine	299.3 $[M+H]^+$	13.0–86.0	10.0–23.0	–	–
Griseofulvin	353.2 $[M+H]^+$	87.0–1598.0	–	210.0	–
Malformin C	530.3$[M+H]^+$	8.0–78.0	–	–	–
Meleagrin	434.3 $[M+H]^+$	14.0–52.0	29.0–67.0	–	–
Monactin	768.8 $[M+NH_4]^+$	4.0–101.0	0.4–2.3	–	0.65
Myriocin	402.4 $[M+H]^+$	52.0–1941.0	–	–	–
Nonactin	754.6 $[M+NH_4]^+$	0.2–50.0	0.5–1.2	0.8	0.2–0.3
Patulin	152.9 $[M-H]^-$	49144.0	–	–	–
Pentoxyfylline	279.2 $[M+H]^+$	11.0–186.0	2.0–101.0	–	–
Physcion	283.0 $[M-H]^-$	409.0–1034.0	231.0–1565.0	–	–
Puromycin	472.4 $[M+H]^+$	40.0–126.0	–	–	–
Roquefortine C	390.2 $[M+H]^+$	83.0–176.4	18.0–350.0	–	–
Stachybotrylactam	386.3 $[M+H]^+$	52.6–104.5	87.0–160.0	–	–
Sterigmatocystine	325.1 $[M+H]^+$	3.0–45.3	6.0–32.0	–	1.6–11.0
Valinomycin	1128.8 $[M+NH_4]^+$	0.05–8.0	0.3–2.0	0.4	0.04–0.6
Viridicatin	238.1 $[M+H]^+$	110.0–920.0	108.0–369.0	–	–

detected in settled floor dust (SFD) samples of control and houses with severe moisture damage (Table 3) along with some other *Fusarium* metabolites. However control and damaged houses had certain metabolite signature pattern. The control houses differed by the presence of metabolites griseofulvin, dechlorogriseofulvin and cyclosapeptide A. The moisture damaged houses were positive for the presence of alternariol monomethyl ether (AME) and monactin which are metabolites of tertiary colonizers *Alternaria alternata* and *Actinomycetes* [14] indicating for water damage. The presence of bacterial metabolites produced by *Streptomyces* and related genera in the damaged houses clearly links to conditions of excess moisture damage and dampness indoors, as this groups of bacteria has been described earlier as being indicative for such indoor conditions [62].

5. Conclusion

The detection and quantification of wider range of metabolites in concentration range of 0.04–49,144.0 μg/kg are evidences for the competency of our developed multi target LC–MS/MS method for the purpose. Occurrence of broader array of metabolites (primary, secondary and tertiary colonizing microbes) in samples of waste handling units (municipal waste (>50%) and paper recycling units (>33%)) is affirmation for microbial succession. Metabolites of *S. chartarum,* which is well known to be indoor specific fungi was found in waste management units in high concentrations (52–160 μg/kg). In the absence of moisture monitoring data of evaluated environments, origin (indoor or outdoor) of stachybotrylactam remains to be an open question. The presence of emodin, griseofulvin and dechlorogriseofulvin along with metabolites of tertiary colonizer are not unexpected findings, considering processes involved in waste handling (collection, transportation, storage) during which moisture accumulation is an obvious possibility. To the best of our knowledge 30 of the 71 identified volatiles are new report in the indoor context, particularly in settled floor dust matrix. Though as many as 20 previously reported MVOCs were found in our study, a direct correlation to secondary metabolite profiles could not be possible due to the known ambiguity in MVOC and the non-availability of authentic environmental control samples and volatile profiles corresponding to them. The applications of AMDIS and Spectconnect for volatile profiling are advantageous identifying major indoor pollutants clouded amidst extremely high number of variables/components. The wide range biogenic and anthropogenic pollutants in dust qualify it as an indicator matrix of indoor status, hence can be valuable for evaluation purposes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.07.043.

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