Volatile organics off-gassed among tobacco-exposed clothing fabrics

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ABSTRACT

This work evaluates the characteristics of short-term release of volatile and semi-volatile organic chemicals from clothing fabrics that are exposed to environmental tobacco smoke (ETS). Various fabrics were concurrently exposed to ETS in a controlled facility, and the chemicals off-gassed were sampled using solid phase micro-extraction coupled with GC/MS analysis. Toluene-reference concentration (TRC) was calculated for nine selected chemicals and compared.

The number of chemicals identified from ETS-exposed fabrics ranged from 13 (polyester and acetate) to 32 (linen). All fabrics off-gassed formaldehyde, tetradecanoic acid and n-hexadecanoic acid, while seven out of eight fabrics emitted furfural, benzonitrile, naphthalene and decanal. Natural fibers of plant origin (cotton and linen) off-gassed higher concentrations (TRC > 100 μg/l) of chemicals that have low molecular weight ($\sim$100 or less) than did natural fibers of animal origin (wool and silk) and synthetic fibers. Conversely, wool and silk off-gassed more chemicals that are of high molecular weight (>200), such as TDA (TRC > 100 μg/l) and n-HDA (TRC > 500 μg/l), than did other fabrics. Fabric structure (for a particular material) significantly affects chemical off-gassing. Cotton typically used for polo shirt (knitted) off-gassed significantly (p < 0.05) higher TRC for chemicals with molecular weight of $\sim$100 (such as furfural) than did other cottons of woven style. The dyeing of fabric (white vs. black) had a limited effect on emission, while increasing contact time with ETS increased the intensity of chemical emissions. The mean TRC for cotton exposed for 12 min was nearly doubled than those exposed for 8 min, but no difference existed for polyester.

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1. Introduction

Environmental tobacco smoke (ETS, or second-hand smoke (SHS)) that has been absorbed by objects and re-emitted, exhaled by smokers after smoking has ceased, or reacts with other chemicals on indoor surfaces to form new species has been described as "third-hand smoke (THS)" [1–4]. THS not only has a distinct odor, but also causes an exposure route to tobacco-related contaminants in the absence of concurrent active smoking.

A used-car provides a good example of the detrimental effects of THS. The surface dusts and air samples collected from the cabins of used cars without smoking ban had significantly higher nicotine levels than those from smoke-free cars, and so sell for less because of the telltale signs such as odor [5]. Similarly, dust and the surfaces in homes of smokers and the index fingers of smoking mothers are contaminated with nicotine, which increases the

risk of infant exposure [6]. These findings demonstrate that constituents of tobacco smoke can be retained and accumulated in the environment such that smoking indoors on one day may expose people to tobacco toxicants on subsequent days [7].

Chemicals in ETS can be grouped into five categories – very volatile organics (VVOCs), volatile organics (VOCs), semi-volatile organics (SVOCs), particulate matter (PM) and associated organics, and gas-phase inorganic chemicals [8]. The sorption of VOCs and SVOCs onto, and their desorption out of, various indoor materials, such as carpet, furniture, wall and drapes, can significantly affect their concentration in indoor air and consequent human exposure, as has been demonstrated by various controlled and field studies [7,9–16]. Accordingly, household fabrics are expected to adsorb and re-emit ETS chemicals such as nicotine, phenol, naphthalene and 3-ethenylpyridine (3-EP).

A study of the uptake of cigarette smoke by clothing fabrics found that natural fabrics such as cotton and linen gained a significantly higher percentage of weight than did man-made materials, such as polyester, upon exposure to SHS [17]. However, chemicals that were absorbed/emitted by each fabric were unknown since no chemical analysis was performed in that investigation, even though moisture likely contributed to most of the weight gained. Similarly,

Table 1
Characteristics of the fabrics under study.

Fabric[a]	Color[b]	Yarn Number		Fabric Count (per inch)[c]		Conditioned Weight (g/m²)[d]	Thickness (mm)[e]	Production method	Structure[f]
		Warp	Filling	Ends	Picks				
Cotton-1	White	7.6	7.3	66.3	41.2	394.7	0.91	Woven[g]	3/1 Twill
Cotton-2	White	44.0	42.6	141.0	71.4	123.8	0.24	Woven	Plain
Cotton-3	White	18.5[h]	–	28.0	42.0	302.7	0.90	Knitted	Double Cross Tuck
Cotton-4	White	21.3	20.5	110.5	55.3	201.9	0.43	Woven	3/1 Twill
Cotton-5	Black	42.8	42.4	139.7	70.7	122.0	0.23	Woven	Plain
Linen	Black	18.1	15.9	58.3	50.0	165.0	0.32	Woven	Plain
Polyester	Black	167.1	166.5	98.9	74.2	136.4	0.40	Woven	2/2 Twill
Rayon	Black	137.0	171.1	138.4	71.1	151.2	0.35	Woven	Plain
PVC	Black	–	–	–	–	306.0	0.67	–	–
Silk	Black	34.2	33.4	339.8	130.0	71.9	0.14	Woven	4/1 Twill
Acetate	Black	71.1	102.7	110.0	72.1	67.7	0.12	Woven	Plain
Wool	Black	57.6	56.1	82.3	70.9	230.2	0.49	Woven	2/2 Twill

[a] Cotton-1: used typically for jeans; Cotton-2: used typically for dress shirt; Cotton-3: used typically for polo shirt; Cotton-4: used typically for trouser; Cotton-5: used typically for dress shirt (identical to Cotton-2, except color).
[b] Color appeared to the researcher; black colors are all dyed.
[c] Tested using ISO 7211-5:1984.
[d] Tested using ISO 7211-2:1984; Environmental condition: 20°C, 65%RH.
[e] Tested using ISO 3801-5:1977.
[f] Tested using ISO 4603:1993; Pressure: 0.5 kPa; Diameter of pressure foot: 57.1 mm.
[g] Tested using ISO 7211-1:1984.
[h] Yarn number as received (Ne) by the tester.

wool fiber was found to have a high capacity to adsorb ETS chemicals, as also measured by weight gained, because of its micro-pores. Hence, treatment of wool with fluorocarbon resin reduces such capacity [18]. Another study examining THS from fabrics found that ETS-exposed cotton and linen emitted more compounds with high volatility (such as ammonia and furfural) and less aromatic organics (such as pyrrole), than acetate [2].

Since clothing fabrics serve as moving sinks of ETS chemicals and potentially expose nearby persons thereto via off-gassing [16], it is beneficial to understand the emission characteristics of such chemicals in order to assess the exposure and potential health hazards of clothing-related THS. This study examines short-term release of volatile organics from ETS-exposed clothing fabrics, and assesses the differences in off-gassed chemicals among various fabrics.

2. Materials and methods

2.1. Study design

Four factors, including fabric type, structure, dyeing and contact time, were independently evaluated. Various fabrics were concurrently exposed to tobacco smoke in a controlled facility, and the chemicals off-gassed immediately following exposure were analyzed qualitatively (i.e., the numbers of species identified) and quantitatively (i.e., toluene-referenced concentrations or TRC), and compared across fabric types and test conditions.

2.2. Test protocol

2.2.1. Fabric

Natural fabrics – including cotton, linen, wool, silk, and man-made fabrics – including rayon, polyester, acetate and synthetic leather (PVC, lined with cotton) that are used for clothing were evaluated. All were purchased from a local fabric market and were used without further treatment/wash. Two identical samples, but in different colors (black and white), of each fabric were obtained, if available, and tested. Additionally, four cotton fabrics (typically used for dress-shirt, polo-shirt, trouser and jeans) were obtained to evaluate the potential effects of fabric structure on off-gassing. The characteristics of the fabrics such as yarn number, fabric count, thickness, density and structure were analyzed by Taiwan Textile

Research Institute (New Taipei City, Taiwan) following standard methods, and are listed in Table 1. Most of the fabrics were woven, but one cotton sample (typically used for polo shirt) was knitted and one synthetic leather (PVC) sample could not be categorized. The conditioned weight (or weight density, g/m²) of the fabrics ranged from 394.7 g/m² for a cotton sample (typically used for jeans) to 67.7 g/m² for acetate (typically used for garment lining), and correlated well ($r = 0.96$) with their thickness. The overall mean (±standard deviation) of weight density was 189.5 ± 101.2 g/m². Fabric colors, black or white, were judged by the researcher.

All fabrics were cut into 2 cm × 8 cm and equilibrated in a desiccator under room temperature for 24 h before testing. Blank fabrics were tested to determine the backgrounds, as carpets made of various fabrics emitted chemicals [19]. The backgrounds were mainly hydrocarbons (such as octane, nonane and tetradecane), aromatics (such as toluene, propylbenzene, trimethylbenzenes), and other compounds (such as p-isopropenylphenol). The backgrounds, if present, were subtracted from the experimental results.

2.2.2. Test facility and analytical protocol

Fabrics were exposed to ETS in a environment-controlled facility (ECF) which was made of stainless steel with internal dimensions of 83 cm(W) × 80 cm(D) × 100 cm(H) for specified periods. The air inside the facility is considered well-mixed as the average air mixing level is 84% [20]. The test conditions were 30 (±5%)°C, 75 (±5%) % relative humidity and one air change per hour. A lit cigarette (of an international brand, with tar and nicotine levels of 10 mg/cig. and 0.7 mg/cig., respectively) was placed upright in a holder, near the center of the air inlet to simulate side-stream smoke (but without exhaled main-stream smoke). Fabric samples were placed (hung) down-stream on a meshed stainless steel (measuring 60 cm × 65 cm) stand using paper clips (Fig. 1). After exposure to ETS (∼14 min, the time for the cigarette to burn completely), the exposed samples were promptly transferred into 22 ml head-space vials that had been pre-purged with pure nitrogen for 5 s, which were then sealed. After equilibration in a water bath at 37 °C (to mimic body temperature) for 15 min, the non-carbonyl organic chemicals that off-gassed from the ETS-exposed fabrics in the head-space of the sample vials were collected passively (in a diffusion-dependent manner) using a solid phase micro-extraction (SPME) fiber (CW/DVB, Supelco/Sigma–Aldrich, Inc., US)
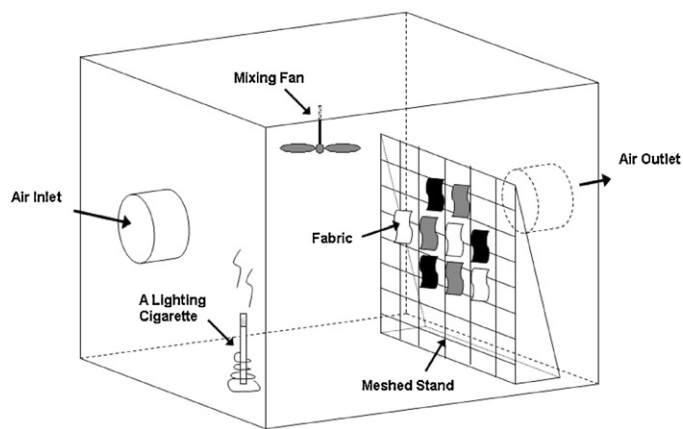
Fig. 1. Schematic representation of the test system.

for 10 min and then desorbed in a GC injector (250 °C for 10 min) for analysis. Sampling via SPME and detection using GC/MS (gas chromatography/mass spectrometry) has been utilized in analyzing mainstream and side-stream smoke components [21,22]. CW/DVB fiber was used as it adsorbed more chemicals than did the other fibers under current settings based on a preliminary test, even though the parameters had not been optimized. Similar procedures were followed to detect carbonyls, except that another SPME fiber (PDMS/DVB, 65 μm, Supelco/Sigma–Aldrich, Inc., US) pre-coated with o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) was employed [23]. Carbonyls can react with PFBHA to form a thermally stable derivative that is suitable for subsequent analysis using a GC.

Samples were analyzed using GC/MS (Model 6890plus GC and 5973 Mass Selective Detector (MSD), Hewlett Packard Inc., US). The GC oven temperature program was as follows: initial temperature of 40 °C, held for 2 min; rising to 120 °C at a rate of 10 °C/min, which temperature was held for 2 min, and then rising to 250 °C at a rate of 8 °C/min, which temperature was held for another 4 min. A capillary analytical column (Model HP-5 MS, 0.25 mm ID × 30 m, 0.25 μm thickness, Hewlett Packard Inc., US) was used for the separation, with helium as the carrier gas, running at 1.0 ml/min. The MSD was set to 250 °C, and 70 eV electron ionization was applied. Mass spectra were obtained by automatic scanning (Scan Mode) in the mass range m/z 40–500 at 2.2 scan/s. The interface between GC and MSD was also at 250 °C. The condition of MSD was ascertained daily before use following the manufacturer's auto-tune instructions. Such analytical application is adequate for current use, as it provides low detection limit (a few ng) and good precision (<5% variation among replicates) based on spiking tests using common aromatics such as toluene, ethylbenzene and xylenes. For calibration purpose, an approach of relative quantification based on toluene response was used. Specifically, a calibration curve of toluene was established by spiking 1 μl of six toluene standard solutions (in methanol, 20–600 μg/ml) into 22 ml head-space vials, with each vial containing a 2 cm × 8 cm piece of aluminum foil to mimic fabric volume, and analyzed following above procedure. The concentrations (TRC) of the target chemicals were estimated based on their respective GC response factors, which can be derived from the equation $y = 0.8891x$ ($r = 0.94$), in which y being the response factor (relative to toluene) and x being the carbon number ratio (relative to 7 for toluene) [24].

2.2.3. Test procedure

Four factors were evaluated by the following procedures. In addition to addressing the test objectives, the test scheme also considered the availability of samples. For example, black and white fabrics were used in sub-tests (1) and (2), respectively, as only black

wool and white cotton (polo-shirt) samples were obtained. In sub-test (3), the three fabrics tested had the same identical samples in both colors.

(1) *Effects of fabric (fiber) type* – One piece of each black fabric sample was hung in a random order on the testing stand in the controlled facility and exposed to tobacco smoke for ∼14 min and then analyzed by following the above protocol.
(2) *Effects of fabric structure* – Four white cotton fabrics (dress-shirt, polo-shirt, trouser and jean; $n = 3$ for each) were hung randomly on the testing stand and concurrently exposed to tobacco smoke in the controlled facility for ∼14 min. They were then analyzed.
(3) *Effects of dyeing* – Two colors, white and black, of the three fabrics, cotton (shirt), linen and polyester ($n = 3$ for each), were hung randomly on the stand, and concurrently exposed to tobacco smoke in the control-facility for ∼14 min. They were then analyzed.
(4) *Effects of contact time* – Two white fabrics, cotton (trouser) and polyester ($n = 6$ for each), were hung randomly on the test stand, and concurrently exposed to tobacco smoke in the controlled facility. At 4, 8 and 12 min, three pieces from each fabric were promptly removed and analyzed.

2.3. Data analysis

In the qualitative analysis, the analyzed chemicals were identified based on the similarity between the mass spectra indices and those of the NIST/Wiley Library System, using a matching scale from 0 to 100. Only compounds with a matching quality of over 80 were identified/reported. For the quantitative analysis, the GC area counts based on total ion current (TIC) from the instrument's Scan Mode for the frequently identified chemicals such as formaldehyde (as PFBHA derivative), furfural (C_5; molecular weight (MW) = 96), benzonitrile (C_7; MW = 103), naphthalene (C_{10}; MW = 128), decanal (C_{10}; MW = 156), tetradecanoic acid (TDA) (C_{14}; MW = 228) and n-hexadecanoic acid (n-HDA) (C_{16}; MW = 256) and common ETS chemicals such as 3-EP (C_7; MW = 105) and phenol (C_6; MW = 94) [21,25] were noted and converted to TRC. However, only GC area counts were used for data interpretation for formaldehyde. Notably, the amounts of these target chemicals were below the detection limits in un-exposed background fabric samples.

The differences between the TRC (or GC area counts) of selected chemicals in the experimental groups were statistically compared using student's t and ANOVA (Analysis of Variance) test with Tukey test as the post-hoc comparisons. The differences between the numbers of chemicals in the experimental groups were tested using the Mann–Whitney U test. A value of $p < 0.05$ was regarded as statistically significant. The coefficient of variation (CV) was used to represent variation in the data both between and within test groups. Error bars in each graph represent the standard deviations of triplicate measurements. Notably, although some fabrics have been used in different sub-tests, comparison of the data across experiments is not performed as between-test variations may exist.

3. Results

Table 2 lists the identified chemical species from the eight black fabrics after concurrent contact with ETS. The numbers of identified chemicals (with a matching greater than 80%) ranged from 13 (polyester and acetate) to 32 (linen). All of the exposed fabrics off-gassed formaldehyde, TDA, z11-hexadecanoic acid and n-HDA while seven out of the eight fabrics released furfural, benzonitrile, naphthalene and decanal. Natural fibers generally yielded more

Table 2
Chemicals off-gassed from various black clothing fabrics treated with tobacco smoke.

Compounds[a]	RT[b]	Fabric[c]								CAS #
		C	W	S	R	PV	P	A	L	
Toluene	3.47					*				000108-88-3
Hexanal	3.89				*					000066-25-1
2-Methyl-pyridine	4.22	*				*				000109-06-8
Furfural	4.35	*	*	*		*	*	*	*	000098-01-1
2-Methyl-1H-pyrrole	4.39					*				000636-41-9
3-Methyl-1H-pyrrole	4.51					*				000616-43-3
2-Furanmethanol	4.64	*		*					*	000098-00-0
Ethyl-benzene	4.79					*				000100-41-4
p-and o-Xylene	4.92	*	*			*		*		000106-42-3
Styrene	5.27		*			*				000100-42-5
2-Methyl-2-cyclopenten-1-one	5.48	*								001120-73-6
5-Methyl-2-furancarboxaldehyde	6.37	*		*			*		*	000620-02-0
1-Ethyl-3-methyl-benzene	6.38					*				000620-14-4
Benzaldehyde	6.43	*	*	*	*				*	000100-52-7
3-Ethenyl-pyridine	6.53	*	*	*		*			*	001121-55-7
Phenol	6.61	*	*	*	*				*	000108-95-2
Benzonitrile	6.78	*	*	*		*	*	*	*	000100-47-0
1,2,4-Trimethyl-benzene	6.93				*	*		*		000095-63-6
2-Propenyl-benzene	6.94					*				000300-57-2
Benzofuran	6.98	*				*				000271-89-6
1-Ethenyl-3-methyl-benzene	7.02					*				000100-80-1
Octanal	7.05	*		*	*					000124-13-0
3-Pyridinecarbonitrile	7.14	*							*	000100-54-9
D-Limonene	7.50	*	*		*	*			*	005989-27-5
2-Methyl-phenol	7.82	*							*	000095-48-7
Acetophenone	8.11	*								000098-86-2
4-Methyl-phenol	8.16			*				*		000106-44-5
Nonyl-cyclopropane	8.44					*				074663-85-7
1-Methyl-4-(1-methylethen benzene)	8.48					*				001195-32-0
2-Ethenyl-1,4-dimethyl-benzene	8.49	*								002039-89-6
Nonanal	8.66			*	*					000124-19-6
2-Ethyl-hexanoic acid	8.76				*	*		*	*	000149-57-5
Naphthalene	10.03	*	*	*	*	*		*	*	000091-20-3
Decanal	10.21	*	*	*	*	*	*		*	000112-31-2
2-methyl-benzofuran	10.60	*								004265-25-2
2-Methyl- 1H-pyrrolo[2,3-b]pyridine	10.64				*				*	023612-48-8
3-Phenyl-2-propenal	10.65		*							000104-55-2
2,3-Dihydro-1H-inden-1-one	11.39			*						000083-33-0
Indole	11.54			*						000120-72-9
2-Methyl-naphthalene	11.64	*	*	*	*				*	000091-57-6
1-Methyl-naphthalene	11.86	*	*	*	*				*	000090-12-0
2,7-Dimethyl-naphthalene	13.16								*	000582-16-1
2,6-Dimethyl-naphthalene	13.32								*	000581-42-0
3-(1-Methyl-2-pyrrolidin)pyridine	12.32			*	*			*		000054-11-5
2-(1-Methyl-2-pyrrolidin)pyridine	12.40			*						023950-04-1
1,2-dibutyl-cyclopropane	12.79								*	041977-32-6
1-Hexadecanol	12.80		*							036653-82-4
Tetradecane	12.90					*				000629-59-4
1,6-Dimethyl-naphthalene	13.37		*		*				*	000575-43-9
3-(3,4-Dihydro-2H-pyrrol)pyridine	13.38		*							000532-12-7
1,3-Dimethyl-naphthalene	13.39		*		*				*	000575-41-7
Nonyl-cyclopropane	14.08		*							074663-85-7
1-Heptadecanol	14.09				*		*		*	001454-85-9
Pentadecane	14.18					*				000629-62-9
2,3,6-trimethyl-naphthalene	14.73			*					*	000829-26-5
Cyclododecane	15.31			*					*	000294-62-2
(E)-9-Eicosene	15.32				*					074685-29-3
Heptadecane	15.40					*				000629-78-7
Tetradecanoic acid	17.24	*	*	*	*	*	*	*	*	000544-63-8
Pentadecanoic acid	18.67	*	*						*	001002-84-2
z-11-Hexadecanoic acid	20.14		*	*	*	*	*	*	*	002416-20-8
n-Hexadecanoic acid	20.61	*	*	*	*	*	*	*	*	000057-10-3
Formaldehyde[d]	7.07	*	*	*	*	*	*	*		086356-73-2
Acetone[d]	9.46	*		*		*	*	*		1000157-01-3
3-Methylbutanal[d]	11.77					*				1000288-17-6
Trans-4-hexenal[d]	12.06			*						1000288-15-3
glycolaldehyde[d]	12.39	*				*	*		*	1000157-01-9
3-Hexanone[d]	12.50		*	*	*		*		*	1000288-11-5
4-Methylpentanal[d]	13.61		*		*		*			1000288-16-6
Total		28	23	29	24	31	13	13	32	

[a] Only compounds with a matching quality of over 80 of the NIST/Wiley Library System are reported.
[b] GC retention time.
[c] C: Cotton–shirt; W: Wool–trouser; S: Silk; R: Rayon; PV: PVC-cotton lined; P: Polyester; A: Acetate; L: Linen. All fabrics appeared in black color.
[d] Identified as PFBHA-oxime (analyzed via PFBHA-coated SPME fiber).
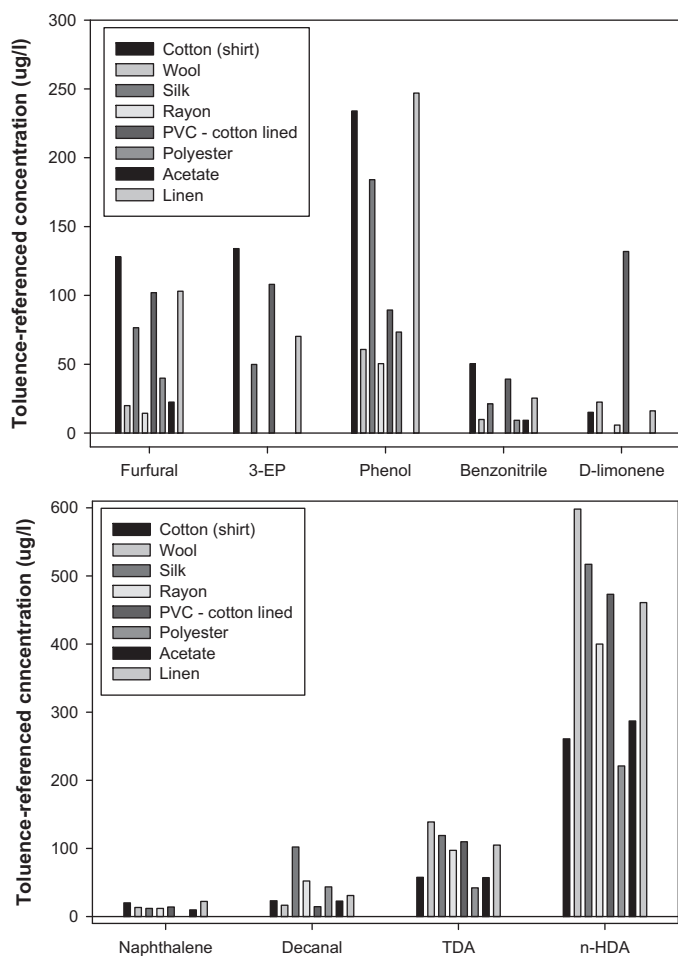* Identified under current analytical setting.

Fig. 2. Comparisons of concentrations (toluene-referenced) of selected chemicals off-gassed from black clothing fabrics treated with tobacco smoke.

identified chemicals than did the man-made fibers, except rayon, which yielded 24 identified chemicals.

Fig. 2 presents concentration profiles of selected chemicals emitted from eight black fabrics. The TRC for the selected chemicals varied greatly among the fabrics. Generally, fabrics emitted higher concentrations of chemicals of both low molecular weight (such as phenol) and high molecular weight (such as n-HDA). Mean CVs of TRC for the selected chemicals among fabrics ranged from ∼34% (phenol) to ∼360% (D-limonene), with an overall mean of 116%.

Fig. 3 shows the TRC of selected chemical off-gassed versus their molecular weights among grouped clothing fabrics. Cotton and linen emitted higher concentration of chemicals of low molecular weight (<100) than did wool, silk and synthetic fabrics, while wool and silk off-gassed higher concentration of high molecular weight (>250) chemicals than other fabrics. Fig. 4 presents the TRC of selected chemical off-gassed versus their respective carbon numbers among eight clothing fabrics.

Fig. 5 displays the test results for four white cotton fabrics (typically used for dress-shirt, polo-shirt, trouser and jeans) following concurrent exposure to ETS. The fabric structures statistically significantly ($p < 0.05$, ANOVA test) affected the amounts emitted on all test chemicals, except decanal and TDA. The fabric used for the polo shirt off-gassed significantly more ($p < 0.05$) furfural, 3-EP and benzonitrile than did the other three fabrics, followed in order by the cotton for trouser, the jean and the shirt, but significantly less ($p < 0.05$) n-HDA than did the other three fabrics. However, the jean emitted more ($p < 0.05$) D-limonene and naphthalene than did the other fabrics, followed in order by the polo-shirt, the trouser and
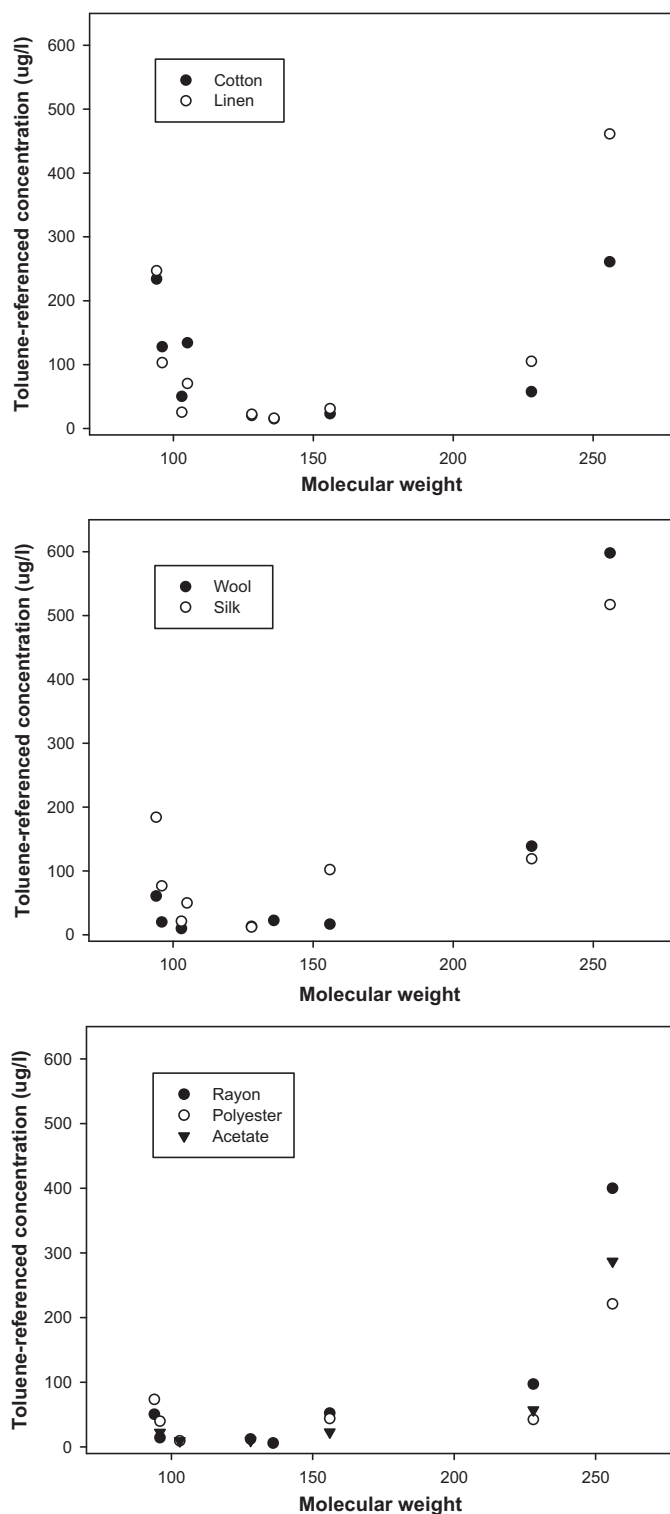

Fig. 3. Concentrations (toluene-referenced) of selected chemical versus their molecular weights off-gassed among grouped clothing fabrics treated with tobacco smoke.

dress-shirt fabrics, which order matched the order of their weight densities. Mean CVs of TRC for the selected chemicals among four cottons ranged from 58.7% (D-limonene) to ∼15.2% (TDA), with an overall mean of 39.4%.

Fig. 6 presents the variation of TRC of each of the selected chemicals emitted with the fabric colors (black and white) for cotton, linen and polyester following concurrent exposure to ETS.
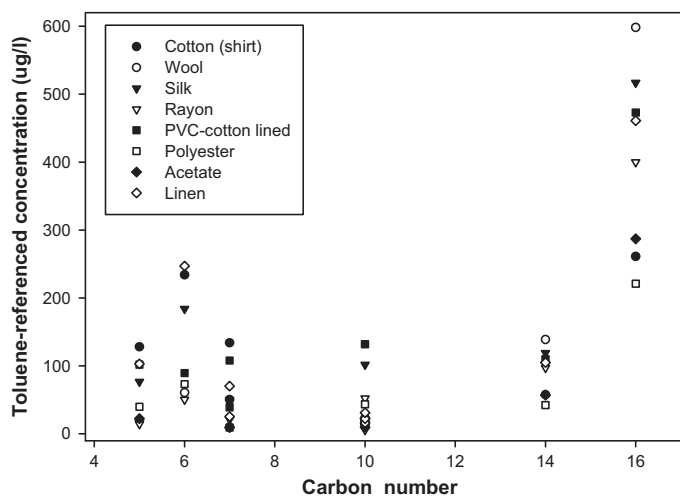
Fig. 4. Concentrations (toluene-referenced) of selected chemical versus their carbon numbers off-gassed from black clothing fabrics treated with tobacco smoke.
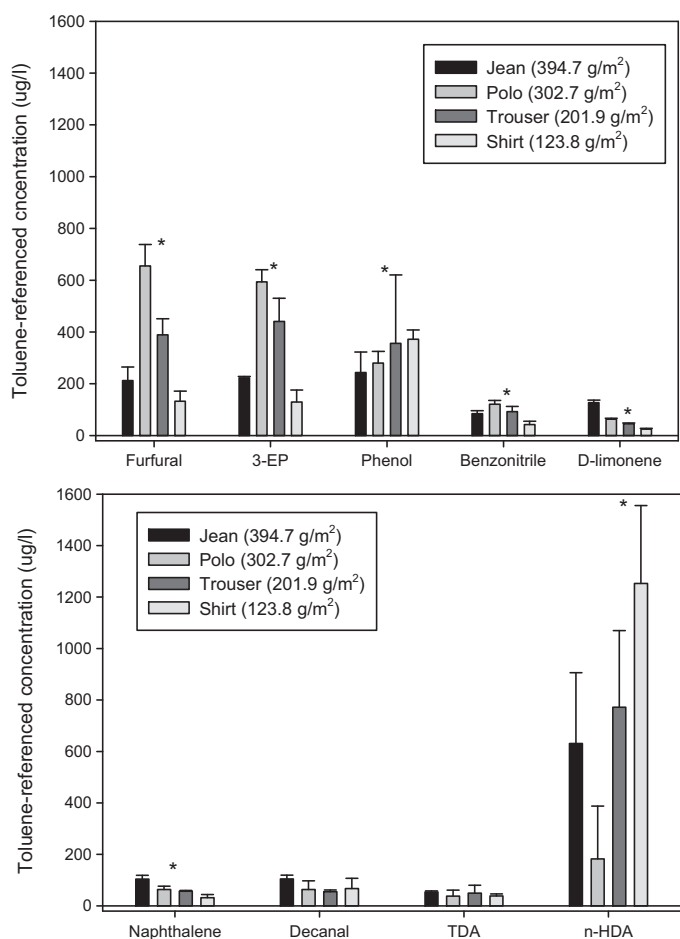

Fig. 5. Effect of fabric structure on the concentrations (toluene-referenced) of selected chemicals off-gassed from ETS-exposed fabrics (* significantly different at $\alpha = 0.05$; Error bars represent standard deviation of triplicates).
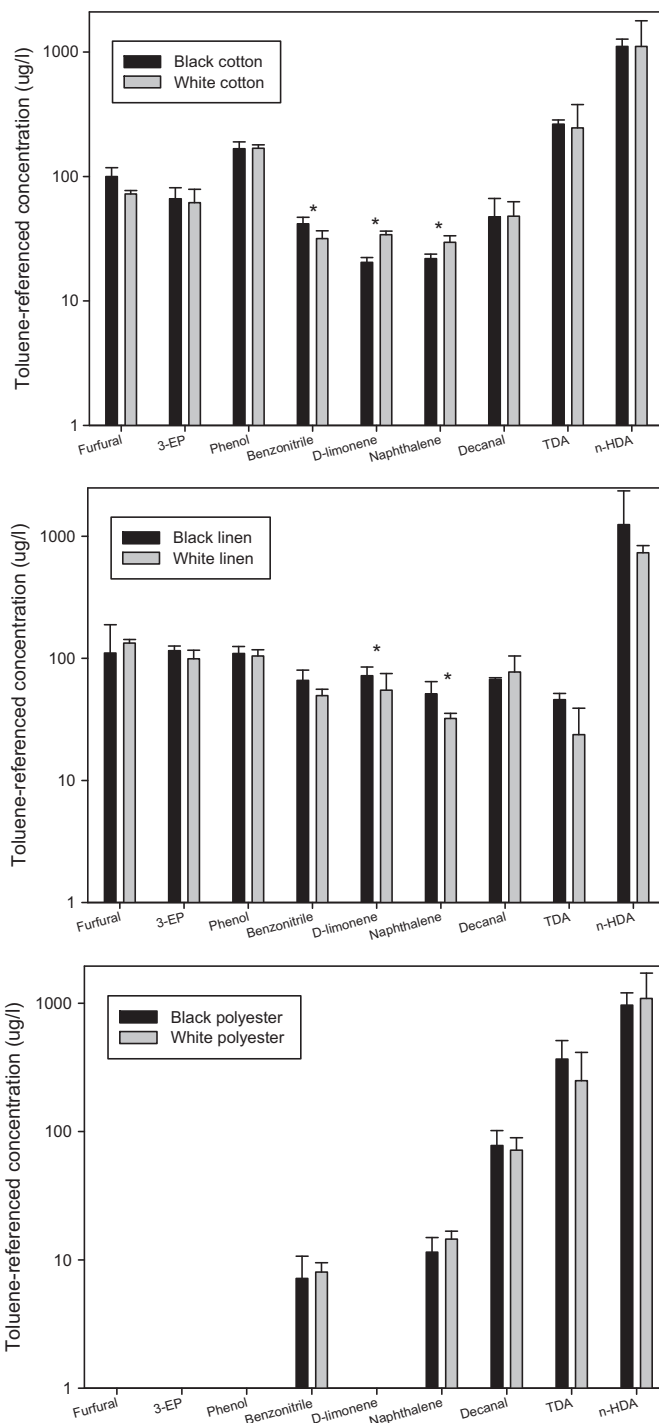

Fig. 6. Effect of dyeing on the concentrations (toluene-referenced) of selected chemicals off-gassed from ETS-exposed fabrics (* significantly different at $\alpha = 0.05$; Error bars represent standard deviation of triplicates).

Table 3 shows the numbers of identified chemicals off-gassed from two ETS-exposed clothing fabrics following exposure for various times. Cotton that was exposed to ETS for 12 min off-gassed statistically significantly more chemical species than did cotton that was exposed for 8 min ($p < 0.05$, Mann–Whitney U test), but for 4 min contact time the data could not be compared statistically due to high variation. However, the exposure time did not significantly ($p > 0.05$) affect the number of identified chemicals from polyester, as well as the four cottons, or the concurrently exposed differently colored fabrics (data not shown).

Generally, the color did not significantly ($p > 0.05$, t-test) affect the amount of chemicals that were off-gassed from the test fabrics, with exception of benzonitrile, D-limonene, naphthalene and formaldehyde for cotton, D-limonene and naphthalene for linen, and formaldehyde for polyester.

Table 3
Numbers of chemicals off-gassed from ETS-exposed fabrics for different exposure times.

Contact Time (min)	Numbers of compounds[a]	
	Cotton[b,*]	Polyester[b]
8	9	11
	12	14
	15	11
12	19	13
	23	11
	25	14

[a] Compounds with a matching quality of over 80 of the NIST/Wiley Library System, including carbonyl compounds; data represent triplicate result.
[b] Cotton typically used for trouser, same as Cotton-4 in Table 1; Polyester is same as that tested in Table 1, except color.
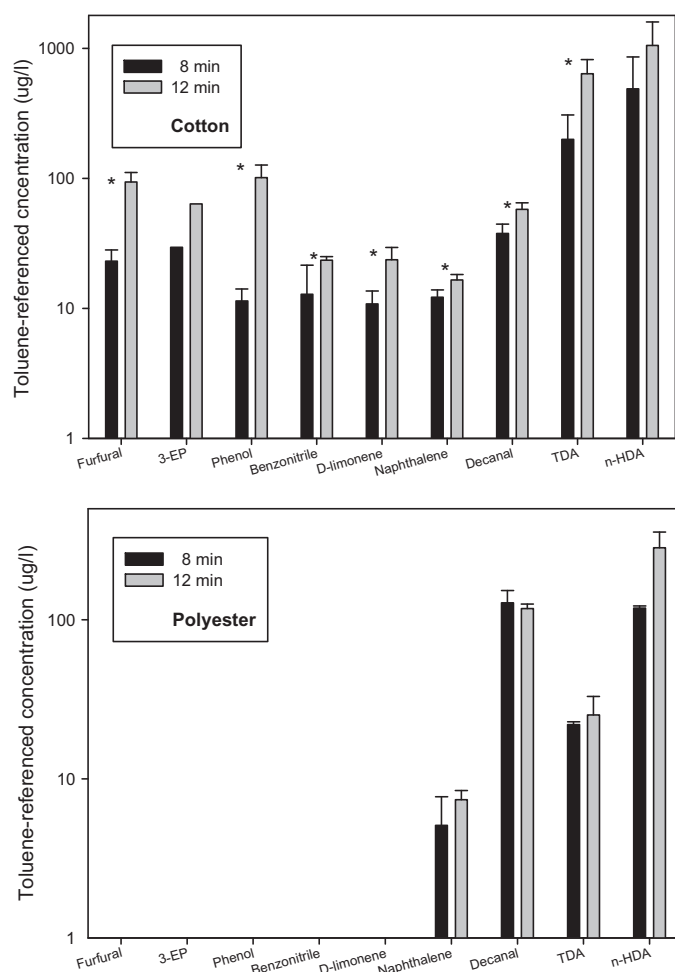[*] Statistically significant ($p < 0.05$), 1-tail Mann–Whitney U test.

Fig. 7. Effect of contact time on the concentrations (toluene-referenced) of selected chemicals off-gassed from ETS-exposed fabrics (* significantly different at $\alpha = 0.05$; Error bars represent standard deviation of triplicates).

Fig. 7 displays the test results concerning the effect of contact time on the TRC of chemicals emitted from cotton and polyester. Samples of cotton that were exposed to ETS for 12 min emitted more ($p < 0.05$, t-test) of the selected compounds, except n-HDA and formaldehyde, than those that were exposed for 8 min. However, no statistical comparison concerning 3-EP could be performed because of failures in the area integrations for the two samples. For polyester, increasing the exposure time (8 vs. 12 min) did not significantly increase ($p < 0.05$) the amounts of chemicals emitted.

The experimental data for Figs. 2 and 5–7 are listed in Appendix.

4. Discussion

The impact of sink phenomena on indoor air quality has attracted increasing attention as the sorption of VOCs/SVOCs to object surfaces and their diffusion into porous materials can significantly reduce peak concentrations, alter their temporal profiles and even cause an episodic release of a chemical. Individual components of ETS are produced in relatively constant ratios, but their concentrations indoors are greatly affected by transformation and removal processes, as well as dilution volume and ventilation. Various controlled studies have investigated the sorption/desorption phenomena of certain ETS-related chemicals, such as 3-EP and nicotine, from different surfaces and textiles [11,16]. SVOCs (such as nicotine) show much greater sorption than VOCs (such as 3-EP) because SVOCs may undergo dual-sink processes with indoor materials [16], while the sorption of VVOCs such as 1,3-butadiene and benzene on indoor surfaces is minimal [7,8]. Nonetheless, the emission characteristics of chemicals off-gassed from ETS-exposed clothing fabrics have not been systematically evaluated. One study revealed that the amounts of chemicals, particularly those of high-volatility, off-gassing from ETS-exposed fabrics declined rapidly after exposure ceased [2], suggesting that VVOCs in the ETS may be retained temporarily on fabric structures and released easily. Thus the current results represent a scenario of ETS-related chemicals released from fabrics shortly following exposure, and therefore may not be applicable to mid- to long-term re-emission of these ETS chemicals.

4.1. Characteristics of chemical released from fabrics

The numbers and concentrations of off-gassed chemicals vary substantially among ETS-exposed fabrics (Table 2 and Fig. 2). Specifically, cotton and linen off-gassed more polar and volatile compounds, such as furfural, phenol and benzonitrile, than did polyester or acetate, but the releasing of less polar and/or less volatile compounds, such as decanal, TDA and n-HDA, from cotton were comparable of those from polyester and acetate. This is compatible with previous result that cotton and linen off-gassed more compounds with high volatility (such as ammonia and furfural) than acetate shortly following contact with ETS [2]. Although these data were not statistically evaluated due to limited sample size, these relationships are considered to be valid as the variation among triplicate measurements in similar settings was generally small.

The relationships of chemical emissions versus the respective molecular weights (Fig. 3) indicate that natural fibers of plant origin, i.e., cotton and linen, off-gassed higher concentrations (TRC > 100 μg/l) of chemical with low molecular weight (~100 or less) than did natural fibers of animal origin, i.e., wool and silk, and synthetic fibers. Conversely, wool and silk off-gassed more chemicals of high molecular weight (>200), such as TDA (TRC > 100 μg/l) and n-HDA (TRC > 500 μg/l), than did cotton, linen and synthetic fibers. However, the sum of the concentration of nine target chemicals for cotton (923 μg/l) was nearly the same as that of wool (880 μg/l), while silk (1082 μg/l) had similar total concentration as linen (1081 μg/l). Wool fibers are known to exhibit extensive sorption and incomplete desorption because the high reactivity of their structure facilitates chemical sorption, while presence of many pores favors physical sorption [26].

Fabrics generally off-gassed higher concentrations of chemical that comprise of six carbons (i.e., phenol) than those of five (i.e., furfural) or seven carbons (i.e., 3-EP and benzonitrile) (Fig. 4). Thus molecular weight appears to be a better predictor,

than carbon number, in terms of short-term chemical emission from ETS-treated fabrics. The differences in emission characteristics (chemical species and concentration) among ETS-exposed fabrics may contribute to the uniqueness of their perceived odors.

Previous study has found that cotton and wool gained nearly the same percentage weight upon exposure to ETS [17], but the characteristics of ETS chemical off-gassing between the two fabrics varied greatly (see above discussion). Conversely, rayon off-gassed more chemical species and higher total concentration of nine target chemicals (632 µg/l), than polyester (430 µg/l) and acetate (409 µg/l) (Table 2 and Fig. 3, bottom), consistent with the previous finding that rayon gained significantly more weight than the other man-made fibers upon exposure to ETS. Thus, the weight-gain of fabrics after contact with tobacco smoke may not be a good indicator of chemical re-emissions, even though a strong correlation has been identified between moisture gained and smoke absorbency [17].

The IARC has confirmed that exposure to second-hand smoke is carcinogenic to humans (Class 1) [27]. The qualitative findings in this study (Table 2) reveal the carcinogenic potential of exposures to THS resulting from ETS-exposed fabrics, since a known human carcinogen, formaldehyde, was identified in all of the current fabric samples, and several possible human carcinogens (Class 2B) such as styrene, ethylbenzene, benzofuran and naphthalene were also identified. Nonetheless, the health risk associated with exposures to these chemicals depends on concentration and time, and consequently warrants further investigation.

4.2. Effects of fabric structure

The data herein indicate that the fabric structure (for a particular material) significantly affects chemical off-gassing. That polo fabric had significantly ($p < 0.05$) higher TRC for chemicals with molecular weight of ~100 (such as furfural, 3-EP and benzonitrile, with mean TRC of 656, 594 and 121 µg/l, respectively) than did other cotton fabrics, (Fig. 5). The knitted pattern is a likely cause of this difference as polo fabric (with a porous style) may have a greater contact surface area, than the other three woven-pattern cotton fabrics, and facilitate adsorption and re-emission of chemicals with low molecular weight. However, for chemicals with higher molecular weight (>250, n-HDA) the TRC for polo fabric was the lowest (183 µg/l). Nonetheless, the variation in the total TRC from nine target chemicals across four cottons was small (CV of 11.6%; means of 1784, 2061, 2257 and 2092 µg/l for jean, polo-shirt, trouser and dress-shirt, respectively).

Moreover, the weight density of the fabric (g/m², Table 1) did not seem to influence off-gassing, except in the cases of D-limonene and naphthalene, for which the TRC were proportional to the weight densities of the fabric. No other relationships between the chemicals releasing and fabric characteristics can be identified.

These data also indicate that the within-fabric variations in the TRC (mean CV of 39.4% for cotton) are less than those between fabric types (mean CV of 126%).

4.3. Effects of dyeing

Color treatments of fabrics, such as by dyeing or printing, may affect the absorption capacity and subsequent releasing of those fabrics [17]. Although the profiles of dye chemicals were unavailable, current results (Fig. 6) indicate that fabric color minimally affected off-gassing since both identical fabrics showed very similar chemical profiles and only some chemicals, specifically benzonitrile, D-limonene, naphthalene and formaldehyde for cotton, D-limonene and naphthalene for linen, and formaldehyde

for polyester, showed statistically significantly difference between the two tested colors of the fabrics. However, such differences were relatively small, with the mean absolute differences in TRC between the two-color cottons of 24%, 67%, 35% for benzonitrile, D-limonene, naphthalene, respectively. These chemicals are characterized with medium polarity/volatility. Additionally, white cotton off-gassed significantly more D-limonene and naphthalene than did black cotton whereas reverse relationships were found for linen.

Moreover, finishing process, such as coating with resin, can also influence sorption/reemission [18], this study evaluated two-color samples from the identical fabrics, so the effects of structure and finishing on emission are considered to be negligible in this subtest.

4.4. Effects of contact time

As the uptake of ETS chemicals by indoor materials is known to be a sorption process, the duration of contact becomes an important factor in determining the amounts of chemicals adsorbed and re-emitted [28]. The current findings (Table 3 and Fig. 7) confirmed that cotton that was exposed for 12 min off-gassed significantly more chemicals (except n-HDA and formaldehyde) than did same cotton that was exposed for 8 min. The mean TRC (of the seven compounds that showed significant differences) for 12-min exposed cotton was 204% (ranging from 35.8% for naphthalene to 790% for phenol) higher than those of 8-min exposed cotton. However, longer contact time (i.e. >12 min) with ETS may result in saturation in adsorption and thus potentially affect the chemical re-emission of fabrics. For polyester, the TRC did not increase significantly with the contact time tested.

Notably, the amounts of formaldehyde off-gassed from either fabric did not increase with contact time from 8 to 14 min. This could be reasonably explained by depletion of the derivatizing agent, PFBHA, which reacted with reactive carbonyls during sampling. The amounts of formaldehyde and other target chemicals off-gassed from cotton exposed for 4 min were lower than those of 8 min (data not shown), evidencing the above postulation. Therefore, exposure of clothing fabrics, and particularly cotton fiber, in a smoking environment should be as brief as possible to minimize sorption and subsequent off-gassing/re-emission.

4.5. Limitations of findings

This work provides information on relative releasing of target chemicals from selected fabrics under the same exposure condition, and was not intended to examine the emission/desorption rate of volatile chemicals from exposed fabrics. Hence, further studies on the emission kinetics of ETS-related chemicals or personal exposures under real-world scenarios will be useful in elucidating the magnitudes of chemical exposures and risks associated with THS via clothing.

Due to the complexity of fabric (Table 1) and the current findings that fiber type, structure, dyeing and contact time affecting the release of ETS chemicals, as discussed above, the results presented herein should be treated as case-specific. Nonetheless, these findings can be applied to other indoor objects such as carpet, chair covering, and drapes that are made of similar fabrics, and related to potential exposures to the general public as all fabrics tested were readily available in fabric markets.

The chemicals identified may not be exhaustive because of analytical and methodological limitations. For instance, nicotine has been found to be adsorbed faster than other gas-phase components and is released more slowly from indoor materials [16]. The samples herein were tested under static conditions immediately following exposure to ETS chemicals, nicotine was likely

to have been retained in the fabrics, and therefore not detected in any of the fabric sample, as also demonstrated previously [2].

5. Conclusion

Exposure to tobacco-related chemicals through ETS adversely affects human health in a manner similar to active smoking. This fact has led to the banning of smoking in public places. Controlling other involuntary pathways, such as those that involve third-hand smoke, may be the next step in further reducing exposure to some ETS carcinogens.

Characterization of the sorption/emission behaviors between ETS chemicals (a few thousands species) and various fabrics is a complicated task. This investigation explored the short-term release of selected volatile and semi-volatile organics from ETS-exposed fabrics, and verified that fiber type, fabric structure, dye applied and contact time significantly affect the retention of ETS chemicals and their subsequent releasing. Natural materials such as cotton and linen generally released more chemicals than do man-made ones. Accordingly, clothing fabrics made from natural fibers may be an important source of tobacco-related chemicals following exposure to ETS. Natural fibers of plant origin emitted differently from those of animal origin.

Acknowledgements

Appendix–Experimental data

Data for Fig. 2 – TRC of selected chemicals emitted from ETS-exposed black fabrics.

Compound	Carbon #	Mol. wt.	Fabric							
			Cotton	Wool	Silk	Rayon	PVC-cotton	Polyester	Acetate	Linen
Furfural	5	96	128[a]	20.0	76.6	14.4	102	39.9	22.5	103
3-EP	7	105	134	ND	49.9	ND	108	ND	ND	70.3
Phenol	6	94	234	60.7	184	50.4	89.4	73.3	ND	247
Benzonitrile	7	103	50.3	9.9	21.2	ND	39.2	9.3	9.3	25.4
D-limonene	10	136	15.1	22.5	ND	5.9	132	ND	ND	16.2
Naphthalene	10	128	20.2	13.3	12.0	12.1	14.3	ND	9.9	22.3
Decanal	10	156	23.1	16.7	102	52.4	14.6	43.7	22.8	31.1
TDA	14	228	57.6	139	119	97.2	110	42.3	57.1	105
n-HDA	16	256	261	598	517	400	473	221	287	461
			Sum							
			923	880	1082	632	1083	430	409	1081

[a] Toluene-referenced concentration (μg/l).

Data for Fig. 5 – TRC of selected chemicals emitted from white cotton fabrics following concurrent exposure to ETS.

Compound	Cotton fabric							
	Jean		Polo		Trouser		Shirt	
Furfural	213[a]	(52.1)[b]	656	(82.3)	389	(62.3)	133	(38.9)
3-EP	223	(5.6)	594	(47.0)	441	(88.9)	130	(46.1)
Phenol	243	(79.4)	280	(44.5)	356	(265)	372	(36.2)
Benzonitrile	84.4	(11.5)	121	(14.7)	92.5	(20.3)	42.3	(12.8)
D-limonene	127	(1.0)	63.1	(3.7)	45.6	(2.8)	24.7	(2.9)
Naphthalene	104	(14.4)	63.4	(13.5)	56.8	(2.9)	32.0	(12.3)
Decanal	105	(14.6)	64.1	(33.4)	55.2	(6.2)	66.9	(40.7)
TDA	54.0	(4.4)	38.0	(23.2)	49.1	(30.8)	38.6	(8.0)
n-HDA	631	(275)	183	(206)	772	(298)	1252	(303)
Formaldehyde	163262272[c]	(23902551)	189751270	(6528571)	185081632	(1377739)	86718992	(17524630)

[a] Mean of toluene-referenced concentration (μg/l).
[b] Standard deviation (SD) of triplicates.
[c] GC area count.

Data for Fig. 6 – TRC of selected chemicals emitted from two-color cotton, linen and polyester fabrics following concurrent exposure to ETS.

Compound	Cotton		Linen		Polyester	
	Black	White	Black	White	Black	White
Furfural	99.6(17.9)[a]	72.3(4.7)	110(7836)	133(9.4)	ND	ND
3-EP	66.1(15)	61.6(17.2)	115(10.9)	99.3(17.4)	ND	ND
Phenol	167(22.2)	168(11.1)	110(15.5)	105(13.0)	ND	ND
Benzonitrile	41.7(5.4)	31.7(4.8)	66.1(14.2)	49.5(6.3)	7.2(3.5)	8.0(1.5)
D-limonene	20.4(1.9)	34.0(2.3)	72.2(12.8)	54.9(20.1)	ND	ND
Naphthalene	21.9(1.9)	29.5(3.8)	51.2(13.3)	32.1(3.3)	11.5(3.5)	14.5(2.2)
Decanal	47.3(19.1)	47.9(14.7)	67.2(2.1)	77.2(27.6)	77.8(24.0)	71.6(17.9)
TDA	263(21.5)	246(132)	45.9(5.8)	23.7(15.3)	366(146)	249(166)
n-HDA	1109(159)	1110(669)	1248(1112)	735(106)	966(240)	1090(629)
Formaldehyde	99267698[b](3282284)	97844781 (19512982)	75345450 (1329432)	76532704 (2756506)	76116760 (942860)	85466618 (2261002)

[a] Mean (SD) of toluene-referenced concentration (μg/l).
[b] GC area count; ND, below detection limit.

Data for Fig. 7 – TRC of selected chemicals emitted from cotton and polyester fabrics with different contact time with ETS.

Compound	Cotton		Polyester	
	8 min	12 min	8 min	12 min
Furfural	23.1(5.1)[a]	93.9(17.3)	ND	ND
3-EP	29.6 (NA)	63.7(NA)	ND	ND
Phenol	11.4(2.7)	101(25.5)	ND	ND
Benzonitrile	12.8(8.7)	23.4(1.6)	ND	ND
ᴅ-limonene	10.8(2.8)	23.7(5.8)	ND	ND
Naphthalene	12.2(1.7)	16.5(1.7)	5.1(2.6)	7.4(1.0)
Decanal	37.7(6.8)	57.8(7.2)	128(25)	117(7.8)
TDA	200(108)	639(180)	21.9(0.9)	25.2(7.8)
n-HDA	489 (373)	1056(543)	118(3.8)	284(71.8)
Formaldehyde	112696157[b](12593972)	121201324 (24537455)	54745491 (4252847)	55352161 (3612418)

[a] Mean (SD) of toluene-referenced concentration ($\mu g/l$).
[b] GC area count; NA, not available; ND, below detection limit.

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