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Impacts of texture properties and airborne particles on accumulation of tobacco-derived chemicals in fabrics

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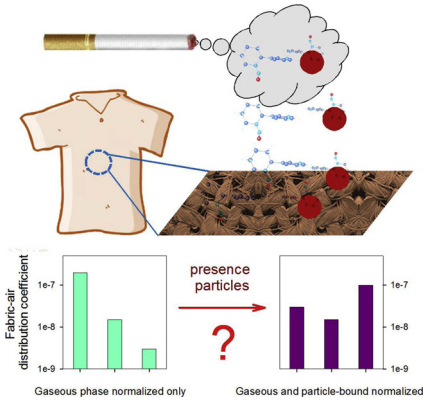
GRAPHICAL ABSTRACT



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ABSTRACT

Vapor-phase constituents of tobacco smoke are known to accumulate on clothing surfaces; however, the significance of texture properties, such as specific surface area, porosity, and surface roughness, and airborne particles to the sorption capacity of fabrics has not been adequately addressed. In the present study, cotton (t-shirt) and polyester (pajama and lab coat) fabrics were exposed to cigarette smoke containing gaseous and particulate tobacco-derived compounds (e.g., N-nitrosamines). Fabric-air distribution coefficients and particle deposition fluxes were then determined to evaluate the accumulation of the target analytes. Appreciable amounts of N'-nitrosoanabasine (NAB) and 4′-(nitrosomethylamino)-1-(3-pyridyl)-1-butanone (NNK) were detected in all three fabric types although particle-bound NAB and NNK were found only in cigarette smoke. In addition, the root mean square surface roughness heights for three types of clothes were within the same order of magnitude. As such, the deposition fluxes of particle-bound N'-nitrosonornicotine (NNN) and NNK to fabric surface may have contributed to 6–20% and 56–100% of total NNN and NNK in fabrics, respectively, estimated based on the assumed deposition velocity of 0.65 m h^{-1}. Apparently, the sorption capacity of fabrics can be greatly influenced by particle-bound compounds on clothing surfaces, resulting in either over- or under-estimation of fabric-air distribution/partitioning coefficients.

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1. Introduction

There is a growing worldwide concern regarding dermal exposure to airborne chemicals via fabrics-mediated transport in a non-occupational exposure context, particularly related to tobacco smoke exposure [1–5]. Fabrics are well known to accumulate/adhere substantial amounts of various substances, such as phenols, indoles, tobacco-specific N-nitrosamines, and polycyclic aromatic hydrocarbons (PAHs), many of which possess carcinogenic and tumor accelerating properties [4,6,7]. For example, urine samples from individuals wearing clothes pre-exposed to tobacco smoke contained greater amounts of nicotine and its metabolites (cotinine and 3OH-cotinine) than those from the participants wearing clean clothes [3]. Similarly, dermal uptake from clothes pre-exposed to phthalates (diethyl phthalate and di(n-butyl) phthalate) also exceeded that from bare-skinned participants [8]. Even more alarming is that mouthing of a small piece of fabric pre-exposed to tobacco smoke by a toddler resulted in the child receiving up to 2.2 μg d^{-1} of nitrosamines, a concentration approximately 16 fold greater than the inhalation exposure of a passive smoker (0.14 μg d^{-1}) [9].

Airborne particles may carry semi-volatile organic compounds (SVOCs) via sorption, coagulation, and /or condensation and deposit on or into the surfaces of fabrics [10]. Furthermore, previous simulations indicated that particles can be captured when depositing on rough surfaces [11,12], and enhance the mass transfer [13]. For example, the time scale for di(2-ethylhexyl) phthalate to reach equilibrium between the gaseous phase and a sorptive surface could be decreased from 3.0 to 0.45 years at the presence of particles [13]. However, such added contributions of SVOCs are overlooked either in fabrics-mediated transport modeling or in field sampling [14–17]. This is especially concerning, as some SVOCs have shown a greater dermal permeability than air-skin mass transferability [15,18], which could lead to substantial erroneous risk assessments results.

The equilibrium fabric-air distribution coefficient is a key parameter describing the sorption of airborne compounds by fabrics [14,19,20]. The sorption capacity of a fabric is mostly related to the fabric's chemical and physical properties [21–23], such as the type and number of functional groups and irregular surfaces or porous structures in the fabric [21–24]. Specific fabric-air distribution coefficients include those normalized by the mass, volume, and planar surface area of fabrics or Brenauer-Emmett-Teller (BET) based surface area [25–27]. However, these normalization methods have not been examined adequately at the presence of particles, as fabrics are supposedly exposed to both gaseous and particulate chemicals in commonly encountered scenarios.

The present study was conducted to examine the significance of airborne particles to the sorption of fabrics by quantifying the fabric-air distribution coefficients of tobacco-derived compounds in an occupied indoor environment via cigarette smoke generated by participants. Gaseous and particle samples, as well as clothing samples, were collected and analyzed for phenol, indole and their methyl-derivative compounds, menthol (cigarette additive), and N-nitrosamines. The impacts of the texture properties (e.g., specific surface area, porosity, surface roughness. and micro-surface structure of fabrics) and airborne particles on the accumulation and fabric-air distribution were examined, and the deposition fluxes of these compounds to fabric surfaces were estimated.

2. Materials and methods

2.1. Materials

Target analytes include liquid phenol-mix 604 (Supplementary Data List S1) purchased from O2si Smart Solutions (Charleston, NC, USA), solid indole from AccuStandard (New Haven, CT, USA), and solid 3-methylindole from Tokyo Chemical Industry (Tokyo, Japan). The solid standards of N'-nitrosoanabasine (NAB), N'-nitrosoanatabine (NAT), 4′-(nitrosomethylamino)-1-(3-pyridyl)-1-butanone (NNK), and N'-nitrosonornicotine (NNN) were obtained from Toronto Research Chemicals (Toronto, Canada). Naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}, benzo(*ghi*)perylene-d_{12}, N'-nitrosoanatabine-2,4,5,6-d_4 (NAT-d_4), and 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone-d_4 (NNK-d_4) were used as surrogate standards, whereas fluoranthene-d_{10}, pyrene-d_{10}, dibenzo(*a*,*h*) anthracene-d_{14}), N'-nitrosoanabasine-d_4 (NAB-d_4), and N'-nitrosonornicotine-d_4 (NNN-d_4) were used as internal standards. The isotopically labeled N-nitrosamines were purchased from Toronto Research Chemicals Inc. (Toronto, Canada) and all other standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Cigarette and fabric materials were standard commercial products. Two cigarette brands, Double Happiness (flue-cured; China Tobacco Guangdong Industrial) and KENT (blended, menthol-flavored; British-American Tobacco (Singapore)), were purchased from a local supermarket. Both of these products are popular among smokers, but have quite different tar and nicotine contents, i.e., 11 and 1.2 mg cigarette^{-1} for Double Happiness and 1 and 0.1 mg cigarette^{-1} for KENT, respectively. Three types of clothes, i.e., t-shirt (cotton), pajamas, and lab coat (both the pajamas and lab coat were polyester fiber), were purchased from local clothing stores. Before use, all clothes were cut into ~15 × 15 cm^2 pieces, which were pre-cleaned by three sonication cycles with dichloromethane [28]. Dried and cleaned fabrics were then stored at –20 °C to minimize potential contamination until use.

2.2. Sample collection

Sampling was conducted on four consecutive weekends in a room of 73 m^3 with a few furnishings. Windows were open slightly and the room temperature was maintained at 24 ± 1 °C via an air-conditioner during sampling. Indoor air was further agitated with a fan. The 12 to 15 participants in each trial consumed at least 4 cigarettes each during the smoking sessions (70 min), and each brand of tobacco was tested in duplicate. The fabrics (each clothing type in triplicate) were hung vertically 1.2–1.5 m above the floor and the distance between the fabrics and smokers ranged from 0.5 to 2.0 m when smoking was initiated. Eleven size-fractioned particle and gaseous samples were collected using a 10-stage cascade uniform deposit impactor (MSP Corporation, Shoreview, MN) coupled with a polyurethane foam (PUF) sampler [29], from three time points, including pre-smoking (12 h), smoking (70 min), and post-smoking (12 h), whereas clothing samples were collected only during the smoking event (70 min). Sampling for the smoking sessions was ended 10 min after the last cigarette was consumed. Overall, 132 size-fractioned particle samples, 12 gaseous samples, and 36 fabrics samples were obtained (List S2). Particle samples were stored in membrane cell holders, whereas PUFs and clothes were wrapped with aluminum foil and then stored with PE zipper bags. All samples were stored at –20 °C until analysis.

2.3. Sample extraction and instrument analysis

The gaseous and fabrics samples were spiked with the surrogate standards, and then Soxhlet extracted with 200 mL of mixed hexane, dichloromethane, and acetone (2:2:1 in volume) for 48 h. Each extract was concentrated to 5 mL, solvent-exchanged to hexane, filtered, and further concentrated to 1 mL with a Biotage TurboVap II (Uppsala, Sweden). Each extract was fractionated into two fractions using a glass column filled with 2 g of neutral silica gel and 1 cm of anhydrous sodium sulfate from bottom to top. The first fraction containing phenols, indoles, and menthol was eluted from the column with 20 mL of dichloromethane. The resulting eluant was concentrated, solvent-exchanged to hexane, and further concentrated to 500 μL for gaseous samples or 50 μL for fabric samples under a gentle stream of N_2. The second fraction, containing nitrosamines, was collected by further eluting the column with 20 mL of methanol and concentrated to 50 μL

for both sample types. The second fraction was further filtered through a 0.22 μm nylon filter, and two fractions were spiked with the internal standards before instrument analysis. Particle samples were spiked with the surrogate standards and sonicated three times, each with 20 mL of hexane, dichloromethane, and acetone mixture (2:2:1 in volume). The subsequent procedures used for particle samples were identical to those for gaseous and fabrics samples.

The first fraction was analyzed with a Shimadzu GCMS-2010 Ultra with a DB-5MS capillary column (30 m × 0.25 mm i.d. with 0.25 μm film thickness). One microliter of each extract was autosampler-injected into the column. The column temperature was started from 60 °C (initially held for 1 min), elevated to 200 °C at 15 °C min^{-1} (held for 5 min), increased to 250 °C at 20 °C min^{-1} (held for 5 min), and ramped to 300 °C at 30 °C min^{-1} (held for 10 min). Ultra-high purity helium was used as the carrier gas at a flow rate of 1 mL min^{-1}. The ion source temperature was set at 250 °C. The mass selective detection was conducted in the electron ionization mode. Mass spectra were acquired in the full-scan mode from *m/z* 56 to *m/z* 330, with an electron impact energy of 70 eV. As no standards were available for all dimethylphenols of interest as well as menthol, the concentrations of these compounds were estimated based on the response factors of their homologues and internal standards.

The second fraction was quantified with a dual pump Shimadzu DGU-20 A 5R high performance liquid chromatography (Kyoto, Japan) coupled to a AB SCIEX Triple Quad 5500 triple quadruple mass spectrometer (Framingham, MA) equipped with an electrospray ionization ion source. An Agilent Eclipse-C18 column (100 × 2.1 mm-i.d.; 1.8 μm film thickness) was used for separation. The mobile phases were ultrapure water containing 0.1% formic acid for solvent A and acetonitrile for solvent B, with a gradient elution programmed as: 0–1.6 min, 15% solvent B; 1.6–2.1 min, 15-60% solvent B; 2.1–4 min, 60% solvent B; 4–4.1 min, 15% solvent B and 4.1–6 min, 60-15% solvent B. Each extract of 5 μL was autosample-injected into the column where temperature was maintained at 40 °C with a flow rate of 300 μL min^{-1}. Mass spectra were acquired in the multiple reaction-monitoring mode with an ion spray voltage of 5500 V and an ion source temperature of 450 °C.

The effective surface area of the fabric was determined by N_2-BET measurements. Samples were conditioned at 50 °C for 4 h under a dry N_2 flow followed by N surface gas adsorption and desorption measurements at 77 K using a Beishide 3H-2000PS2 surface area analyzer (Beishide Instrument Technology, China). The surface roughness of the fabric samples was analyzed with a 3D optical profilometer (RTEC Instruments, San Jose, CA, USA) in the CF mode at a frame rate of 6.28 fps and an exposure duration of 158.8 ms.

2.4. Quality assurance and quality control

Prior to sampling, preliminary testing had been conducted to select the appropriate size of fabrics needed. The results showed that the concentrations of the compounds under investigation from the fabric size of 10 × 10 cm^2 were similar to those for what was used in the present study (~15 × 15 cm^2). To satisfy the detection limits for the target analytes, a fabric size of 15 × 15 cm^2 was used in the present study.

One procedural blank, one matrix spike, and one field blank were analyzed for every batch of 20 samples. The recoveries of naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}, benzo(*ghi*)perylene-d_{12}, NAT-d_4, and NNK-d_4 were 41 ± 19%, 46 ± 17%, 55 ± 11%, 72 ± 16%, 82 ± 18%, 67 ± 16%, 114 ± 38%, and 65 ± 47% in blank samples and 33 ± 16%, 41 ± 13%, 50 ± 11%, 64 ± 14%, 74 ± 18%, 60 ± 13%, 147 ± 39%, and 62 ± 48% in field samples. Phenol was excluded for further analyses because its concentrations in blank samples were comparable to those in field samples. Concentrations of other analytes in all field samples were corrected with their concentrations in procedural blank samples and the recoveries of the surrogate standards. The reporting limit in the present study was defined as the lowest calibration concentration divided by the actual sample mass. For example, the reporting limits for N-nitrosamines were 0.2 and 2 pg m^{-3} for particle samples without smoking (25.2 m^3 of sampling volume) and with smoking (2.1 m^3 of sampling volume), respectively and 1 pg g^{-1} for 5 g fabric sample.

2.5. Data analysis

The fabric-air distribution coefficient (K) or partition ratio, normalized to fabric mass (K_{mass}; L kg^{-1}), planar surface area ($K_{planar\ surface\ area}$; m), and BET specific surface area ($K_{BET\ surface\ area}$; m), respectively, was calculated by

$$K_{mass} = \frac{m_{target}}{m_{fabric} \times C_{target}} \quad (1)$$

$$K_{planar\ surface\ area} = \frac{m_{target}}{A_{planar\ surface\ area} \times C_{target}} \quad (2)$$

$$K_{BET\ surface\ area} = \frac{m_{target}}{A_{BET\ surface\ area} \times C_{target}} \quad (3)$$

where m_{target} is the mass of a target analyte accumulated by fabric, m_{fabric} is the mass of the fabric sample, C_{target} is the air concentration of the target analyte in the gaseous and/or particulate phase, and $A_{planar\ surface\ area}$ and $A_{BET\ surface\ area}$ are the planar (one-side) and BET specific surface areas of the fabric sample, respectively. These distribution coefficients were used in the present study to describe air-fabric partitioning at equilibrium or non-equilibrium steady state. It should be noted that the particulate phase normalized fabric-air distribution coefficients were used to examine the influences of airborne particles to fabric-air distribution coefficient, rather than to characterize the processes of particle deposition.

3. Results and discussion

3.1. Occurrence of airborne particulate matter and smoking-related chemicals

As expected, the concentrations of airborne particulate matter and all target compounds were the greatest during smoking periods (Table 1 and Table S1). Tobacco smoking in the present study contributed substantially to the increase in the amount of particles sized smaller than 1.0 μm (when compared to particles greater than 1.0 μm), accounting for 75–85% of the total airborne particles collectively (data not shown). These results are similar to the reported size-specific tobacco particle emissions for cigarettes and cigars [30]. The concentrations of airborne particles in the present study (1.7–3.8 mg m^{-3}; Table 1) were greater than those found in indoor smoking environments reported previously (i.e., 10–45 μg m^{-3}) [30], which presents a 'worst-case' scenario.

The partitioning of the target analytes between the gaseous and particulate phases was positively correlated with their log-based octanol-air partition coefficient (log K_{oa}), e.g., phenols, indoles, and menthol occurred only in the gaseous phase, while nitrosamines mostly partitioned in particulate matter (Fig. S1). It should be noted that the concentrations of airborne particulates as well as gaseous phenols, cresols, and nitrosamines (except for NNN) were comparable between the flue-cured and blended cigarettes (Student's *t*-test; $p > 0.05$; Table S1). Moreover, there was no linear correlation between the total concentrations of nitrosamines and the contents of tar and nicotine, similar to the findings by Zhang et al. [31], although the contents of tar and nicotine in Double Happiness (flue-cured) were eleven times higher than those in KENT (blended).

Table 1
Contents of particulate matter (mg m^{-3}) and gaseous and particle-bound concentrations (ng m^{-3}), particle ratio (%), and geometric mean diameter (GMD; μm) of phenols, indoles, menthol, and nitrosamines for two types of tobacco during pre-smoking, smoking, and post-smoking intervals.

Cigarette type	Gaseous		Particle		Particle ratio		GMD	
	Flue-cured	Blended	Flue-cured	Blended	Flue-cured	Blended	Flue-cured	Blended
Pre-smoking								
Particle matter	na[a]	na	0.22 ± 0.17[b]	0.04 ± 0.01	na	na	1.5 ± 0.06	1.2 ± 0.4
Phenols	nd	8 ± 12	nd	nd	nd	nd	nd	nd
Indoles	54 ± 27	120 ± 54	nd	nd	nd	nd	nd	nd
Menthol	nd[c]	nd	nd	nd	na	na	na	na
Nitrosamines	0.080 ± 0.077	0.04 ± 0.02	0.3 ± 0.06	0.5 ± 0.03	81 ± 29	97 ± 5	1.5 ± 1.1	0.9 ± 0.3
Smoking								
Particle matter	na	na	3.0 ± 0.8	2.2 ± 0.5	na	na	0.63 ± 0.02	0.58 ± 0.05
Phenols	34,000 ± 9000	28000 ± 1700	4.3 ± 2.5	20 ± 9.2	0.05 ± 0.05	0.33 ± 0.35	0.39 ± 0.08	0.39 ± 0.12
Indoles	7100 ± 450	10000 ± 2600	9.8 ± 1.5	24 ± 8.4	0.21 ± 0.17	0.25 ± 0.07	0.54 ± 0.15	0.41 ± 0.01
Menthol	nd	35000 ± 5900	nd	nd	na	na	na	na
Nitrosamines	1.4 ± 0.2	2.7 ± 1.7	170 ± 29	190 ± 53	91 ± 10	91 ± 13	0.66 ± 0.14	0.67 ± 0.14
Post-smoking								
Particle matter	na	na	0.09 ± 0.01	0.06 ± 0.02	na	na	1.0 ± 0.06	1.3 ± 0.2
Phenols	180 ± 230	350 ± 220	nd	nd	nd	nd	nd	nd
Indoles	300 ± 280	1000 ± 460	nd	nd	nd	nd	nd	nd
Menthol	nd	nd	nd	nd	na	na	na	na
Nitrosamines	0.18 ± 0.14	0.12 ± 0.03	0.6 ± 0.5	1.6 ± 1.5	90 ± 19	98 ± 2	0.7 ± 0.3	0.7 ± 0.2

[a] "na" is the abbreviation of not available.
[b] (A ± B) represents the mean (A) and standard deviation (B).
[c] "nd" is the abbreviation of not detected.

3.2. Impacts of the properties of fabric materials on accumulation

In general, the concentrations of fabric-accumulated phenols, indoles, and nitrosamines in all three types of clothes were statistically indistinguishable (Kruskal–Wallis H test; $p > 0.05$) when normalized to per unit mass and planar surface area (Fig. 1). For example, the per unit mass normalized concentrations of 3-methylphenol were 29000, 30000, and 34,000 pg g^{-1} in t-shirt, pajamas, and lab coat and planar surface area normalized ones were 750, 510, and 510 pg cm^{-2}, respectively. In contrast, the concentrations of the target analytes accumulated in pajama and lab coat (both polyster; i.e., 14,000 and 22,000 pg cm^{-2} for 3-methylphenol) were statistically different (Kruskal–Wallis H test; $p < 0.05$) from those in cotton t-shirt (i.e., 8500 pg cm^{-2} for 3-methylphenol) when normalized to BET specific surface area. These results (Fig. 1) were consistent with a study by Saini et al. [25], which also reported similar planar surface area normalized concentrations of

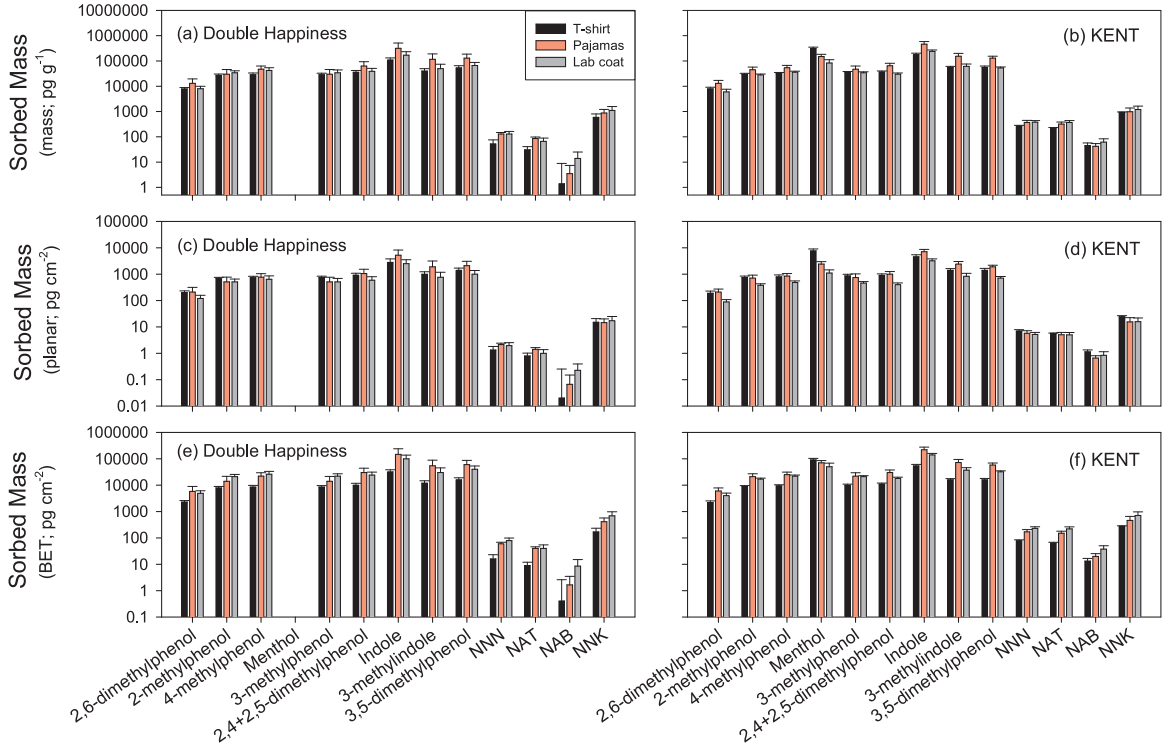

Fig. 1. Masses of chemicals sequestered in fabrics normalized to fabric mass, planar surface areas, and BET specific surface areas for cotton (t-shirt) and polyster (pajamas and lab coat) fabrics for two tobacco products (Double Happiness and Kent cigarettes). The target analytes are arranged in the order of increasing K_{oa} (Table S2). NAB, NAT, NNK, and NNN are the acronyms for N'-nitrosoanabasine, N'-nitrosoanatabine, 4′-(nitrosomethylamino)-1-(3-pyridyl)-1-butanone, and N'-nitrosonornicotine, respectively.

polybrominated diphenyl ethers between cotton and polyester fabrics, but greater BET specific surface area normalized concentrations in polyester than in cotton. This difference was presumably due to either dilution by a greater cotton specific surface area or the aromatic-rich texture of the polyester fabric [25].

Although the present study and Saini et al.'s study [25] both showed a significant difference between the two fabrics (cotton and polyester) when normalized to BET specific surface areas, the BET specific surface areas for the two fabrics were quite different between the present study and Saini et al.'s study. The difference in the BET specific surface areas of cotton ($3.4\ m^2\ g^{-1}$) and polyester (pajama ($2.1\ m^2\ g^{-1}$) and lab coat ($1.6\ m^2\ g^{-1}$)) in the present study was quite similar (1.6–2.1 times), while the difference in Saini et al.'s study [25] was 10 fold between cotton ($0.72\ m^2\ g^{-1}$) and polyester ($0.07\ m^2\ g^{-1}$). Also in the present study, menthol concentrations (without a benzene ring) in cotton fabric was slightly greater than those in pajama and lab coat fabric, regardless of which normalizing factor was used. The results of the present study as well as the past study suggested that the properties of fabric materials can greatly affect the accumulation of chemicals in fabrics [21–25], e.g., menthol binds to cotton through hydroxyl functional groups, while phenols and indoles form pi-pi interactions through the benzene ring of polyester.

3.3. Airborne particles mediate accumulation processes

The amounts of phenols and indoles accumulated in fabrics were comparable between flue-cured and blended cigarettes based on all three normalization factors (Fig. 1). The fabric contents of nitrosamines (except NNK), however, were slightly greater in blended cigarettes than in flue-cured cigarettes when smoked (Fig. 1). Interestingly, appreciable levels of NAB and NNK were detected in all three types of fabrics (Fig. 1) even though only particle-bound NAB and NNK were found in cigarette smoke (Table S1). This demonstrated the effective deposition of particles on fabrics, while a previous study showed the surface-mediated reaction of sorbed nicotine with gaseous nitrous acid as a source of NNK on fabric surface [32]. The amounts of accumulated NAB and NNK were similar between these cigarettes, which was not surprising as the particle-bound concentrations and geometric mean diameters of NAB and NNK were within the same order of magnitude (Table S1). Airborne particles of 0.1—2 μm are often categorized as belonging to the accumulation mode, within which greater-sized particles have higher deposition loss-rate coefficients, which can be enhanced upon mixing with air [33]. Furthermore, the fabric accumulated amounts of NNN and NAT in all three forms of normalization were 3.6–5.4 times greater for exposure to smoke from blended cigarettes than from flue-cured ones, consistent with the differences with airborne particle-bound (2.7 times) concentrations (Table S1).

3.4. Dependence of fabric-air distribution on fabrics specified surface area and airborne particles

In general, all three distribution coefficients, K_{mass}, $K_{planar\ surface\ area}$, and $K_{BET\ surface\ area}$, for gaseous phenols, menthol, and indoles for each of the three fabrics types increased with log K_{oa} (Fig. 2) and decreased with vapor pressure (Fig. S2). It should be noted that the BET specific surface area normalized distribution coefficients were comparable for menthol among the three types of clothing, while the mass and planar surface area normalized distribution coefficients were more variable. This implies that the distribution of gas-phase compounds in fabrics can also be driven by physical characteristics such as surface area and porosity of a sorbent or fabric in this case. Noble [4] reported that uptake of tobacco smoke by clothing fabrics was more closely related to the surfaces of fabrics than their weights. This result is similar to a previously reported finding that daily wet/dry or wash/dry processes, which would affect the surface of the fabric, could influence the fabric sorption [34]. Other processes, such as charring, have also been shown to enhance the aromaticity of cellulose and create additional surface areas and micropores on the char surface, resulting in increased sorption of naphthalene and phenanthrene [35]. Furthermore, nanoparticle thin-films and coatings have been increasingly utilized in the textile industry (for intelligent textiles and antibacterial fabrics), which can further enhance the absorbency of fabrics, as these nanoparticles have a large surface area per unit mass, volume, and planar surface area [36,37]. These results collectively implicate that the fabric-air distribution/partitioning coefficients for gaseous compounds may not be accurately predicted from K_{oa} or vapor pressure alone without also considering the sorbent properties of fabrics, namely specific surface area and porosity.

In regards to nitrosamines, fabric-air distribution coefficients for NAB and NNK could not be calculated when normalized by gaseous NAB and NNK concentrations (Fig. 3a–b) as they were below the reporting limits. The same distribution coefficients were available when normalized by the particulate or total NAB and NNK concentrations (Fig. 3c–f). Furthermore, the root mean square surface roughness heights were similar for cotton (174 μm), pajamas (182 μm), and lab coat (97 μm) in the present study. In addition, the micro-surface structure of the cotton and pajamas fabrics was of concave slope or U-shaped valley type with large contact areas (Fig. 4a–b). The average inter-rim distance ranged from 580 to 760 μm, so particles may easily attach on the fabric surface but are difficult to be retained. The lab coat has a net/pocket micro-surface structure (Fig. 4c) with a measured inter-rim distance of 120 μm, which allows smaller particle to easily entrap/settle inside/around the rim of net/pocket and thereby remain in the fabric surface. Obviously, the fabric-air distribution coefficients for nitrosamines may be overestimated or underestimated (as these particle-bound compounds in fact occurred on clothing), depending on the gas-particle partitioning.

The fabric-air distribution coefficient, concerning either the fabric-air gap between skin surfaces or outer fabric-room air, is a key parameter used to predict chemical exposure from textiles by dermal uptake. In common daily scenarios, fabrics are exposed to both gaseous and particulate chemicals, rather than gaseous ones alone. If the chemicals are distributed between the gaseous and particulate phases, any increase in the gas-particle partition coefficient would lead to an increase or decrease in the fabric-air distribution coefficient normalized by gaseous or particulate concentrations of the target analytes. On the contrary, if the chemicals occur only in the gaseous phase, the fabric-air distribution coefficient would maintain constant. Apparently, the contributions of airborne particles to fabric surfaces should be carefully dealt with, particularly for SVOCs.

3.5. Depositional fluxes of particle-bound NNN and NNK to fabric surfaces

Among N-nitrosamines, both NNK and NNN are regarded as powerful carcinogens in laboratory animal testing, and have also been classified as "carcinogenic to humans" by the International Agency for Research on Cancer [38]. The particle-bound NNN and NNK concentrations during smoking in the present study ranged from 3.5 to 10.3 ng m^{-3} and 130 to 230 ng m^{-3}, respectively (with means of 6.9 and 180 ng m^{-3}, respectively; Table S1). Meanwhile, the airborne geometric mean diameters for NNN and NNK were 0.5 and 0.7 μm, respectively (Table S1). The deposition velocity of particles with an aerodynamic diameter of 0.5 μm to clothing surface was assumed as 0.65 m h^{-1} based on a previous study [39], although the deposition velocity could be different among different densities of particles and also depend on the roughness of the surface itself or ambient conditions (such as air speed, temperature, and humidity). As such, the total particle depositional fluxes of NNN and NNK were estimates, which were calculated from the analyte concentration multiplied by the related deposition velocity of particles, but even so the fabric surface flux was as high as 0.3–0.8 and 10–17 pg cm^{-2} d^{-1} and contributed up to 6–20% and 56–100% of total NNN and NNK in fabric, respectively.

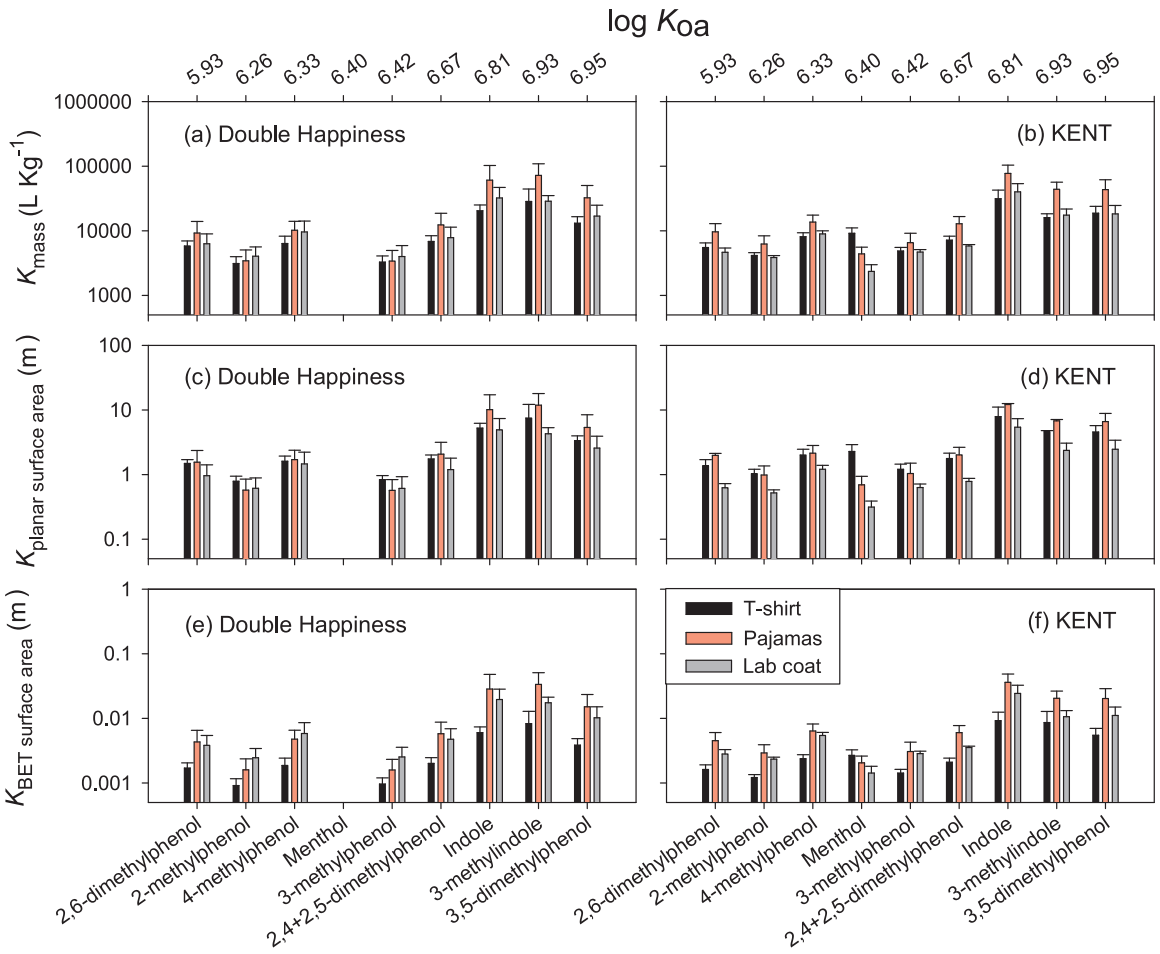

Fig. 2. Three fabric-air distribution coefficients, K_{mass}, $K_{planar\ surface\ area}$, and $K_{BET\ surface\ area}$ for phenols, indoles, and menthol among cotton (t-shirt) and polyster (pajamas and lab coat) fabrics for two tobacco products (Double Happiness and Kent cigarettes). The target analytes are arranged in the order of increasing log K_{oa} (Table S2).

Based on a real-life scenario, the concentrations of NNN and NNK in a poorly ventilated office were reported to be 4.9 (ranging from not detected to 14 ng m^{-3}) and 2.8 (ranging from not detected to 6.0 ng m^{-3}) ng m^{-3}, respectively [40]. In a separate study, the concentrations of particle-bound NNN and NNK in 10 different locations, including bars, trains, offices, and a smoker's home, ranged from not detected to 22.8 and 1.4 to 29.3 ng m^{-3}, respectively [41]. Meanwhile, aerosol particles from tobacco smoking are known to remain airborne for approximately 8–10 h [42]. Using this information collectively, the resulting depositional fluxes of NNN and NNK to the fabric surface under these scenarios could be up to 15 and 19 pg cm^{-2} d^{-1}, respectively (if fabric surfaces were consistently exposed to tobacco smoke). For a susceptible individual, like an infant (assuming a mean total body surface area of infants under 1 year of age is 3600 cm^2 [43], and that the child would be covered by fabrics daily), they would be contacted to approximately 54–69 ng d^{-1} of NNK and NNN. These high levels are concerning and show the importance of considering fabric surface in particle-bound flux models as it is certainly an important pathway of exposure for non-smokers to nitrosamines.

4. Conclusions

Clothing is increasingly being recognized to play an influential role in human exposure to toxic chemicals, either directly or indirectly. Although the results from the present study were derived from controlled tobacco smoking experiments, at least two implications are evident. First, sorbent properties, such as specific surface area and porosity need to be taken into account in calculating the normalized fabric-air distribution/partitioning coefficients for gaseous compounds. Second, the presence of particle-bound compounds on clothing surfaces can inflate the sorption capacity, resulting in either over- or under-estimated fabric-air distribution/partitioning coefficients. Consequently, texture properties seem to be the main factor affecting the distribution process for compounds with relatively small log K_{oa} (i.e., $< 10^7$), while the role of particles on fabric-air distribution should not be overlooked for compounds with large log K_{oa} (i.e. $\geq 10^7$). In this context, the importance of understanding the properties for both fabrics and the airborne particle-bound compounds attached on those fabrics remains to be adequately examined, so that more accurate assessments of potential health risk due to fabric-air mediated transport of SVOCs are conducted in the future.

Conflict of interest

The authors declare no competing financial interest.

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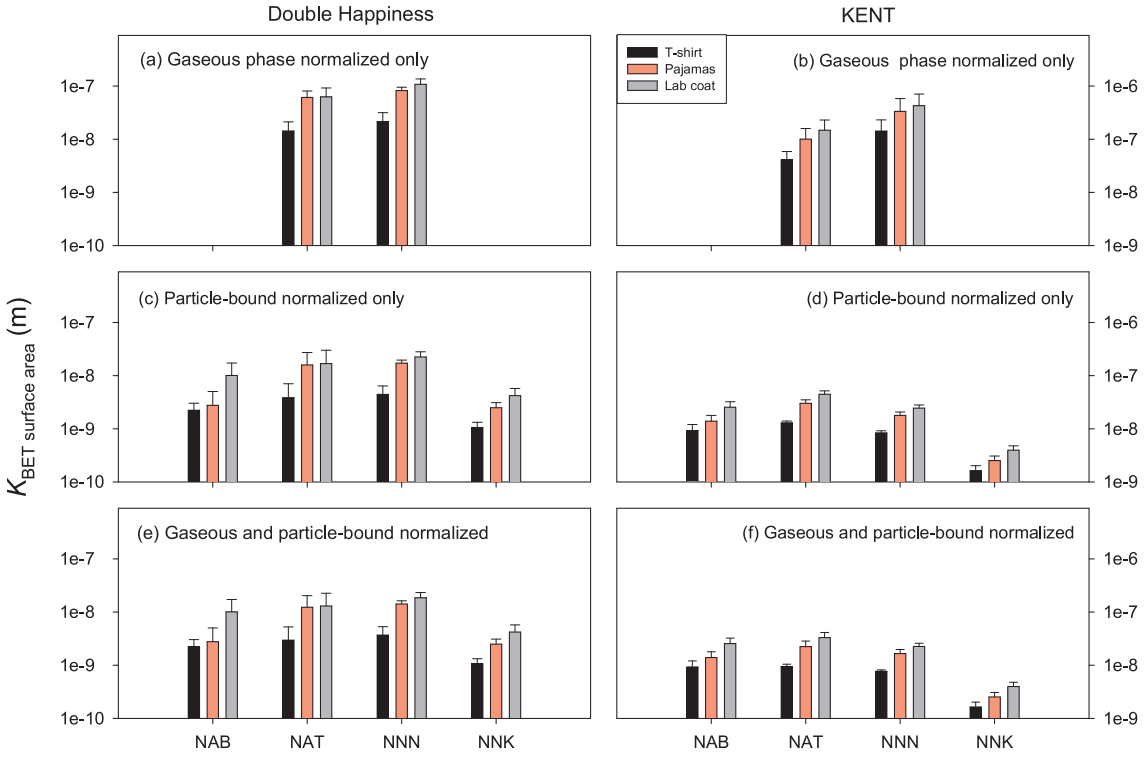

Fig. 3. The BET specific surface area normalized fabric-air distribution coefficients for nitrosamines (NAB, NAT, NNN, and NNK) among cotton (t-shirt) and polyster (pajamas and lab coat) fabrics for two tobacco products (Double Happiness and Kent cigarettes). The target analytes are arranged in the order of decreasing vapor pressures. NAB, NAT, NNN, and NNK are the acronyms for N'-nitrosoanabasine, N'-nitrosoanatabine, N'-nitrosonornicotine, and 4′-(nitrosomethylamino)-1-(3-pyridyl)-1-butanone, respectively.

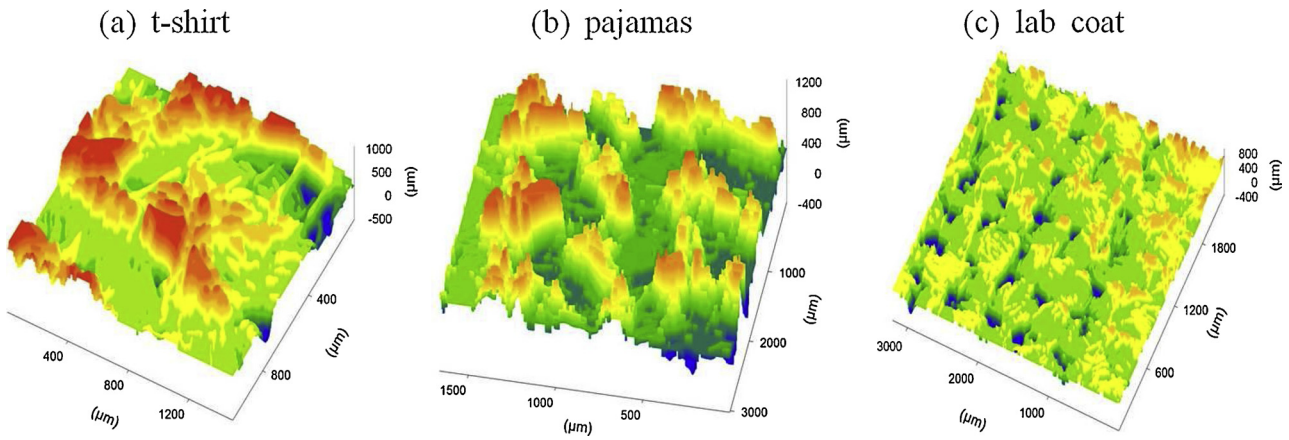

Fig. 4. 3D profiles for surface roughness of (a) cotton (t-shirt), (b) pajamas, and (c) lab coat.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2018.12.107.

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