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keywords: nicotine, heterogeneous chemistry, SVOC, indoor surfaces, sorption, thirdhand tobacco smoke

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ABSTRACT

Exposure to tobacco pollutants that linger indoors after smoking has taken place (*thirdhand smoke, THS*) can occur over extended periods and is modulated by chemical processes involving atmospheric reactive species. This study investigates the role of ozone and indoor surfaces in chemical transformations of tobacco smoke residues. Gas and particle constituents of secondhand smoke (SHS) as well as sorbed SHS on chamber internal walls and model materials (cotton, paper, and gypsum wallboard) were characterized during aging. After smoldering 10 cigarettes in a 24-m³ room size chamber, gas-phase nicotine was rapidly removed by sorption to chamber surfaces, and subsequently re-emitted during ventilation with clean air to a level of ~10% that during the smoking phase. During chamber ventilation in the presence of ozone (180 ppb), ozone decayed at a rate of 5.6 h⁻¹ and coincided with a factor of 5 less nicotine sorbed to wallboard. In the presence of ozone, no gas phase nicotine was detected as a result of re-emission, and higher concentrations of nicotine oxidation products were observed than when ventilation was performed with ozone-free air. Analysis of the model surfaces showed that heterogeneous nicotine-ozone reaction was faster on paper than cotton, and both were faster than on wallboard. However, wallboard played a dominant role in ozone-initiated reaction in the chamber due to its large total geometric surface area and sink potential compared to the other substrates. This study is the first to show in a room-sized environmental chamber that the heterogeneous ozone chemistry of sorbed nicotine generates THS constituents of concern, as observed previously in bench-top studies. In addition to the main oxidation products (cotinine, myosmine and N-methyl formamide), nicotine-1-oxide was detected for the first time.

1. Introduction

Over the past decade significant progress has been made around the world in controlling involuntary exposures of non smokers to secondhand tobacco smoke (SHS). In some countries, expanding workplace restrictions now protect a majority of working adults, but homes remain the most important exposure setting for children (USDHHS 2006). SHS includes thousands of substances, of which more than 60 are known or suspected carcinogens and several are strong irritants (Jenkins et al. 2000; Hoffmann et al. 2001). Recently, the term *thirdhand smoke* (THS) has been adopted to describe the residues of tobacco smoke that remain adsorbed to indoor surfaces after the smoke clears, react to produce secondary pollutants and/or are re-emitted back to indoor air over extended periods of time (Matt et al. 2004; Winickoff et al. 2009; Fortmann et al. 2010; Sleiman et al. 2010). While inhalation of SHS is a major pathway of exposure indoors, long after smoking has ceased, contact with toxicants in THS can also take place by other routes such as dermal uptake, hand-to-mouth transfer and inhalation of sorbed species that are re-emitted to the gas phase. These pathways of exposure are especially relevant in homes with toddlers because young children have more contact with contaminated surfaces such as carpet and furniture.

Physicochemical transformations of SHS and THS components that occur in indoor environments after smoking takes place - aging - impact both short and long term exposure patterns of nonsmokers because aging can generate secondary pollutants over periods ranging from a few hours to several months. Ozone and other atmospheric oxidants may produce secondary pollutants by reaction with sorbed SHS and THS (Destailats et al. 2006; Petrick et al. 2010). Moreover, nicotine remitted from surfaces

during aging can react with ozone in the gas phase to produce ultrafine aerosol particles that contain oxidized byproducts with high asthma hazard indices (Petrick et al. 2010; Sleiman et al. 2010). Thus, a significant fraction of the widespread respiratory symptoms associated with passive smoking may be associated with irritating gas-phase oxidation products and secondary aerosol particles produced by the reaction of tobacco smoke components with indoor ozone.

Despite its high reactivity, the atmospheric lifetime of ozone is long enough to allow for its transport to the indoor environment, where it reacts at rates that are often higher than typical ventilation removal rates. Weschler (2000) reviewed available information on simultaneous indoor-outdoor (I/O) ozone measurements, finding that in most cases I/O ratios were between 0.2 and 0.7. Ozone may also be generated indoors in large quantities from devices marketed as “air purifiers” (Boeniger 1995; Hubbard et al. 2005). Such devices are commonly used to remove odors related to secondhand tobacco smoke, despite the growing body of evidence showing that they generate products that are more toxic and/or irritating than their precursors (Phillips and Jakober 2006; Waring et al. 2008).

While some homogenous gas phase reactions are important indoors, the available experimental evidence indicates that the most important decay processes for indoor ozone involve surface reactions that are major sources of secondary pollutants (Morrison and Nazaroff 2002; Aoki and Tanabe 2007; Zhao et al. 2007) and sorbed chemicals (Fan et al. 2003; Fick et al. 2005; Singer et al. 2006; Wang and Morrison 2006; Coleman et al. 2008; Petrick and Dubowski 2009). The characterization of ozone-initiated chemical reactions on indoor surfaces will contribute to understanding their link to health effects

and provide important insights into design of effective engineering solutions that eliminate or reduce exposure to toxic chemicals generated by these reactions (Weschler 2004; Weschler and Wells 2004; Weschler 2006; Morrison 2008).

Our previous work showed that nicotine sorption is affected by substrates (Petrick et al. 2010) and that it can be substantially depleted by its reaction with ozone over timescales that are competitive with desorption and re-emission into the gas phase (Destailats et al. 2006; Petrick et al. 2011). As a consequence, re-emitted nicotine gas phase levels decreased by 1-2 orders of magnitude compared with similar conditions in the absence of ozone, and stable oxidation products such as N-methylformamide, cotinine, nicotinealdehyde and myosmine were emitted to the gas phase. This study investigates whether similar processes occur when SHS ages in a scaled-up environmental chamber that contains several indoor materials. The present study also tracks a wider range of SHS constituents in the gas phase, on airborne particles, and on the model surfaces gypsum wallboard, cotton cloth, and cellulose paper. The effect of substrate type on nicotine surface oxidative kinetics is also examined.

2. Experimental

Chamber smoke aged in clean air (RH = 44 to 63%, T = 20 to 27 °C, no ozone) was compared with smoke that aged in the presence of ozone under otherwise identical conditions. After smoke generation the following types of samples were collected and analyzed: a) gas (and particulate) phase compounds on Tenax TA in sorbent tubes, b) semi-volatile organic compounds (SVOCs) on XAD-coated denuders, c) particles on filters and d) SVOCs sorbed to model surfaces (cotton cloth, wallboard, and paper).

2.1 Chamber parameters

The walls and ceiling of the 24 m³ smoking chamber were covered with 42 m² of painted gypsum wallboard, while the floor (10 m²) was covered with vinyl tiles; all surfaces had previously been exposed to tobacco smoke over a period > 10 years. An axial fan (52 cm diameter) was operated inside the chamber to ensure rapid mixing. Filter cigarettes from a leading US brand were purchased from local California retailers and used for SHS generation. At experimental onset 10 cigarettes were smoldered simultaneously. The chamber was housed within a small building and outdoor air ventilation was continuously supplied to the chamber through a dedicated system that had a carbon trap to remove organic gases, and held the chamber at a slightly positive pressure. The ventilation rate was 0.75 h⁻¹ determined using CO₂ as a tracer gas (EGM-4, PP systems). Temperature and relative humidity in the chamber were logged continuously (HOBO® U10-003, Onset Corp., USA).

Experiments were performed in 2 phases: a smoking phase and a ventilation phase, as shown in Figure 1 and Table S1 in Supplementary Information (SI). The

smoking phase started at the point of cigarette lighting, and lasted for ~2.5 h, corresponding to roughly 3 air exchanges. Clean air was introduced continuously during both phases. However, oxidation studies were performed by adding ozone during the ventilation phase ('ozone'), for comparison with ventilation by clean air ('clean'). Ozone was generated by flowing Ultra High Purity O₂ (Airgas) through a corona discharge ozone generator (Yanco Industries M/N GE30/FM100) at a rate of 100 mL min⁻¹. The ozone flow was introduced at the center of the chamber. Gas phase ozone concentrations in the chamber in the absence of tobacco smoke were ≤ 200 ppb (steady state of [O₃] = 180 ppb was reached after 24 h), and were monitored with a continuous ozone monitor (2BTechnologies Model 202.). These ozone levels are higher than typical concentrations associated with infiltration from outdoor air, but consistent with those observed during operation of ozone-generating indoor "air cleaners" (Phillips and Jakober 2006; Waring et al. 2008).

2.2 Model surfaces and wall wipes

Wallboard specimens were cut and the edges sealed with Teflon tape to limit direct exposure to the gypsum core. Strips of chromatography paper of 17.5 × 13.5 cm² (Whatman 3MM, No. 3030-153), cotton cloth samples of 10 × 3 cm, and wallboard samples of 9 × 1 × 1.3 cm were placed in the center of the chamber for exposure, at a distance of ~1 m from the smoldering cigarettes. Multiple equivalent samples of each model surface were exposed simultaneously to the same chamber air, and were retrieved at different times to follow their SHS/THS loading as a function of time. The effective surface areas of the substrates were determined by N₂-BET measurements. Samples were

conditioned at 50 °C for 20 h under a dry N₂ flow (FlowPrep 060, Micromeritics) followed by analysis of N₂ surface gas adsorption at 77 K (TriStar 3000 Micromeritics).

Wall wipes. During experiments the chamber walls were wiped using laboratory lint-free tissues (KimWipes®) at selected times during chamber studies (sampling conditions described in Table S2). The extracts were analyzed following procedures that were similar to those used for the surface materials (described below).

2.3 Sample collection and analysis

Extraction. Model samples exposed to SHS were extracted twice at 100 °C at 1500 psi, in methylene chloride (OmniSolv, spectrophotometric grade) in an accelerated solvent extractor (ASE200 Dionex Corp.) using a total volume of up to 30 mL. A methanol aliquot of 0.5 mL (JT Baker, reagent grade) was added to each extract to ensure transfer of polar compounds (Swartz et al. 2003), followed by concentration with N₂ using a TurboVap II system (Caliper LifeSciences) at 35 °C to a total volume of 1 mL.

Extraction efficiency. Prior to chamber studies, extraction efficiency tests were performed in order to obtain optimal conditions for nicotine extraction at the low quantities of sorbed nicotine expected under realistic smoking conditions. Using the accelerated solvent extraction system, optimal conditions resulted in extraction efficiencies of cotton = 30 ± 5%, paper = 10 ± 5%, wallboard = 20 ± 5 % when spiked with 600 - 40 ng of nicotine. Low recovery efficiencies may be due to the fact that these experiments were carried out at levels that were near the limits of quantification, due to constraints associated with performing experiments in room-size conditions. For that reason, the data for surface-bound compounds are semi-quantitative. While multiple SHS

constituents were expected to have sorbed to the model substrates, only nicotine was quantified due to analytical limitations.

Partitioning of semi-volatile compounds. Particles and gases were collected during smoking and ventilation phases using an Integrated Organic Gas and Particle Sampler (IOGAPS), (Gundel et al. 1995; Swartz et al. 2002). A cyclone removed particles $> 2.5 \mu\text{m}$, allowing gases and respirable particles to pass through. In experiments #5- #7, the denuder section contained two XAD-4-coated denuders (eight-channel, 52 mm OD; 30 cm length) in series, upstream of the filters. Unless otherwise stated, a KI coated denuder preceded the XAD-4 denuders during ozone experiments. The KI and XAD-4 coated denuders scrubbed ozone and collected semi-volatile organic gases, respectively, while the particles (with both particulate SVOC and non-volatile species) deposited downstream on a pre-weighed Teflon-coated fiberglass filter. SHS was collected by the IOGAPS at $100 \pm 5 \text{ L min}^{-1}$. After sampling, the XAD-4 coated denuders were spiked with an internal standard mixture (phenanthrene- d_{10} and flouranthrene- d_{10}), extracted with 60 mL of methanol, and the extracts filtered through 47 mm, $0.45 \mu\text{m}$ Teflon filters (Millipore FHUP047). The extract volumes were reduced to 5 mL using the TurboVap system. The Teflon-coated glass filters (90 mm diameter) were weighed before and after exposure to SHS using an analytical balance (precision of 0.1 mg) to determine the SHS $\text{PM}_{2.5}$ concentration. Filters were extracted with methanol and analyzed using GC-MS.

Analysis of extracts. A gas chromatograph equipped with an ion trap – tandem mass spectrometric detection (GC-IT-MS/MS, Varian 4000) was used for quantification of nicotine (98% Toronto Research Chemicals, (+/-)-nicotine) using a multipoint

calibration and quinoline (Aldrich 98%) as an internal standard (Sleiman et al. 2009). Nicotine oxidation products were identified by comparison to the online NIST library, followed by analysis of authentic standards when they were available. Instrumental parameters included an injector temperature of 270 °C run in splitless mode. Samples were eluted on a Factor Four VF-5ms column (Varian 30m × 0.25 mm ID, Df = 0.25 µm). After a 3 min hold at 60 °C, oven temperature was ramped to 300 °C (8 °C min⁻¹). The MS ion trap detected analytes in the electron impact mode over the range 50-425 *m/z*.

Nitrogenated compounds in SHS. Chamber air was sampled at specific flow rates of 50-500 mL min⁻¹ into stainless steel sorbent tubes containing 200 mg Tenax-TA. Flows were maintained downstream to within ± 5% by a vacuum pump and mass flow controller. The sorbent tubes were analyzed using a Perkin Elmer ATD 400 automatic multi-tube desorber/injector connected to a Hewlett-Packard (now Agilent) Model 5890 gas chromatograph that had a DB1701 column, 30 m length, 0.53 mm diameter, film thickness 1.0 µm (part number 125-0732, J&W, Folsom, CA) and a nitrogen-phosphorous detector (NPD, Model TID-4, DETector Engineering and Technology, Walnut Creek CA). Quinoline was added to each tube as an internal standard, and multi-point calibration curves were constructed from analysis of a standard mixture of pyridine, pyrrole, 2-, 3- and 4-picoline, N-methylformamide, 3-ethylpyridine, 4-ethenylpyridine, nicotine aldehyde, nicotine, 3-hydroxypyridine, myosmine and cotinine. The response factor for 4-ethenylpyridine was used to quantitate the SHS tracer 3-ethenylpyridine, which eluted within 0.2 min of its isomer.

3. Results and Discussion

3.1 Smoking phase versus clean air ventilation.

Nitrogenated species. Average concentrations of nitrogenated SHS compounds (i.e. pyridine, N-methylformamide, pyrrole, 3-ethenylpyridine, and myosmine) decreased over time while apparent SHS PM_{2.5} simultaneously decreased during the smoking phase ($t_0 - t_{150}$ min), as shown in Figure 2 (corresponding to data from Exp #2), primarily due to removal by ventilation ($AER = 0.75 \text{ h}^{-1}$). The average loss rates ($\mu\text{g m}^{-3} \text{ min}^{-1}$) for each compound during the smoking phase (150 min) are as follows: $14.4 \text{ (PM}_{2.5}\text{)} > 0.29 \text{ (Pyrrole)} > 0.15 \text{ (Pyridine)} > 0.13 \text{ (N-methyl formamide)} > 0.1 \text{ (myosmine)} > 0.07 \text{ (3-ethenylpyridine)}$. During the same period, SHS PM_{2.5} decreased from 2.5 mg m^{-3} (t_0-t_{40} min) to 1.4 mg m^{-3} ($t_{40}-t_{90}$ min) and 0.37 mg m^{-3} during $t_{90}-t_{150}$ min. While initial nicotine concentrations were 1.5 orders of magnitude greater than those of the other species, nicotine was no longer detected after only 40 min into the smoking phase, corresponding to a loss rate of $2.4 \mu\text{g m}^{-3} \text{ min}^{-1}$ during the first 40 min of smoking phase. Similar trends were observed in the other experiments carried out in the absence of ozone. This is in agreement with very fast sorptive losses to surfaces reported previously (Singer et al. 2003; Singer et al. 2004).

It is worth noting that the apparent PM_{2.5} concentrations described here overestimated the actual concentrations because the filter in Exp #2 was not preceded by a denuder to capture the SVOCs upstream of the filters. During the periods of PM collection, SVOCs from the gas phase were likely to have been trapped by the SHS

particles collected on the filter, and to a smaller extent by the filter itself. Figure S2 (Supporting Information) shows estimates of the magnitudes of the artifacts for SVOCs identified in the extracts of SHS-loaded filters, which were typically small (~10%), except for nicotine (~50%).

Nicotine sorption to model substrates. Net sorption of nicotine to cotton was less than to wallboard with gypsum core and cellulose paper (Figure S1a). However, when normalized to the effective surface area of the substrates (0.72, 1.52, and 1.96 m² g⁻¹ for cotton, paper, and wallboard paper, respectively) sorption was similar (Figure S1b) for each of these materials, in agreement with our previous bench-top studies (Petrick et al. 2010) that utilized only the first layer of wallboard paper. This chamber study included the multi-layer piece with gypsum core. Consistent with the observations of Meininghaus and Uhde (2002), the high surface area of the gypsum (21.4 m² g⁻¹) accounted for substantial nicotine sorption into the gypsum core. This drastically reduced the normalized sorption (ng m⁻²) by approximately 2 orders of magnitude. Additionally, nicotine sorption to the samples appeared to level at $t \geq 90$ min, indicating that equilibrium had been reached early in the smoking phase.

Gas/particle partitioning of SVOCs. Semivolatile constituents and oxidation byproducts identified in denuder and filter extracts of the IOGAPS system are listed in Table 1. Concentrations of main SVOCs from denuder and filter samples are shown in Figure 3, with compounds ordered by increasing chromatographic retention time. The mass concentrations (in $\mu\text{g m}^{-3}$) of compounds on the filter (MnF) and on the denuder (MnD) measured in Exps #5 and #2 were used for comparing their relative loadings, using the calculations described in the SI. With or without denuders, filter-derived

concentrations were highest during the first 40 min of the smoking phase (Figure 3), as previously observed for nitrogenated SHS constituents. While high concentrations of gaseous semi-volatile constituents were observed in the smoking phase, lower and roughly constant concentrations were observed during the clean air phase (i.e., sampling at 150-260 min and 260-350 min), due to ventilation and continuous desorption from other indoor surfaces in the chamber. Artifacts associated with loss of small-sized (<50 nm) ultrafine particles to the denuder using the IOGAPS system are expected to be less significant for samples collected in the absence of ozone, because most of the particles in SHS are in the accumulation mode (Sleiman et al, 2010b).

Asthma Hazard Indices for SHS constituents. Species identified in extracts from the IOGAPS are listed in Table 1 (See Table S3 for structures and CAS numbers). Table 1 includes predicted values of the asthma hazard, based on the model developed by Jarvis et al. (2005) in which 0 is a low hazard and 1 is a definite hazard. Values ranged from 0.01 to 0.99, with approximately 50% of the compounds likely to cause or exacerbate asthma (hazard index > 0.5).

3.2 Effect of added ozone.

As nicotine is the major constituent of SHS and highly reactive to ozone, nicotine-ozone reaction in the chamber is expected. This may proceed via several pathways 1) as a homogeneous reaction in the gas phase, 2) as a heterogeneous reaction between airborne particulate nicotine and gaseous ozone, or 3) as a heterogeneous reaction between chamber surface bound nicotine and gaseous ozone. Because the AER in the chamber was much greater than the estimated homogeneous rate constant (Tuazon et al. 1994);

Petrick et al (2010), and gaseous nicotine concentrations immediately dropped due to sorption, reaction by pathway 1 was not likely to be significant. Therefore, nicotine transformations should occur predominately via heterogeneous reactions. Assuming that the ozonolysis rates are similar on particles and on the surfaces of the chamber, reactions taking place on chamber surfaces dominated for this experiment since the exposed chamber surface area was ~2 orders of magnitude higher than the total surface area of the particles.

Gas phase concentrations differed during ventilation in the presence of ozone versus clean air alone. During clean air ventilation, gaseous nicotine was detected long into the ventilation phase (Table S4), as a result of continued desorption from chamber surfaces (Figure 3). Average gas phase nicotine concentrations in the clean air ventilation phase were ~10% of those during the smoking phase. On the other hand, during ventilation in the presence of ozone, no re-emission of gaseous nicotine was detected while the concentrations of gaseous oxidation byproducts increased (e.g., N-methylformamide and myosmine) and were higher than those measured during ventilation in absence of ozone. This is consistent with heterogeneous oxidation and off-gassing of reaction byproducts from the surfaces, as observed previously in bench scale laboratory experiments (Destailats et al. 2006). 3-ethenylpyridine, a semi-volatile marker for SHS not known to be highly reactive to ozone, showed similar gaseous concentrations under either condition.

In addition to changes in gas phase composition, the amount of nicotine sorbed to the model surfaces was affected by the presence of ozone. Figure 4 shows the fraction of sorbed nicotine $[\text{Nic}]/[\text{Nic}]_0$ during ventilation phases using clean air or ozone, as a

function of time. In all surfaces, a greater fraction of the initial nicotine remained in the absence of ozone than in its presence, indicating loss via heterogeneous reaction. Furthermore, for each substrate, the difference between the nicotine fraction remaining on the surface in the absence of ozone and the presence of ozone provides a qualitative comparison of surface kinetics. These results indicate that surface nicotine oxidation rates are in the order: paper > cotton > wallboard. Overall, about half of the nicotine sorbed to cotton and wallboard appeared to be protected from reaction with O₃. This is likely due to diffusion of nicotine molecules into pores of the gypsum core of wallboard, and to their association with the large amount of water sorbed to the cotton fabric. In addition, cotinine, the major product of nicotine-ozone oxidation (Destailats et al. 2006; Petrick et al. 2010), was identified on paper substrates when ventilation was performed in the presence of ozone.

The total geometric surface area of wallboard in the chamber was four orders of magnitude larger than the other model surfaces. Thus, while kinetically not as favorable, nicotine-ozone surface reaction on wallboard was probably the dominant player in this chamber. In addition, since chamber walls were previously exposed to nicotine and continuously exposed during these experiments, they most likely contained nicotine residues that reacted with the ozone.

Additional evidence of ozone-initiated heterogeneous chemistry was obtained from the ozone chamber deposition rate. After the ozone concentration reached steady-state in the chamber ([O₃] = 180 ppb, at the end of Exp #3 and #4), the ozone generator was shut off, and the ozone concentration was monitored as a function of time (Figure S3). The ozone decay rate (5.6 h⁻¹) was much faster than the chamber AER (0.75 h⁻¹), and

ozone decay rate due to reaction with wallboard alone (published value of 0.2 h^{-1}) (Kunkel et al. 2010). Thus, the observed ozone loss in the chamber was most likely due to ozone reactions with SHS residues freshly deposited during Exp #3 and #4.

3.3 Reactions on chamber walls.

Further support of significant nicotine loading on the wallboard and ozone uptake by surfaces is provided in the analysis of the wall wipes where compounds associated with ozone surface reaction were identified and semi-quantitatively compared. Calculations for the relative concentrations are described in the SI, and chemical structures and CAS numbers are shown in Table S5.

Prior to initiation of the set of smoking experiments described here, wall sampling identified methyl nicotinate, thiazolidine, 2-ethyl-,bicyclo,octa-1,3,5-triene-7,8-dione, and carbamodithioic acid–diethylmethylester. Their levels were reduced by one cycle of smoking and ventilation, and no longer detected after two cycles. Given the long history of tobacco exposure to the chamber walls, these compounds were most likely due to long-term aging of SHS on wallboard, and can be considered persistent thirdhand smoke constituents. For example, methyl nicotinate has previously been identified as a secondary product of surface nicotine nitrosation (Sleiman et al. 2010).

During the smoking and ventilation cycles, nicotine was identified as the major constituent of all the wallboard wipe extracts, in support of the previous nicotine wallboard loading assumptions. Furthermore, maximum surface concentrations of nicotine, myosmine, and cotinine were observed on the wallboard immediately after the smoking phase, not surprising given that they are primary constituents of SHS. Clean

ventilation reduced the sorbed nicotine concentration by a factor of 2 consistent with desorption. However, ventilation in the presence of ozone reduced nicotine surface concentrations by a factor of 10, in support of enhanced nicotine loss due to heterogeneous reaction. In addition, nicotine-1-oxide was identified in wall wipes (Figure S4) only following O₃ exposure. This intermediate is formed during nicotine-ozone reaction at the pyridinyl nitrogen, a secondary reaction pathway only observed previously in solution (Hoigne and Bader 1983). Nicotine-ozone surface reaction is suspected to occur mainly via electrophilic attack on the amino group (Tuazon et al. 1994; Sleiman et al. 2010) and includes the formation of cotinine and myosmine (Destailats et al. 2006; Petrick et al. 2010).

While present after the smoking phase, cotinine and myosmine were not identified in wall wipes after ventilation in the presence of ozone. This is not surprising since initial cotinine surface concentrations (after smoking) were near the limit of detection. In addition, desorption during clean ventilation reduced initial myosmine surface concentration by a factor of 5 to near its limit of detection. While very low concentrations contributed greatly to analytical limitations, it is also possible that surface reaction may follow different mechanistic pathways or that water at gas-surface interface may play a role in wallboard nicotine-ozone surface kinetics.

Additionally, other compounds were identified in wall wipe samples that did not originate in tobacco smoke. Two organophosphate esters were identified in all samples: tris(2-chloroethyl)phosphate (CAS nr. 115-96-8) and 2-propanol, 1-chloro-phosphate (CAS nr. 13674-84-5). These compounds are present in the formulation of flame retardants, can be emitted from indoor furnishings and electrical equipment, and have

been reported in indoor air and dust (Staaf and Ostman 2005; Saito et al. 2007). Concentrations of these semivolatile organophosphorous compounds on wallboard surfaces remained relatively constant throughout smoking and clean ventilation phases. However, in the presence of ozone, surface concentrations of the organophosphate esters decreased to 20-25% of the post-smoking values, suggesting that these compounds are also susceptible to oxidation.

4. Conclusions

Common indoor surfaces such as painted wallboard and cotton furniture can act as significant sinks for SHS constituents. With high concentrations of sorbed pollutants, these materials act as substrates for ozone-initiated reactions that may release secondary byproducts back to the gas phase and impact indoor air quality over periods of time that are significantly longer than smoking. This study illustrates the importance of gypsum wallboard as a dominant medium for ozone-initiated loss and aging of indoor pollutants. Our findings show, for the first time using a room sized chamber and under realistic conditions, that the reactivity of sorbed nicotine towards indoor ozone leads to the formation of secondary byproducts that remain adsorbed to materials or are re-emitted to the gas phase. While ozone commonly occurs indoors as a consequence of infiltration from polluted urban outdoor air (at a few tens of ppb), even higher levels (hundreds of ppb) can be produced by ozone-generating “air purifiers” that are often used in residences, hotels and other indoor environments. In both cases we expect to observe formation of the oxidation byproducts described here. The asthma hazard indices of the non-volatile and semi-volatile smoke constituents and ozone byproducts identified in this

study raise concerns about the potential health effects associated with the presence of thirdhand smoke pollutants. Future work in this field should provide a quantitative assessment of the incremental risks attributed to chemical transformations of indoor tobacco residues.

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Supplementary Information

Further explanation of experimental conditions and wall wipe sampling, gaseous and sorbed SHS concentrations as a function of time, chemical structures and CAS nr. of identified constituents on denuders, filters, and wallwipes, denuder, filter, and wallwipe normalization calculations, chamber ozone loss due to surface reactivity, nicotine-1-oxide MS spectrum.

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1 TABLES2 **Table 1.** SHS and THS semivolatile constituents and oxidation products identified in denuder and filter extracts of IOGAPS system^a

#	Name	Filter (F) or Denuder (D)	Retention Time	MS Ion	Asthma Hazard Index
Heterocyclic compounds					
1	1,3 diazine or pyrazine	F	5.4	<u>80</u> , 110 / 53, <u>80</u>	0.26
2	4-pyridinol	F	7.6	<u>95</u>	0.09
3 ^b	Nicotine	F, D	12.0	84, <u>133</u> , 162	0.64
4	Indazole	F	13.1	91, <u>118</u>	0.21
5	2,4-Bipyridyl	F, D	15.0	130, <u>156</u>	0.52
6	9H-Pyrido[3,4-b] indole,1-methyl/ 9H-Pyrido[3,4-b]indole	F, D	20.9/21.0	154, <u>182</u> / 140, <u>168</u>	0.43/ 0.36
7	2,2':6',2''-Terpyridine	F, D	25.6	<u>233</u>	0.98
Phenolic compounds					
8	Hydroquinone	F	10.8	81, <u>110</u>	0.01
Nicotine oxidation byproducts					
9	2,5, pyridinecarboxylic acid/nicotinic acid	F	10.3	<u>123</u>	0.99/ 0.92
10	Nicotinamide	F	12.7	78, <u>106</u> , 122	0.53
11 ^b	Myosmine	F, D	13.3	<u>118</u> , <u>145</u> , 146	0.53
12	N-methylnicotinamide	F	13.5	78, 106, <u>135</u>	0.61
13	β-Nicotyrine	F, D	14.1	130, <u>158</u>	0.56
14 ^b	Cotinine	F, D	17.4	<u>98</u> , 119, 176	0.76

3 (cont'd)

4

1 **Table 1.** (cont'd)

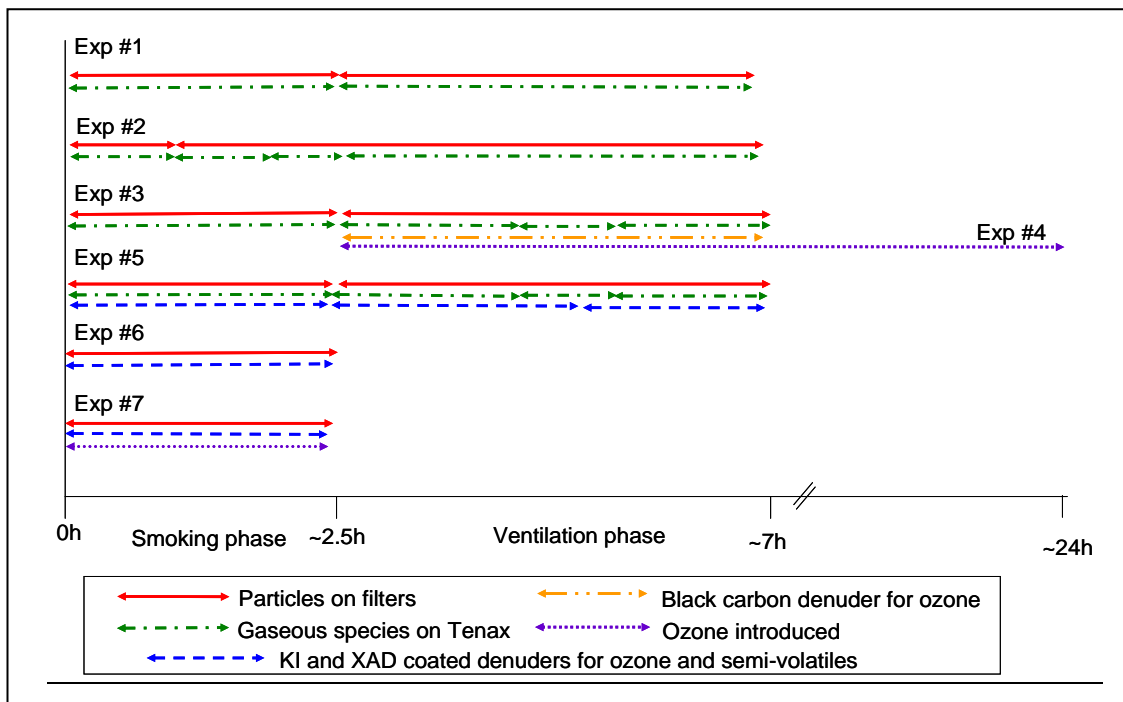
PAHs					
15	Naphthalene, 1,3-dimethyl-	F, D	13.3	141, <u>156</u>	0.08
16	1H-Phenylene/fluorene	D,	15.5	<u>165</u>	0.04
17	Pyrene/Fluoranthene	F, D	22.0/22.6	<u>202</u>	0.06/ 0.08
18	Phenanthrene, 1-methyl-7-(1-methylethyl)-	F	23.6	204, <u>219</u> , 234	0.04
19	Naphthacene/Benzo(a)anthracene/ Triphenylene	F, D	26.2	<u>228</u>	0.17/ 0.13
20	1,2-Dihydrobenzo[b]fluoranthene / 1,2'-Binaphthalene	F	32.0	127, <u>253</u>	0.84
Other					
21	Dibenzofuran	F	16.8	139, <u>168</u>	0.01
22	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	F	18.9,19.2, 20.4, 20.5	70,125, <u>154</u>	0.93

2

3 ^a Compounds identified by comparison of sample spectrum with NIST library mass spectrum unless otherwise stated4 ^b Compounds identified by comparison between NIST library mass spectrum, authentic standards mass spectrum, and retention time.

1 FIGURES

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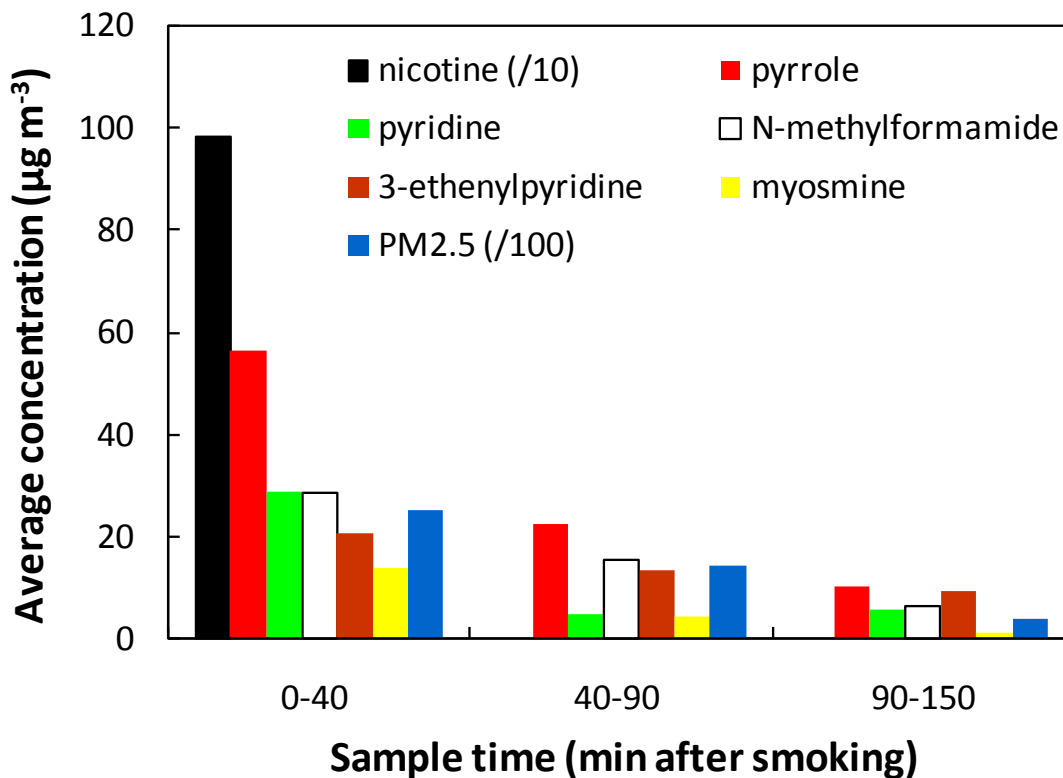


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8 **Figure 1.** Sampling and chamber experimental conditions

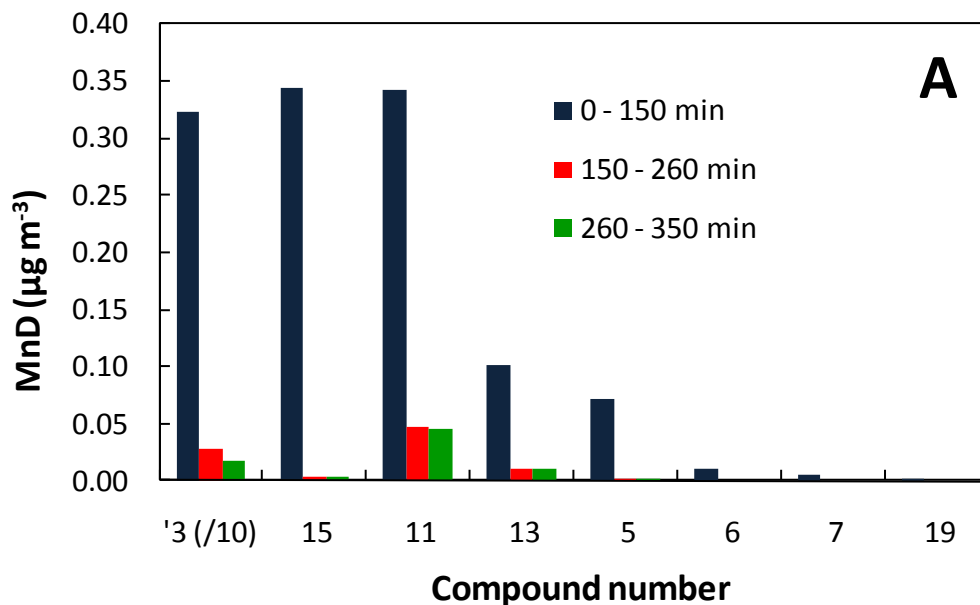
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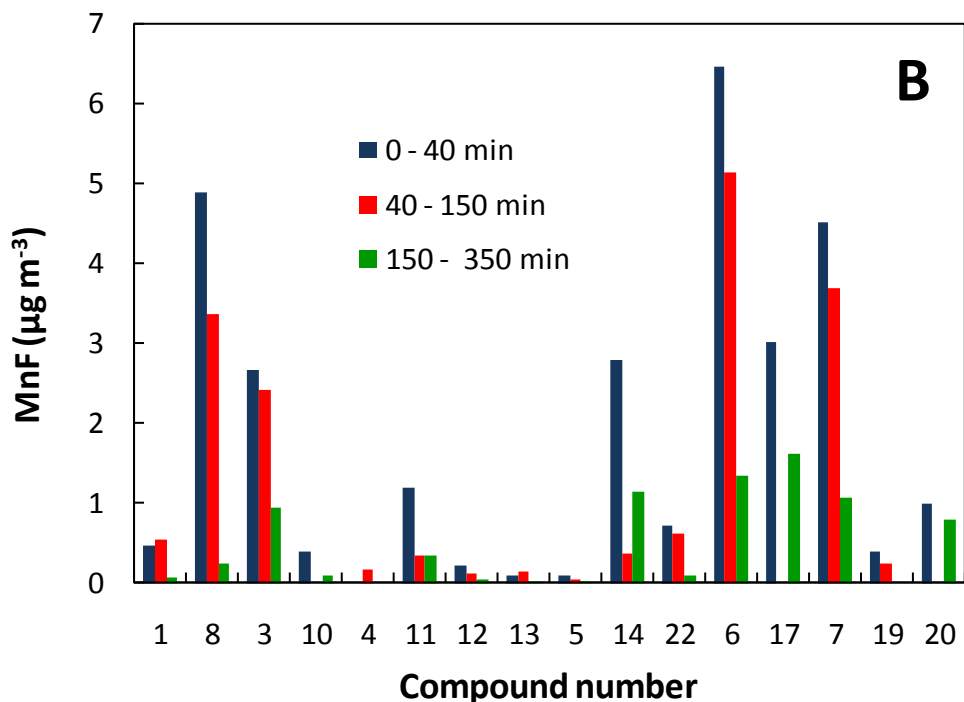


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Figure 2. Concentrations of selected gaseous SHS components and PM_{2.5} during the smoking phase (0-40 min) and clearing periods (40-90 min and 90-150 min). Nicotine and PM_{2.5} concentrations are divided by 10 and 100, respectively for scaling (Exp #2).



1

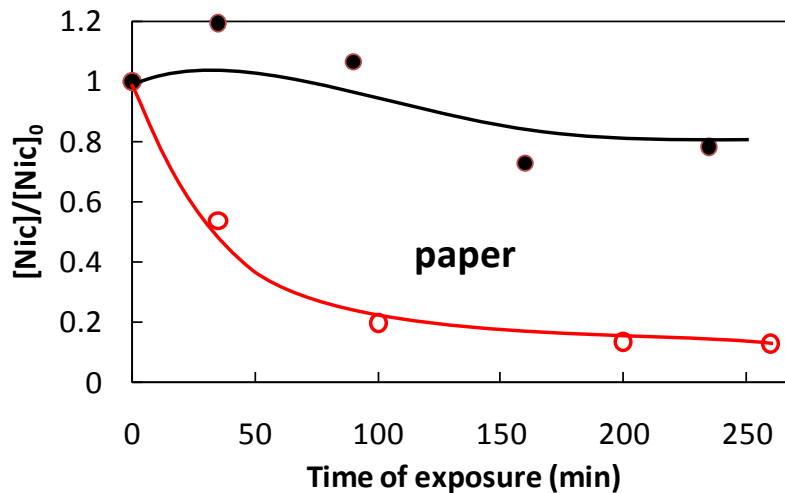


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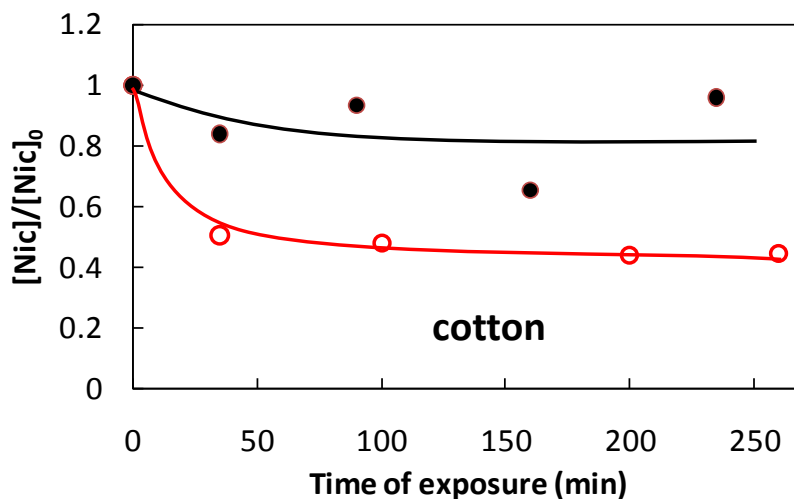
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4 **Figure 3.** Normalized quantification of SHS semivolatile constituents during various
 5 sampling durations on: (A) XAD-coated denuders (Exp #5), and (B) filters not preceded
 6 by denuders (Exp #2). The x-axis compounds are numbered as in Table 1, and ordered by
 7 increasing GC retention time (left to right). In Figure 3a, gaseous nicotine quantity
 8 (compound #3) is divided by 10 for scaling.

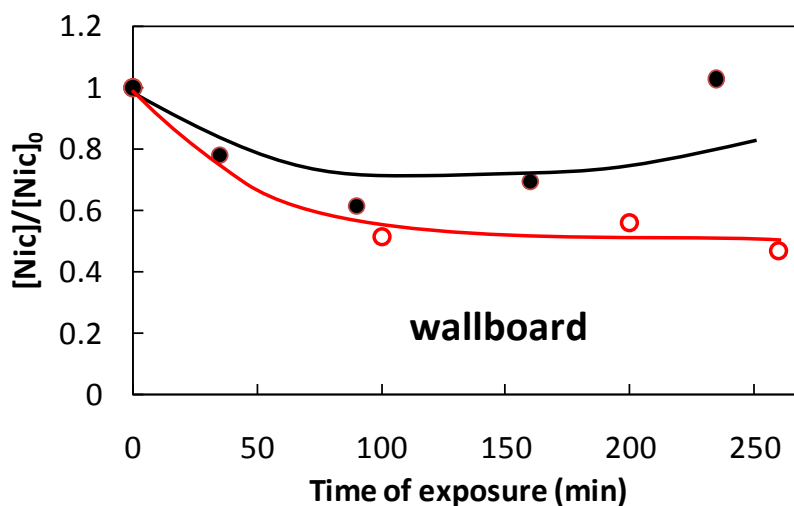
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4 **Figure 4.** Nicotine fraction remaining on model surface upon exposure to clean air (black
 5 data points, Exp #5) or ozone (open data points, Exp #3).