E-cigarette nicotine deposition and persistence on glass and cotton surfaces

Cheryl L. Marchama, Evan L. Floyd, Beverly L. Wood, Susan Arnold, and David L. Johnson

ABSTRACT
Nicotine from electronic cigarette aerosol will deposit on surfaces immediately after vaping, but how long deposited nicotine will persist on various surfaces is unknown. This work exposed glass and terrycloth (cotton) materials to electronic cigarette aerosols for 1 hr, assessed the initial nicotine sorption, and characterized surface persistence over a 72-hr period. Exponential decay of surface concentration was observed for both materials. Terrycloth had higher initial nicotine deposition and retained nicotine substantially longer than glass. Residual nicotine concentrations persisted on both surface types for 72 hr. Statistical modeling predicted surface concentrations to reach background levels after 4 and 16 days for glass and terrycloth, respectively. Nicotine persistence was long enough to pose a potential thirdhand nicotine exposure risk, and reactions to produce tobacco-specific nitrosamines may be possible from nicotine deposition from electronic cigarette aerosols, but further study is needed.

Introduction
Nicotine and other contaminants from tobacco cigarette smoke have been shown to deposit on room surfaces and contribute to thirdhand exposure. Over time, this residual nicotine from tobacco smoke on indoor surfaces can also react with ambient ozone and nitrous acid to form carcinogenic tobacco-specific nitrosamines (TSNAs). Sleiman et al. showed that TSNAs can form in as little as 3 hr with traditional cigarette smoke in a controlled environment with known concentrations of HONO or other nitrogen oxides. Nicotine and TSNAs have also been shown to remain on fabrics for many months after exposure to cigarette smoke. Electronic cigarette (EC) “vapor,” which is actually comprised primarily of fine droplets, typically contains nicotine as well as acrolein, formaldehyde, and acetaldehyde. EC nicotine residues have been measured on surfaces in an exposure chamber immediately after EC aerosols were introduced and in homes where occupants were puffing ECs 50–500 times daily. Floyd also showed that EC aerosols can spread through HVAC systems. If deposited nicotine or other hazardous EC aerosol components persist on surfaces, then thirdhand exposure is possible. However, this surface persistence has not been well characterized.

Some of these studies suggest, however that nicotine from EC aerosols may dissipate much faster than nicotine deposition from traditional cigarette smoke. Goniewicz and Lee reported that in a chamber study, only three of four EC tested showed elevated concentrations of surface nicotine immediately after a puff test. Bush and Goniewicz found that measurable levels of surface nicotine was found in only half of EC user’s homes studied, whereas nicotine was found in all of the tobacco cigarette smokers’ homes. It is possible that nicotine deposited from EC aerosol may dissipate faster than nicotine from secondhand tobacco smoke, since there is no persistent (smoke) particle providing a sorption surface for the nicotine as there is with traditional tobacco smoke. Nicotine is a semi-volatile compound and can be present in both the gas and particulate phases at normal indoor temperatures. When concentrated, as in mainstream and sidestream tobacco cigarette smoke, nicotine is primarily in the particle phase. When dilute, as in environmental tobacco smoke, 95% is in the gas phase. This concentration-dependent nicotine partitioning appears to be true for concentrated EC aerosol as well, with 76–100% of the nicotine in the droplets. These droplets will deposit on surfaces. However, it is unclear how long the nicotine will
persist on the surface. Surface concentration might be expected to decline over time, as determined by processes such as adsorption, desorption, evaporation, solvation and chemical reaction.\textsuperscript{[10]}

The existing literature indicates nicotine accumulates on different materials to differing degrees\textsuperscript{[4,10]} but no studies have been conducted to determine differences in persistence by material type. The objective of this study was to characterize the persistence of surface-deposited EC nicotine over a short aging period of 72 hr on two common surface materials: terrycloth (cotton) and glass.

**Methods**

Glass and cotton were selected as sampling materials in this study for continuity with similar studies. Glass and cotton deposition surfaces were exposed to EC aerosol in an acrylic containment chamber for 1 hr, then aged under active aerosol-free ventilation for 72 hr. Randomly selected samples of each material were periodically removed for analysis to determine nicotine persistence by material type.

Forty-two pairs of glass plate (GP) and 100% cotton terrycloth (TC) surfaces, in pairs, were placed on the floor of a 1 m\textsuperscript{3} volume glove box exposure chamber as shown in Figure 1. GP samples were 90-mm glass petri dishes with an internal surface area of 58.1 cm\textsuperscript{2}. GPs were washed in a laboratory dish washing machine using Cascade liquid dish detergent (Walmart, Edmond, OK), then triple sonicated in deionized water for 30 min. TC patches were cut from a new, freshly washed towel to match the nominal surface area of the GPs, i.e., 3 x 3 inches or 7.6 x 7.6 cm. To ensure the cleanest, nicotine-free cotton material possible, a new terrycloth towel was washed in a residential washing machine two full cycles using laundry detergent (Gain original powdered laundry detergent, unscented; Walmart, Edmond, OK), then one full cycle without detergent. Afterward, the towel was soaked in 0.5 M HCl (ACS grade, Fisher Scientific, Waltham, MA) for 2 hr, wrung dry, then triple rinsed in deionized water with pH checked for neutral on final rinse. After air drying, the towel was cut into squares with clean shears.

After sealing the chamber, three material pairs were collected from randomly selected chamber locations to establish the pre-exposure nicotine background in the materials. EC aerosol was manually generated using a 500-mL syringe connected to a
Smok VCT Pro sub-ohm atomizer powered by a Smok R200TC battery unit (Smoktech, Shenzhen, China). The atomizer was loaded with a laboratory-prepared solution of 70%v vegetable glycerin, 30%v propylene glycol, and 12 mg/mL nicotine, and operated at 40 watts. Each puff was approximately 3 (±0.1) sec long and 500 (±20) mL in volume. Alternating sets of five puffs were introduced into the chamber, upward through the left and then right access ports (Figure 1), to distribute the aerosol evenly and avoid bias due to loading. A total of 49 puffs, totaling 2.569 g (2.20 mL) of aerosolized solution, were added to the chamber via the access ports over 15 min, and the chamber air then briefly mixed by vigorously puffing the syringe within the chamber until no swirling could be seen in the aerosol. The aerosol was allowed to deposit for an additional 45 min without ventilation, followed by rapid chamber clearing at a ventilation rate of approximately 28 cfm (0.79 m³/min) for 15 min (~12 air changes). During clearing, another three randomly selected sample pairs were collected to establish the initial post-exposure nicotine concentration. The ventilation rate was reduced to approximately 6.8 cfm (0.19 m³/min) for the duration of the experiment. Three randomly selected material pairs were also collected at 1, 2, 4, 8, 18, 24, 36, 48, and 72 hr post-exposure. A second set of three pairs was collected at 1 and 36 hr to provide additional measurement variability information. Temperature and relative humidity were maintained at 23°C +/- 1.5°C and 60% RH +/-5% RH throughout the experiment.

TC samples were placed in a pre-weighed 40-mL Volatile Organic Analysis (VOA) vial with PTFE-lined lid, while GP samples were covered with the petri dish lid to minimize evaporation. Samples were extracted for nicotine immediately after collection and stored at ~20°C. TC samples were spiked with 50 μg of internal standard (25 μL of 2000 μg/mL quinolone, reagent grade, Sigma-Aldrich, St. Louis, MO) while in the VOA vial and extracted with 20 mL dichloromethane (DCM) (VWR, Radnor, PA, U.S.A.) for 20 min while tumbling. After extraction, TC samples were drained of DCM and packed into a 10-mL all-polypropylene disposable syringe and squeezed back into the same VOA vial. Recovery volumes (approximately 15 mL) were precisely determined by weight gain of the VOA vial + solvent, and density of DCM. DCM extracts were then evaporated by nitrogen blow-down to approximately 1 mL and post-weighed to determine the final volume.

GP samples were spiked with 50 μg of internal standard (ISTD) then extracted by quadruplicate rinsing of each plate with 4 mL DCM on a hotplate at 35–40°C. Each rinse volume was transferred to a pre-weighed VOA vial. The hotplate was necessary to prevent water condensation from forming on the GP vial during transfer of each rinse due to evaporative cooling of the DCM. Collected rinsate (approximately 16 mL) was evaporated to approximately 1 mL and post-weighed to determine final volume, as above. All completed samples were stored at ~20°C until ready for gas chromatography–mass spectrometry (GC–MS) analysis.

TC calibration standards were prepared by spiking clean TC samples with 0.2–124 ug nicotine in a spike volume of 10–100 uL, then allowed to evaporate for 10 min. GP calibration standards were prepared by spiking clean GPs with 0.1–217 ug nicotine in 100 or 300 uL of a nicotine/DCM solution, then allowing the DCM to evaporate completely (while on the warm hotplate). Calibration standards were extracted in the same manner as samples, as previously described. Method limit of quantification (LOQ) for TC samples was determined as nine times the standard deviation of nine replicates prepared at low end of the calibrated range. LOQ for TC samples was 1.56 ug/sample (0.027 ug/cm²). The LOQ for GP samples was determined to be 1.41 ug/sample (0.024 ug/cm²).

Nicotine GC–MS analyses were performed using an Agilent 6890 gas chromatograph with 5973N mass selective detector (Agilent Corp., Alpharetta, GA) operated in scan mode from 20–330 m/z. Sample results were ISTD-corrected and final concentration estimates were adjusted for sample-specific extraction volumes and evaporation final volumes. Nicotine concentrations in the extract (μg/mL) were converted to surface concentrations (μg/cm²) by multiplying by final volume and dividing by sample surface area (58.1 cm²).

Nicotine surface concentration decay was modeled using the SAS 9.4 GLM procedure (SAS Institute, Cary, NC). Log-transformed surface concentration was modeled on hours post-exposure, material type, and their interaction. The resulting model allowed an estimate of the length of time required, by material type, for nicotine concentration to return to background levels found in samples unexposed to EC aerosol.

Results

Laboratory method blanks analyzed prior to conducting the experiment averaged 0.27 μg per sample (0.004 μg/cm²), which was below the method limit of
quantitation (LOQ) for both materials. Pre-exposure samples collected immediately before EC aerosol exposure, which served as field blank samples, were also < LOQ; therefore, no background correction was applied to the sample results.

Nicotine on GP samples ranged from 0.290 to 0.030 μg/cm² and decreased over time, with a rapid decline observed in the first hour followed by a slower decline for the duration of the trial (Figure 2). Nicotine on TC samples ranged from 0.949 to 0.323 μg/cm², also decreasing over time but without the initial rapid decline seen for GP. Nicotine concentration was substantially greater on TC than GP at all time points, which was unexpected. Variability within each time point ranged from 7 to 31% relative standard deviation (RSD) for GP and 3 to 24% RSD for TC. Analysis of the 1- and 36-hr double-sampling events (n = 6 each) confirmed lower variability in TC samples at both time points (RSD: TC = 11.6 and 4.8%, GP = 22.6 and 14.6%, at 1 and 36 hr, respectively).

Statistical modeling showed the main effects (time and material type) and their interaction to be statistically significant (α < 0.05), indicating differences by material in nicotine initially sorbed to the surfaces as well as in the rate of surface concentration decay over time. From the model, the time that would be required for nicotine levels to return to background levels were estimated to be 95.5 hr (4 days) for GP and 385 hr (16 days) for TC.

**Discussion**

Both the amount of nicotine sorbed and the nicotine decay rates were significantly different for TC and GP, with higher sorption and more rapid average decay with TC than GP. Initial deposition results were consistent with those of Schick et al. [3] who found that nicotine deposition was 14% greater for TC than paper or stainless steel. Sorption by diffusion is surface-area mediated, and it is possible that the complex loop structure of TC simply provided a greater surface area than the smooth glass plates. It is also possible the hydrophilic surface of the cotton (cellulose) acted as a diffusion sink for nicotine vapor.

The persistence of nicotine on TC of 16 days is four times longer than the persistence on GP, which confirms that type of material has a great effect on nicotine retention. Cellulose is known to have a water monolayer at low relative humidity (RH) and polylayer at moderate RH [22], which can solvate nicotine as long as minimal humidity is present in the ambient environment and thereby inhibit its subsequent evaporation. Furthermore, Bahl et al. [10] noted that TC has a hydrophilic cellulose backbone that can participate...
in direct hydrogen bonding with nicotine. Both characteristics may have contributed to the greater TC persistence.

The GP and TC persistence times of 4 and 6 days, respectively, may be long enough for TSNA s to form by environmental nitrosation, but further study is needed. Thus, nicotine sorption on clothing and furniture upholstered with natural fibers might result in not only thirdhand nicotine exposures, but also potentially TSNA exposures. However, this should be verified with long-term studies.

**Limitations**

The EC liquid used in this experiment was prepared from laboratory chemicals of high quality and contained no flavorings. The impact of flavoring compounds on deposition and retention of the EC aerosol was not explored or evaluated in this study. Also, the nicotine concentration used in the EC liquid is higher than most users of sub-ohm ECs, which was done to ensure sufficient deposition on the samples within the 1-hr deposition period.

It should be noted that the level of EC aerosol in the test chamber was quite high compared to what is likely to be produced in residences by casual vapers. Based on estimates from St. Helen et al., the concentration of EC nicotine and aerosol components exhaled by a vaper are expected to be approximately 6–16% of what was introduced into the study chamber, but their work did not evaluate vaping with high-powered ECs such as that used in this study. It is therefore unknown what exhaled fraction should be expected, and how it might compare to the conditions used in this study.

Finally, this pilot laboratory study was limited to nicotine sorption and persistence on only two material types after a single 1-hr aerosol exposure. Nicotine, and other contaminant, sorption and persistence on other surfaces and under other conditions was not determined due to the project’s limited scope.

**Conclusions**

The objective of this study was to characterize nicotine sorption and persistence on two common surface materials following exposure to EC aerosol. This study shows that nicotine from e-cigarettes can sorb to and persist upon indoor surfaces. There were significant differences in initial sorption, with terrycloth (cotton) sorbing much more than glass. There were also significant differences in persistence, with terrycloth retaining nicotine longer than glass. Decay rates observed in this study indicate EC nicotine persistence are potentially long enough to pose a risk for third-hand exposures to nicotine, especially if continued deposition from continued use is present. Given the absence of any evidence that the constituents of e-cigarette aerosols prevent nitrosation reactions on indoor surfaces, it is appropriate to assume that reactions to produce tobacco-specific nitrosamines are possible in sorbed e-cigarette aerosols containing nicotine, but further study is needed.

**Recommendations**

Additional research is needed to assess the risk of exposure to nicotine and its reactive products, as well as other EC aerosol contaminants. If nicotine persists on a surface or is continually replenished, it may reside long enough to react with ambient ozone and nitrous acid to form TSNA s and other carcinogenic byproducts. Therefore, further research is needed to study long-term deposition of nicotine from ECs to determine whether TSNA s form over time. Following the precautionary principle, use of ECs should be avoided in confined spaces such as vehicles and homes where children are present or likely to occupy. Use of EC should be consistent with smoking policies.

**References**

[1] Matt, G.E., P.J.E. Quintana, M.F. Hovell, et al.: Households contaminated by environmental tobacco smoke: Sources of infant exposures. Tob. Control. 13: 29–37 (2004).

[2] Matt G.E., P.J.E. Quintana, A.L. Fortmann, et al.: Thirdhand smoke and exposure in California hotels: Non-smoking rooms fail to protect non-smoking hotel guests from tobacco smoke exposure. Tob. Control. 23(3):264–72 (2014).

[3] Schick, S.F., K.F. Farraro, C. Perrino, et al.: Thirdhand cigarette smoke in an experimental chamber: Evidence of surface deposition of nicotine, nitrosamines and polycyclic aromatic hydrocarbons and de novo formation of NNK. Tob. Control. 23: 152–59 (2014).

[4] Bahl, V., H.J. Sim, P. Jacob, K. Dioas, S.F. Schick, and P. Talbot: Thirdhand smoke: Chemical dynamics, cytotoxicity, and genotoxicity in outdoor and indoor environments. Toxicol. in Vitro. 32: 220–31 (2015).

[5] Matt, G.E., P.J.E. Quintana, H. Destaillats, et al.: Thirdhand tobacco smoke: Emerging evidence and arguments for a multidisciplinary research agenda. Environ. Health Perspect. 119: 1218–26 (2011).

[6] Sleiman, M., L.A. Gundel, J. Pankow, P. Jacob, B. Singer, and H. Destaillats: Formation of
carcinogens indoors by surface-mediated reactions of nicotine with nitrous acid, leading to potential third-hand smoke hazards. Proc. Nat. Acad. Sci. U.S.A. 107(15):6576–81 (2010).

[7] Destaillats, H., B.C. Singer, S.K. Lee, and L.A. Gundel: Effect of ozone on nicotine desorption from model surfaces: Evidence for heterogeneous chemistry. Environ. Sci. Technol. 40:1799–805 (2006).

[8] Petrick, L.M., A. Svidovsky, and Y. Dubowski: Thirdhand smoke: Heterogeneous oxidation of nicotine and secondary aerosol formation in the indoor environment. Environ. Sci. Technol. 45:328–33 (2011).

[9] Petrick, L.M., M. Sleiman, Y. Dubowski, L.A. Gundel, and H. Destaillats: Tobacco smoke aging in the presence of ozone: A room-sized chamber study. Atmos. Environ. 45:4959–65 (2011).

[10] Bahl, V., P. Jacob, C. Havel, S.F. Schick, and P. Talbot: Thirdhand cigarette smoke: Factors affecting exposure and remediation. PLoS One 9(10):e108258 (2014).

[11] Czogala, J., M.L. Goniewicz, B. Fidelus, W. Zielinska-Danch, M.J. Travers, and A. Sobczak: Secondhand exposure to vapors from electronic cigarettes. Nicotine Tob. Res. 16(6):655–62 (2013).

[12] McAuley, T.R., P.K. Hopke, J. Zhao, and S. Babaian: Comparison of the effects of e-cigarette vapor and cigarette smoke on indoor air quality. Inhal. Toxicol. 24(12):850–57 (2012).

[13] Goniewicz, M.L., J. Knysak, M. Gawron, et al.: Levels of selected carcinogens and toxicants in vapour from electronic cigarettes. Tob. Control. 23:133–39 (2014).

[14] Geiss, O., I. Bianchi, F. Barhona, and J. Barrero-Moreno: Characterisation of mainstream and passive vapours emitted by selected electronic cigarettes. Int. J. Hyg. Environ. Health. 281(1):169–80 (2014).

[15] Uchiyama, S., K. Ohta, Y. Inaba, and N. Kunugita: Determination of carbonyl compounds generated from the e-cigarette using coupled silica cartridges impregnated with hydroquinone and 2,4-dinitrophenylhydrazine, followed by high-performance liquid chromatography. Anal. Sci. 29(12):1219–22 (2013).

[16] Goniewicz, M. L., and L. Lee: Electronic cigarettes are a source of thirdhand exposure to nicotine. Nicotine Tob. Res. 17(2):256–58 (2015).

[17] Bush, D., and M.L. Goniewicz: A pilot study on nicotine residues in houses of electronic cigarette users, tobacco smokers, and non-users of nicotine-containing products. Int. J. Drug Policy. 26:609–11 (2015).

[18] Floyd, E.: “When cloud chasing spills over: A different kind of ’vapor intrusion.’” Presented at the American Industrial Hygiene Conference and Exposition, Seattle, Washington, June 6, 2017.

[19] Seeman, J.L., P.J. Lipowicz, J. Piade, et al.: On the deposition of volatiles and semivolatiles from cigarette smoke aerosols: Relative rates of transfer of nicotine and ammonia from particles to the gas phase. Chem. Res. Toxicol. 17(8):1020–37 (2004).

[20] Van Loy, M.D., W.J. Riley, J.M. Daisey, and W.W. Nazaroff: Dynamic behavior of semivolatile organic compounds in indoor air. 2. Nicotine and phenan-threne with carpet and wallboard. Environ. Sci. Technol. 35(3):560–67 (2001).

[21] Sundahl, M., E. Berg, and M. Svensson: Aerodynamic particle size distribution and dynamic properties in aerosols from electronic cigarettes. J. Aerosol Sci. 103:141–50 (2017).

[22] Hill, C.A.S., A. Norton, and G. Newman: The water vapor sorption behavior of natural fibers. J. Appl. Polym. Sci. 112:1524–37 (2009).

[23] St. Helen, G., C. Havel, D.A. Dempsey, P. Jacob, and N. Benewitz: Nicotine delivery, retention and pharmacokinetics from various electronic cigarettes. Addiction 111, 535–44 (2016).