

Siloxane Emissions and Exposures during the Use of Hair Care Products in Buildings

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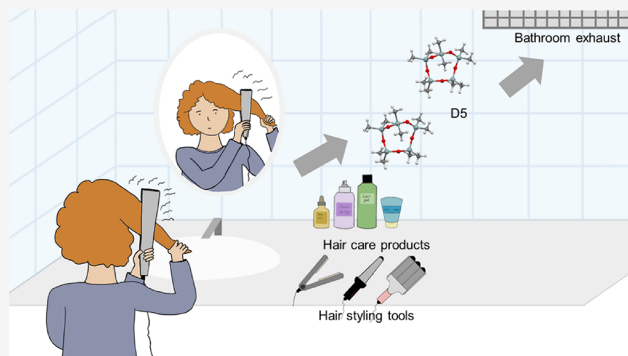
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ABSTRACT: Cyclic volatile methyl siloxanes (cVMS) are ubiquitous in hair care products (HCPs). cVMS emissions from HCPs are of concern, given the potential adverse impact of siloxanes on the environment and human health. To characterize cVMS emissions and exposures during the use of HCPs, realistic hair care experiments were conducted in a residential building. Siloxane-based HCPs were tested using common hair styling techniques, including straightening, curling, waving, and oiling. VOC concentrations were measured via proton-transfer-reaction time-of-flight mass spectrometry. HCP use drove rapid changes in the chemical composition of the indoor atmosphere. cVMS dominated VOC emissions from HCP use, and decamethylcyclopentasiloxane (D5) contributed the most to cVMS emissions. cVMS emission factors (EFs) during hair care routines ranged from 110–1500 mg/person and were influenced by HCP type, styling tools, operation temperatures, and hair length. The high temperature of styling tools and the high surface area of hair enhanced VOC emissions. Increasing the hair straightener temperature from room temperature to 210 °C increased cVMS EFs by 50–310%. Elevated indoor cVMS concentrations can result in substantial indoor-to-outdoor transport of cVMS via ventilation (0.4–6 tons D5/year in the U.S.); thus, hair care routines may augment the abundance of cVMS in the outdoor atmosphere.

KEYWORDS: indoor air quality, volatile organic compounds, personal care products, proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF-MS), chemical emissions, siloxanes



INTRODUCTION

Hair care products (HCPs) include a diverse array of shampoos, conditioners, sprays, creams, lotions, gels, oils, waxes, and pomades. Surveys indicate that a large population of people routinely use HCPs for cleaning, treating, and styling their hair in their home environment.^{1–4} A study on household personal care product (PCP) usage patterns in California, U.S., reported that 29 to 70% of respondents of various genders and age groups claimed to use hair styling products (e.g., hair gels, hair sprays, and hair waxes) in their homes.³ A survey on PCP usage patterns in the Netherlands indicated that 97% of participants use HCPs, and 50% of the participants use leave-on HCPs, including hair gels, lotions, and waxes, among which 80% of the HCP consumers apply them more than once per week and ~40% apply them more than once per day.¹ High-frequency HCP use patterns were observed across participants of all ages and genders.^{1–4} Given the complex chemical formulations of these products, potential emissions of volatile organic compounds (VOCs), such as siloxanes, during indoor use of HCPs may be an issue that affects a large percentage of the global population.

Siloxanes are organosilicon compounds that contain $[-\text{Si}(\text{CH}_3)_2-\text{O}-]$ groups and have been widely used in the hair cosmetics industry over the past few decades.^{5,6} Cyclic volatile methyl siloxanes (cVMS, denoted by “D” followed by the number of Si atoms in the compound) and linear volatile methyl siloxanes (IVMS, denoted by “L”) are two important subgroups of siloxanes. Due to their low surface tension, inertness, high thermal stability, and smooth texture,^{7–9} cVMS, including octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), or dodecamethylcyclohexasiloxane (D6), are ubiquitous in PCPs.¹⁰ cVMS can be used as carriers in HCPs to uniformly deliver high-molecular-weight fluids to hair.⁵ D5 is often listed first or second in the ingredient lists of some HCPs, indicating that it can be one of the most abundant ingredients in these products.

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cVMS can persist and bioaccumulate in aquatic organisms¹¹ and it has been detected in aquatic environments and various marine animals.^{11,12} D4 is considered to be “persistent, bioaccumulative, and toxic” and “very persistent and very bioaccumulative”, while D5 is classified as the latter by the European Chemicals Agency.¹³ D4 has been shown to cause fatal liver and lung damage in mice.¹⁴ Inhalation exposure to D5, which is the major route of cVMS exposure while applying PCPs,¹⁵ can lead to adverse effects on the respiratory tract, liver, and nervous system of laboratory animals.^{16,17} Nevertheless, the impact of cVMS on human health has remained poorly characterized. Other ingredients commonly found in HCPs, such as monoterpenes and propylene glycol, may potentially impact human health. Inhalation exposure to some monoterpenes is associated with respiratory symptoms.^{18,19} Dermal exposure to propylene glycol has been found to cause skin irritation and sensitization; however, contradictory results suggesting that propylene glycol is not related to skin irritation have also been reported.²⁰

Most existing environmental studies on siloxanes in PCPs are focused on wash-off products,^{21–24} which are designed to be removed from the skin or hair with water after application, such as shampoos and cleansers. Considering their impact on aquatic ecosystems, the European Union has established regulations for wash-off PCPs, limiting D4 and D5 to less than 0.1% by weight.¹³ However, studies or regulations on siloxane emissions and exposures from leave-on products, which are designed to be left on the skin or hair after application, such as hair creams, hair gels, and hair sprays, are very limited. Usage of these products in confined indoor spaces, such as residential bedrooms or bathrooms, could potentially cause high indoor siloxane concentrations, which might raise concerns for human inhalation exposure in the indoor atmosphere. In addition, indoor-to-outdoor emissions from PCPs may also be of concern for urban air quality in densely populated cities. Recent studies have revealed the existence of cVMS in both urban and rural atmospheres.^{25–29} For example, urban D5 concentrations were found to increase in the early morning in North American cities, indicating a strong association between urban outdoor D5 mixing ratios and the use of PCPs.²⁷ Volatile chemical products may be the largest source of VOCs in urban areas,^{30,31} which can be precursors to ozone formation and contribute to the generation of other secondary products.^{31–35} As a subclass of volatile chemical products, hair care products could potentially impact the atmospheric environment, with cVMS and monoterpenes as their ingredients, which can produce secondary products.^{36–40} cVMS can be oxidized by OH radicals with a lifetime of 4 to 10 days, leading to the formation of secondary oxidation products and secondary organic aerosol (SOA).^{41,42}

Existing studies on siloxane emissions from PCPs^{43,44} and siloxanes in indoor air or indoor dust have been primarily conducted using offline gas chromatography–mass spectrometry (GC–MS) measurements.^{45–50} Despite providing a knowledge base on the relative abundance of siloxanes in indoor environments and PCPs, such offline measurements cannot capture rapid changes in indoor air composition during active hair care routines. Real-time measurements of indoor VOCs via proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF-MS) have emerged in recent years.^{51–60} Real-time indoor siloxane concentrations have been reported for several indoor environments and indoor activities,

including applying PCPs, disinfecting, cleaning, and cooking.^{51,52,54,55,60} Among these studies, Tang et al. (2015) and Molinier et al. (2022) specifically investigated VOC emissions from the use of PCPs in residences.^{51,52} However, hair care routines can be unique indoor activities compared to the use of other PCPs. HCPs are commonly used with hair styling tools operated at high temperatures (148.9–210 °C), such as hair straighteners, hair curlers, and hair wavers. These products are commonly applied close to the breathing zone, where VOC concentrations can be significantly higher as compared to the bulk indoor air during active use of consumer products.⁵⁷ These factors may intensify VOC emissions and human exposure to these products. However, studies on real-time VOC emission profiles during hair care routines are limited.²⁴

The objective of this study is to characterize indoor emission profiles, human inhalation exposures, and indoor-to-outdoor transport of siloxanes and other VOCs during indoor hair care routines. A composite matrix of realistic hair care experiments was designed and conducted in a mechanically ventilated, zero-energy tiny house laboratory. Real-time indoor VOC measurements via PTR-TOF-MS were combined with a material balance model to evaluate the impact of HCP type, hair styling tools, their operation temperatures, and hair length on cVMS and VOC emission factors (EFs). EFs provide a generalizable output that can be used by the indoor air quality, atmospheric chemistry, and exposure science research communities to further understand how HCP emissions affect indoor and outdoor atmospheric environments and human health.

MATERIALS AND METHODS

Description of the Study Site. The measurement campaign was conducted in a residential architectural engineering laboratory—the Purdue zero Energy Design Guidance for Engineers (zEDGE) Tiny House.^{56–58} zEDGE is located on the campus of Purdue University in West Lafayette, Indiana, U.S.A. (Figure S1). zEDGE is built on a mobile trailer according to guidelines established by the Recreational Vehicle Industry Association (RVIA) and holds a National Organization of Alternative Housing (NOAH) certificate.

zEDGE is a mechanically ventilated single-zone residential building with a conditioned interior volume of 60 m³. A single-zone ductless heating and cooling system (FTX12NMVJU, Daikin North America LLC, Houston, Texas, U.S.A.) and a portable air conditioner were used to maintain a nominal indoor air temperature of 20 °C (68 °F). The indoor air temperature and relative humidity were measured with a hand-held humidity and temperature meter (HM70, Vaisala Oyj, Helsinki, Finland). A variable-speed powered ventilator with two MERV 13 filters directed filtered outdoor air to the interior of zEDGE (Figure S1), while a variable-speed bathroom exhaust fan (FV-0511VKS2, Panasonic Eco Solutions of North America, Newark, New Jersey, U.S.A.) directed indoor air to the outdoors. The settings of the powered ventilator, bathroom exhaust fan, and portable air conditioner were adjusted to achieve the desired air change rate (ACR) for each experiment (Table S1). Four mixing fans were set up on the main floor and loft in zEDGE to promote indoor air mixing (Figure S1).

Real-Time Indoor VOC Measurements via PTR-TOF-MS. Mixing ratios of VOCs were measured with a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS, PTR-TOF 4000, Ionicon Analytik Ges.m.b.H., Innsbruck,

Austria).^{56–58} Hydronium (H_3O^+) was used as the reagent ion. In the drift tube, compounds with proton affinities (PA) greater than the PA of water will collide with H_3O^+ and be ionized through a proton transfer reaction.^{61,62} Then, the ionized molecules are separated and detected by a TOF-MS. During the experiments, mass spectra for mass-to-charge ratios (m/z) from 20 to 450 were recorded at a sampling rate of 1 Hz. The chemical formula with the closest exact mass to a m/z peak was determined as the chemical formula corresponding to that m/z value, and then a tentative identification of compounds can be determined based on their chemical formulas. Pressure, voltage, and temperature for the drift tube were set at 2.2 mbar, 600 V, and 70 °C, respectively, and the ionization field energy (E/N) was kept at 139 Td. The indoor sampling inlet was located near the center of zEDGE, and the outdoor sampling inlet was extended to the outdoor air intake of the powered ventilator, as shown in Figure S1. An automated multipoint valve sampling system (VICI Valco Instruments, Houston, Texas, U.S.A.) was built to switch the sampling location between indoors and outdoors, sampling indoors for 55 min and outdoors for 5 min. The active hair care period of the experiments was ensured to take place when the PTR-TOF-MS was sampling indoor air. PFA tubing (3/8 in. OD) was used as the sampling line. A PTFE membrane filter (1 μm pore size) was installed at the intake of the sampling line to remove particles. The filter was replaced daily to ensure its efficacy. D5 and monoterpenes were calibrated with a D5 gas standard and a limonene gas standard, respectively. Details on the calibration of PTR-TOF-MS can be found in Jiang et al. (2021)⁵⁶ and also in the Supporting Information. VOC concentrations in the Results and Discussion are reported using a 10 s moving average of the measured data.

Protocol for Hair Care Routine Emission Experiments.

A total of $n = 46$ emission experiments were conducted during the measurement campaign in zEDGE over a period of two months, including three experiment types: (1) realistic hair care experiments ($n = 35$) that replicate actual hair care routines in the home environment, including different combinations of HCPs, hair styling tools, operation temperatures of the hair styling tools, occupancy, and ventilation conditions. These experiments were conducted following a Purdue University Institutional Review Board (IRB)-approved experimental protocol (IRB-2022-157). Volunteers who were generally healthy, between the ages of 18 and 65, and routinely used hair care products were recruited to participate in this study. Participants were allowed to participate in this study multiple times if they had several different hair care routines. Supporting Information experiments include: (2) hot plate emission experiments ($n = 8$) that explore the relationship between the temperature of the hair care tools and VOC emissions; and (3) surface area emission experiments ($n = 3$) that investigate how hair surface area impacts VOC emissions during hair care events. The experimental sequences and conditions for each HCP emission experiment are summarized in Figure S2. Details of the supplemental experiments are provided in Supporting Information.

Realistic Hair Care Routine Emission Experiments. For the realistic hair care routine emission experiments, the participants were asked to bring their own HCPs and hair styling tools (if that is part of their hair care routine) to replicate their hair care routines in zEDGE (Figure S1). Eight siloxane-based HCPs and three hair styling tools were used

during the hair care routines. Products A–G include hair creams, hair serums, hair lotions, and hair sprays, which are promoted to reduce hair damage and breakage. These HCPs were used with heated hair styling tools, including hair straighteners, curlers, and wavers. Product H is a hair oil to repair dry hair and calm frizz. It was applied to the hair directly by hand without any hair styling tools. Detailed information for each HCP is provided in Table S1. Additional hair care events were conducted with different outdoor ACRs and occupancy levels to study the impact of both factors on indoor VOC emissions.

Prior to each experiment, the participants were instructed to separate their hair into four sections. The hair length of each participant was categorized as long hair (below the shoulder) or short hair (above the shoulder). The sequence of each experiment consisted of four periods to replicate a real-life indoor HCP application event: (1) a 10 min unoccupied background period to account for emissions from the building itself; (2) a 10 min background period with occupants in zEDGE to account for human-related VOC emissions; (3) a 25 min active hair care period for long hair or a 15 min active hair care period for short hair, in which the hair styling appliance was preheated for the first 3 min, and then two pumps of the HCP were applied to one section of hair every 5 min for long hair and 150 s for short hair, respectively. The mass and volume of each pump of each HCP were measured three times after the experiments, and the averaged values are provided in Table S1. The active hair care period closely replicates the participants' hair care routines in their own homes. After hair styling, the participants had 2 min to collect the tools and leave zEDGE; and (4) a 60 min concentration decay period in which zEDGE was unoccupied and the PTR-TOF-MS monitored the decay in indoor VOC concentrations. The indoor air was purged at an outdoor ACR of 9 h^{-1} for at least 30 min between experiments to help remove indoor air pollutants. The experiments and subsequent analysis focused on indoor VOC concentrations and emissions during and after active hair care routine periods and did not account for emissions from residual HCPs on the human body during the remainder of the day.

Material Balance Model for the Determination of VOC Emission Factors and Emission Rates. Emission factors (EFs) are a generalizable metric to quantify the total amount of species emitted, normalized by the amount of product applied or the number of people. Emission rates (ERs) generalize the amount of VOC emitted by time (mg min^{-1}), which describe how fast a specific VOC is emitted during an emission event. EFs and ERs are useful in modeling VOC concentrations for different indoor emission scenarios with different outdoor ACRs, room volumes, and amounts of HCP applied. For consumer products, EFs can be expressed as mass emitted per mass or volume of product applied (mg g^{-1} or mg mL^{-1}) or per person applying the product (mg person^{-1}).⁵⁶

To calculate speciated emission factors (EFs) and emission rates (ERs), the Purdue zEDGE Tiny House was treated as a single zone completely mixed flow reactor (CMFR).⁵⁶ As shown in Figure S3, a material balance model was developed to determine EFs and ERs for VOCs (e.g., siloxanes, monoterpenes and monoterpenoids, and glycols) released from hair care products (HCPs), as previously done to determine EFs and ERs for VOCs released from botanical disinfectants.⁵⁶ To estimate speciated EFs and ERs during the hair care routines, the material balance model was simplified based on the

following three assumptions: (1) the transport of outdoor VOCs into zEDGE via building ventilation is negligible relative to indoor generation of VOCs during the hair care routines for target VOCs (e.g., siloxanes, monoterpenes and monoterpenoids, and glycols), (2) siloxane (D5) loss via indoor oxidation with OH is negligible relative to loss via building ventilation, and (3) VOC adsorption and desorption processes with indoor surface sinks in zEDGE have a negligible effect on the estimation of EFs and ERs.

The simplified material balance model can be expressed as

$$\frac{dC_{m,in}(t)}{dt} = \frac{S_m(t)}{V} - ACR \times C_{m,in}(t) \quad (1)$$

where the subscript m represents the compound of interest, $C_{m,in}(t)$ is the indoor mass concentration of compound m (mg m^{-3}), $S_m(t)$ is the indoor source rate (mg h^{-1}), V is the well-mixed interior volume of zEDGE (m^3), and ACR is the outdoor ACR of zEDGE (h^{-1}). The simplification process and a sensitivity analysis of the assumptions are detailed in the [Supporting Information](#).

The EF of compound m can be expressed as

$$EF_m = \frac{1}{N} \int_{t_1}^{t_2} S_m(t) dt \quad (2)$$

where EF_m is the emission factor of compound m normalized by the number of people (mg person^{-1}), N is the number of people applying HCPs in zEDGE, t_1 is the start of the emission period, and t_2 is the end of the emission period. A time-averaged ER of compound m during the emission period can be expressed as

$$ER_m = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} S_m(t) dt \quad (3)$$

where ER_m is the emission rate of compound m (mg min^{-1}).

The EFs derived from the realistic experiments in zEDGE were further applied in a material balance model of a simulated bathroom with and without an exhaust fan to estimate indoor-to-outdoor VOC mass fluxes and inhalation exposures to VOCs during hair care routines, as discussed in the [Supporting Information](#).

RESULTS AND DISCUSSION

Indoor Emissions of VOC Mixtures during the Use of Hair Care Products. Figure 1 serves as an illustrative example of the net increase in the PTR-TOF-MS mass spectrum (background corrected) during the active use of an HCP (two participants conducting hair straightening with HCP A). Figure 1 demonstrates how PTR-TOF-MS enables the

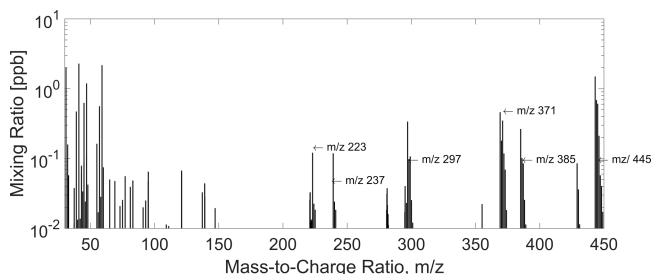


Figure 1. Net increase of the PTR-TOF-MS mass spectrum during experiment SA2.

detection of a complex mixture of VOCs during hair care events in a residential environment. Over 100 ions increased by 100% during the hair care routine compared to the background period with two occupants inside zEDGE ([Table S4](#)). These ions can include parent ions, fragment ions, and water clusters. 75% of these ions have a m/z greater than 200. These ions increased the most and are likely to have Si atoms. For example, cVMS and IVMS mixing ratios, including m/z 223.06 (D3), m/z 297.08 (D4), m/z 371.10 (D5), m/z 385.15 (L5), and m/z 445.12 (D6), increased 65- to 2700-fold compared to their occupied background levels. m/z 355.11, a fragment ion of D5,^{63,64} increased with m/z 371.10 during the hair care event.

Considering the diverse spectrum of ions detected, VOC emissions during hair care routines were categorized into the following three VOC categories: (1) volatile methyl siloxanes, consisting of both IVMS and cVMS, including m/z 237.12 ($\text{C}_8\text{H}_{24}\text{O}_2\text{Si}_3$, L3), m/z 385.15 ($\text{C}_{12}\text{H}_{36}\text{O}_4\text{Si}_5$, L5), m/z 223.06 ($\text{C}_6\text{H}_{18}\text{O}_3\text{Si}_3$, D3), m/z 297.08 ($\text{C}_8\text{H}_{24}\text{O}_4\text{Si}_4$, D4), m/z 371.10 ($\text{C}_{10}\text{H}_{30}\text{O}_5\text{Si}_5$, D5), and m/z 445.12 ($\text{C}_{12}\text{H}_{36}\text{O}_6\text{Si}_6$, D6); (2) monoterpenes and monoterpenoids, typically added as fragrances to HCPs, including m/z 137.13 ($\text{C}_{10}\text{H}_{16}$), m/z 151.11 ($\text{C}_{10}\text{H}_{14}\text{O}$), m/z 153.13 ($\text{C}_{10}\text{H}_{16}\text{O}$), m/z 155.14 ($\text{C}_{10}\text{H}_{18}\text{O}$), and m/z 157.16 ($\text{C}_{10}\text{H}_{20}\text{O}$); and (3) other primary emissions, which mainly include other compounds listed in the ingredients, including m/z 77.06 ($\text{C}_3\text{H}_8\text{O}_2$, propylene glycol), m/z 93.05 ($\text{C}_3\text{H}_8\text{O}_3$, glycerin), and m/z 119.11 ($\text{C}_6\text{H}_{14}\text{O}_2$, hexylene glycol).

Temporal Variations in Indoor VOC Concentrations during the Use of Hair Care Products. Four experiments with different combinations of HCPs and hair styling tools were selected as case studies to investigate the temporal variations in indoor VOC concentrations during hair care routines. A comparison of the emissions from different hair care routines is discussed in detail in the following section. Siloxane mass concentration time series during these four experiments are shown in [Figure 2](#): (1) experiment SA2: hair straightening with product A; (2) experiment SC1: hair straightening with product C, (3) experiment CC: hair curling with product C, and (4) experiment NH1: hair oiling with product H. Details on the experiment ID can be found in [Figure S2](#). VOC concentrations presented here have been subtracted by the unoccupied background VOC concentrations. During experiments SA2, SC1, and CC, two participants were conducting the same hair care routine at the same time, respectively. Experiment NH1 was conducted with one participant. To account for the impact of the number of participants on indoor VOC concentrations, the VOC concentration time series presented here was normalized by the number of participants conducting the hair care routines. VOC concentrations for all three VOC categories were elevated during the four hair care events, with the estimated peak total concentration ranging from 1.2 to 6.1 mg m^{-3} , among which siloxanes dominated the emissions by mass. During the hair care events, a sudden increase in VOC concentrations was observed each time the product was applied to one section of the participants' hair; this was enabled by the high-time resolution of the PTR-TOF-MS (1 Hz). Among the VOC emissions, siloxane concentrations contributed 76, 97, and 96% to the total VOC concentration during experiments SA2, SC1, and CC, respectively, with peak concentrations estimated at 0.9, 6.0, and 3.8 mg m^{-3} . Siloxane concentrations during the HCP application were 330- to 2300-

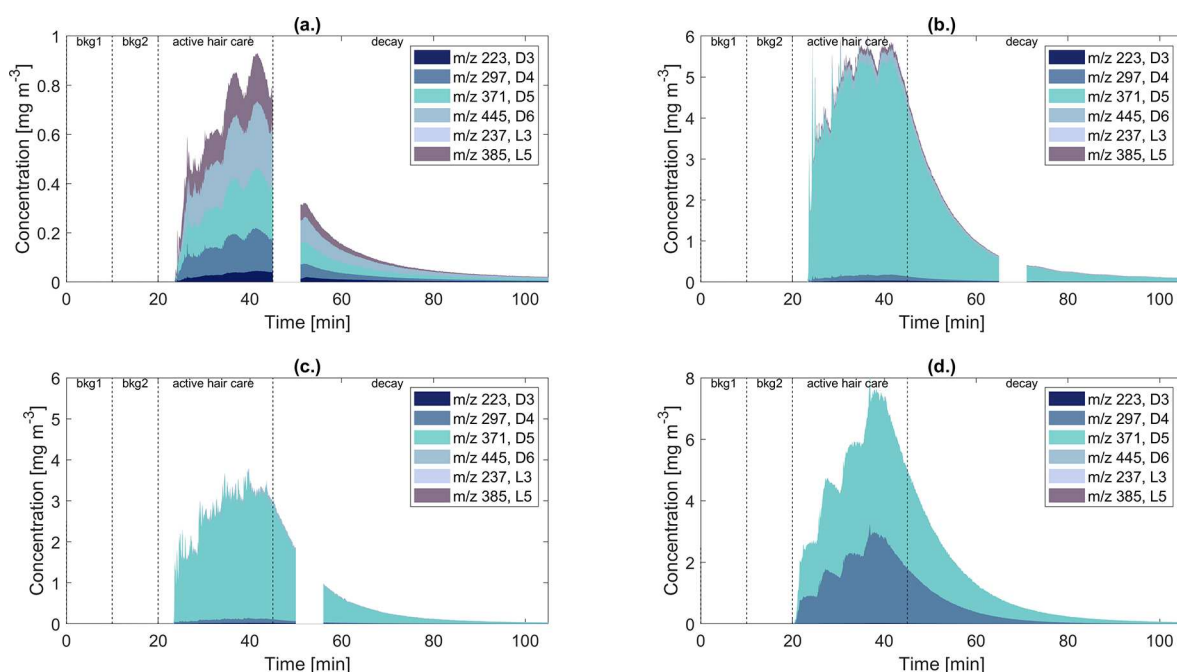


Figure 2. Time-series of indoor mass concentrations for cVMS during the use of (a) hair care product A with hair straightening at 187.8 °C; (b) hair care product C with hair straightening at 187.8 °C; (c) hair care product C with hair curling at 182.2 °C; and (d) hair care product H, which was directly applied by the hands without heat. Data during outdoor PTR-TOF-MS sampling were removed from the plots (blank area).

fold higher than background concentrations, while zEDGE was not occupied.

Siloxane emissions were primarily associated with cVMS, while IVMS concentrations were comparatively lower. cVMS concentrations observed during hair care routines were substantially higher than typical indoor concentrations.^{46,48,52} Participant-normalized cVMS concentrations during the three experiments were comparable or higher than the peak concentrations reported during PCP application in a residential house with multiple occupants, as reported by Molinier et al.⁵¹ Considering that the ACR during our experiments was relatively higher than those of typical residences, HCPs can potentially be a stronger source of indoor cVMS in home environments where occupants routinely use siloxane-based HCPs in their bathrooms and bedrooms as compared with other PCPs. Estimated concentrations of monoterpenes, monoterpenoids, and other primary emissions were 1 to 2 orders of magnitude lower than siloxane concentrations but still substantially elevated compared to both unoccupied and occupied background periods in zEDGE. Participant-normalized concentrations of monoterpenes and monoterpenoids peaked at 0.03, 0.12, and 0.05 mg m⁻³ during the three events, respectively, 50 to 180% higher than their background levels (Figure S4(I)). Limonene, a monoterpene, was listed as an ingredient of product A; however, product C did not specify which compounds were added as a fragrance. The estimated concentration of propylene glycol, another ingredient that is ubiquitous in PCPs,^{65–67} was also found to increase by 70 to 170% during the application of HCPs (Figure S4(II)). The propylene glycol concentration could be overestimated, as acetone emitted by humans can be detected at the same masses (*m/z* 59.049 and *m/z* 77.060).

The temporal trends, concentrations, and breakdown of cVMS and other VOCs varied with the HCP type and the hair styling tool used. By comparing hair straightening events between products A and C, D4, D5, and D6 share similar

proportions of the total siloxane emission during the use of product A, with peak concentrations at 0.18, 0.25, and 0.28 mg m⁻³, accounting for 19, 26, and 29%, respectively. Emissions of L5, an IVMS (peaked at 0.20 mg m⁻³), were detected during the use of product A as well, accounting for 21% of the total siloxane (cVMS + IVMS) emissions. While for product C, D5 peaked at 5.4 mg m⁻³, which dominated siloxane emissions, contributing to 89% of the total siloxane emissions. When comparing hair straightening events (operated at 187.8 °C, Figure 2b) with hair curling events (operated at 182.2 °C, Figure 2c) using product C, small spikes in VOC concentrations were observed more frequently during the hair curling event, while during hair straightening, the emission profiles were relatively smoother. Hair straightening resulted in higher cVMS and monoterpene concentrations as well. Considering the hair straightening iron was firmly clipped on the hair during application, the long, stable, and tight contact between the hair straightener and hair could enhance the evaporation of HCPs applied to the hair and might explain the stable emission profiles observed. Interestingly, during experiment NH1 using product H without heat, the cVMS concentrations were comparable to or even higher than those in the other experiments, with D4 and D5 concentrations peaking at 3.3 and 5.0 mg m⁻³, respectively. Occupant-normalized background concentrations and average and peak concentrations during the HCP application events are summarized in Table S5. Each event exhibited different emission profiles, and each VOC contributed differently to HCP emissions, as determined by the styling technique following HCP application to hair with the hands. While the impact of HCP type and hair styling tools is already evidenced in this section, other factors that impact VOC emissions during HCP application will be discussed more in the next section.

VOC Emission Factors for Indoor Hair Care Events.

VOC emission factors (EFs) and emission rates (ERs) are generalizable parameters that can be extrapolated to model

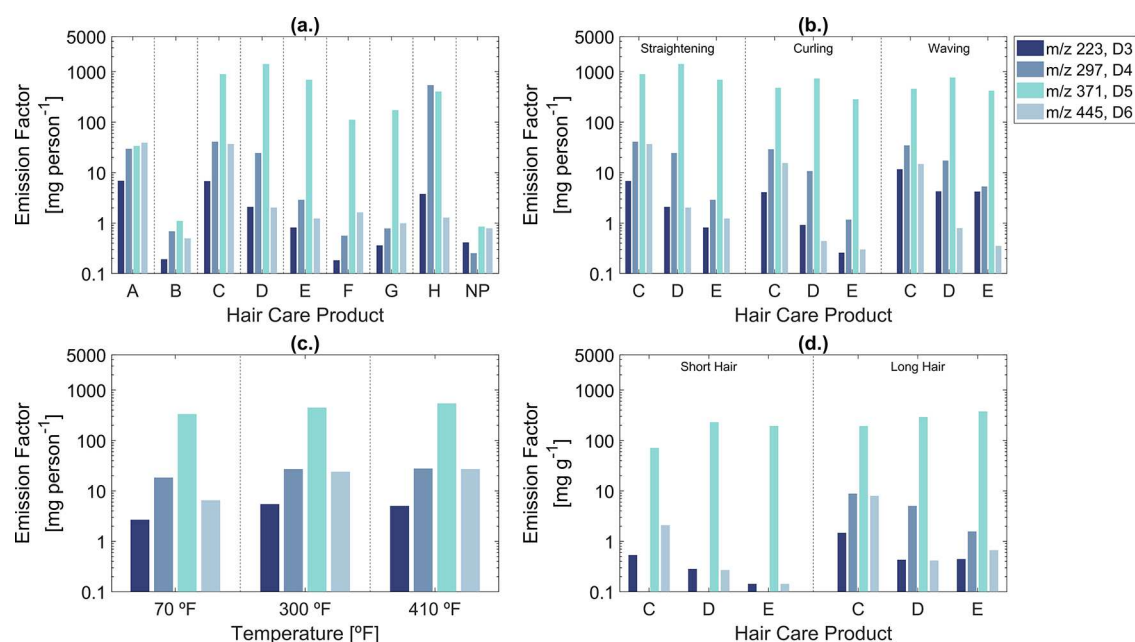


Figure 3. Emission factors of cVMS emissions for (a) hair care products A to G using a hair straightener at 187.8 °C and hair care product H by hand at room temperature; “NP” represents “no product”; (b) different hair styling tools; (c) different temperatures for product C with a hair straightener; and (d) different hair lengths.

HCP concentrations and exposures for different indoor environmental settings, e.g., different room volumes and ventilation rates. EFs were categorized by HCP type, hair styling tool, temperature of the tool, hair length, and outdoor ACR, as shown in Figure 3. EFs normalized by different terms and ERs are summarized in Table S6, expressed in mg person^{-1} , mg pump^{-1} , mg g^{-1} , and mg min^{-1} .

Figure 3a shows EFs as mg person^{-1} and the apportionment of the various siloxanes during the use of different HCPs. Siloxane emissions dominated VOC emissions during the use of most HCPs, contributing 71 to 99% of the total VOC emissions, except for hair spray B, which was sprayed to the hair directly and then applied by hand to spread the product evenly onto the hair. Among all eight HCPs, the estimated total siloxane emissions of products C, D, and E were the highest, with EFs of 1000, 1500, and 700 mg person^{-1} (ERs of 50, 73, and 35 $\text{mg person}^{-1} \text{ min}^{-1}$), respectively. D5 is listed as the first ingredient for product H and the third ingredient for products C, E, and G, while it is not listed as an ingredient for the other products. IVMS emissions, including L3 and L5, were relatively low compared to cVMS emissions, ranging from 0.02 to 0.39 mg person^{-1} and 0.04 to 30 mg person^{-1} , respectively. Among cVMS emissions, D5 was the most dominant cVMS for most of the HCPs, with EFs 1 to 2 orders of magnitude higher than those for D4 and D6. The cVMS emission rates from the use of HCPs were substantially higher than per-capita ERs reported in previous studies, e.g., 3 to 5 orders of magnitude higher than ERs measured from engineering students who were not actively applying PCPs in a classroom,⁵² and 2 to 4 orders of magnitude higher than ERs reported for various PCPs, including shampoos, conditioners, and shower gels.⁴³ The high temperature of the hair styling tools during their operation and the high surface area of human hair may explain such high ERs, along with the cVMS content of the products. It should be noted that even though product H was applied without heat, it still resulted in relatively high D4 and D5 emissions, with EFs of 560 and 420 mg person^{-1} , respectively.

Despite the high molecular weights of D4 and D5, their volatility is relatively high,^{69,70} allowing them to evaporate easily at room temperature.

In addition to siloxanes, high EFs of other VOCs, including monoterpenes, monoterpenoids, and propylene glycol, were observed during most of the hair care events (Figure S5). Product G resulted in the highest monoterpene and monoterpenoid emissions (51 mg person^{-1} or 6.3 mg g^{-1}), which is comparable to monoterpene EFs from the use of botanical disinfectants (Figure S5(I)).⁵⁶ Propylene glycol dominated the emissions of product E (550 mg person^{-1}) and was the highest among all the HCPs (Figure S5(II)). Skin contact with propylene glycol can potentially sensitize human skin,^{65,68} but inhalation toxicity is still unclear.

A comparison of EFs for different hair styling tools is shown in Figure 3b. For D5, EFs for hair straightening were 900, 1400, and 700 mg person^{-1} while using products C, D, and E, respectively, 65 to 145% higher than hair curling and waving with the same product. This is possibly due to the longer contact time and higher contact surface area between the hair straightening iron and hair during the hair care routines.

The same group of participants applied the same hair care product (product C) with hair straighteners without heat (~ 21 °C), at 148.9 °C, and at 210 °C, respectively (Figure 3c). When the temperature increased from ~ 21 to 148.9 and 210 °C, EFs of D4 increased by 48 and 51%, respectively, and EFs of D5 increased by 34 and 63%, respectively. Temperature had a stronger impact on D6 emissions, with EFs 2.7 and 3.1 times higher when increasing the hair straightener temperature from room temperature to 148.9 and 210 °C, respectively. With the increase of temperature,⁷¹ the evaporation of cVMS from the hair and hair straightener surfaces to indoor air was enhanced.

Figure 3d compares the emission profiles of products being applied to different hair lengths. Interestingly, HCPs applied to longer hair resulted in siloxane EFs that were 2.5 to 5.4 times greater than applications to short hair. Participants with long hair applied twice the amount of the product as applied to

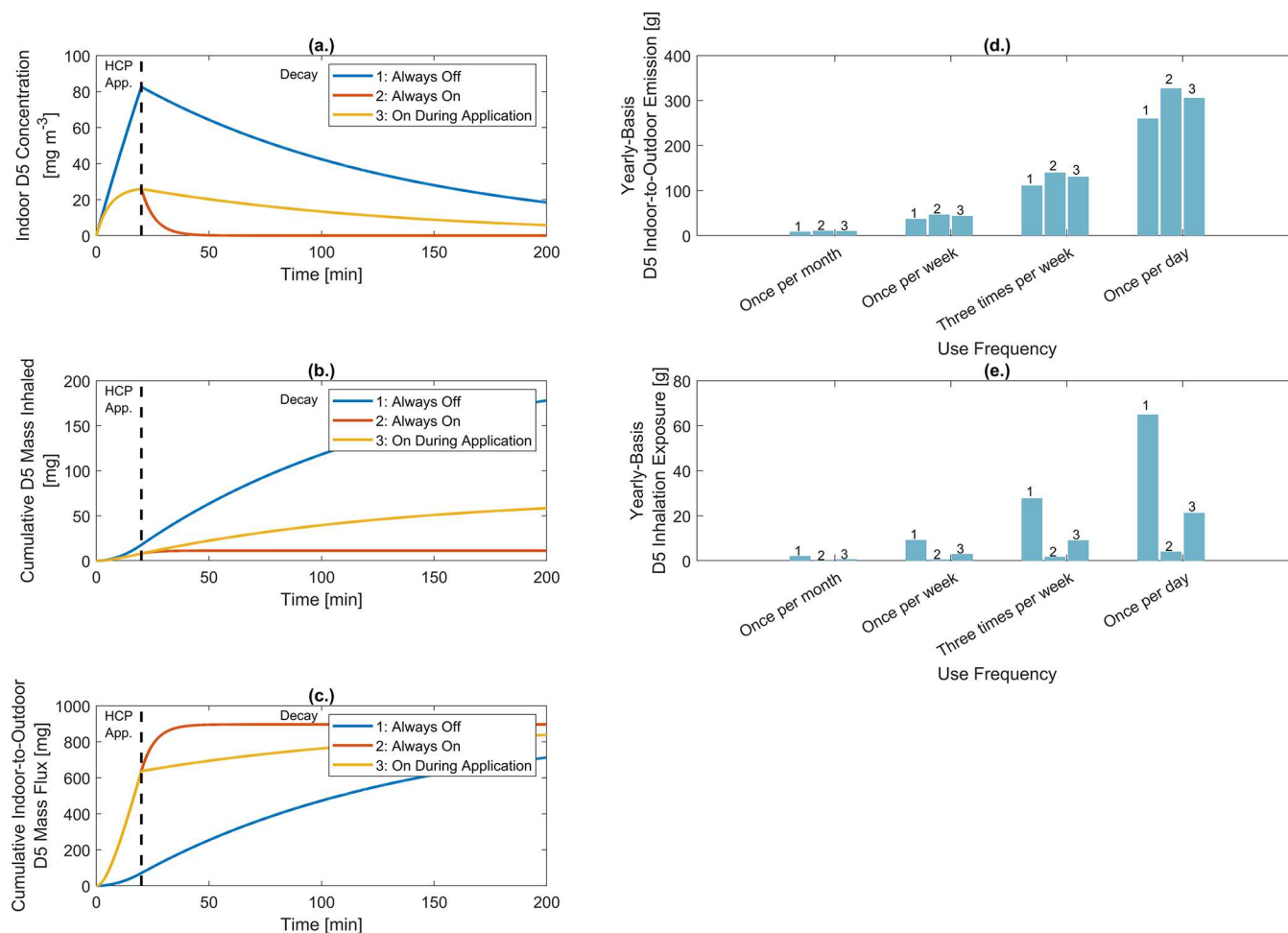


Figure 4. Time-series of (a) indoor D5 mass concentration during a 20 min hair care routine in a residential bathroom under three ventilation conditions; (b) cumulative D5 inhalation exposure during and after HCP application; and (c) cumulative indoor-to-outdoor D5 mass flux during and after HCP application. Annual (d) D5 indoor-to-outdoor VOC emissions per person and (e) D5 inhalation exposures for an adult with different HCP use frequencies per person.

shorter hair. To account for the difference in the amount of product applied, the mass emitted during the experiments was normalized by the mass of product applied in Figure 3. Long hair still resulted in higher EFs after normalization, which indicates that a larger surface area could enhance the evaporation of VOCs. Other factors, such as hair density and hair diameter, could also impact the hair surface area that is in contact with the applied product.⁷² Supplementary hot plate evaporation experiments and surface area experiments, which are detailed in the Supporting Information, verified the dependence of EFs on the hair styling tool temperature and hair surface area. The EFs increase with an increase in temperature and hair surface area.

EFs from the same HCP are not sensitive to the outdoor ACR when it was relatively high ($>3 \text{ h}^{-1}$) (Figure S6), as the ACR does not strongly impact the localized evaporation process of products from the hair, thus the total mass emitted during the same hair care sequence should remain similar. However, this may not stand true for low ACRs, as mass transfer could be affected. With ACR determining the amount of air exchanged between indoors and outdoors, it can affect the buildup speed and the temporal trend of indoor VOC concentrations and further impact indoor-to-outdoor emissions and human exposures (see following sections).

Human Exposure Implications of VOC Emissions during Hair Care Routines. Figure 4a shows the time-series of simulated D5 concentrations during a 20 min hair care routine using product C with a hair straightener at 187.8°C and its subsequent decay period in a residential bathroom for each ventilation scenario. When the exhaust fan is off, the D5 concentration in the bathroom peaks at 82 mg m^{-3} . Turning on the exhaust fan reduces the peak indoor D5 concentration by $\sim 70\%$. Keeping the exhaust fan always on after finishing the use of the HCP accelerates the decay of the indoor D5 concentration. The D5 concentration drops by 95% to $<1 \text{ mg m}^{-3}$ within 20 min after completing the hair care routine when the exhaust fan is on, while the D5 concentration still remains elevated ($\sim 6 \text{ mg m}^{-3}$) even after 3 h with the exhaust fan off. The cumulative D5 mass inhaled by the occupant built up to 17 and 8 mg with the exhaust fan off and on during the 20 min hair care event, respectively (Figure 4b). It should be noted that the cumulative inhalation exposure to D5 will continue to increase if the occupant stays in the same space after finishing their hair care routines, e.g., for skin care routines. Exposure to siloxane residual on the hair after the hair care event may also be an important contributor to daily siloxane exposures, which have not been accounted for in this model.

Figure 4e shows the integrated inhalation exposures for D5 under different bathroom ventilation scenarios and for

different HCP use frequencies on an annual basis. One would be exposed to 65 g of D5 via inhalation per year if a siloxane-based HCP was applied everyday with the exhaust fan always off. Keeping the exhaust fan always on helps to significantly reduce exposures, with the D5 inhalation exposure dropping to 4 g if the HCP is used daily. The annual exposure to D5 can be translated to inhalation intake rates ranging from 1 to 20 mg day⁻¹. Considering the high annual siloxane doses, studies of the long-term impact of siloxane exposures on human health are urgently needed.

Indoor-to-Outdoor Siloxane Emissions during Hair Care Routines. The use of PCPs and other volatile chemical products could be a major siloxane source in the urban atmosphere.^{27,30} Ventilation is likely the major pathway for indoor-to-outdoor siloxane transport. Three ventilation scenarios were considered for both the indoor-to-outdoor mass transport and exposure analysis: (1) exhaust fan always off; (2) exhaust fan always on; and (3) exhaust fan only turned on during the use of HCPs.

Figure 4c shows cumulative indoor-to-outdoor D5 mass fluxes during and after the same hair care event in a residential bathroom, as previously described. The cumulative indoor-to-outdoor D5 emission with the exhaust fan always off reaches 710 mg within 3 h, while the indoor-to-outdoor D5 emission with the exhaust fan always on reaches 900 mg within only 1 h. Improving ventilation can reduce human exposure to VOC emissions during hair care events; however, the VOCs would be exhausted in the proximate outdoor atmosphere at a faster rate.

Figure 4d shows indoor-to-outdoor D5 emissions under different ventilation scenarios and different HCP use frequencies on an annual basis. When the exhaust fan is off, 260 g of D5 would be exhausted to the outdoors per year with the siloxane-based HCP applied daily, while 310 g of D5 would be exhausted to the outdoors when keeping the exhaust fan on. However, this model only estimated the indoor-to-outdoor D5 emissions within 200 min of the hair care routines. Given a long enough time, the impact of ventilation on indoor-to-outdoor D5 transport would be small. The annual D5 flux to outdoors from the indoor use of siloxane-based HCPs in a city or country can be estimated based on the use patterns of HCPs by multiplying the average of HCP use per year by the population of HCP consumers, then by the emissions per event. Surveys on different population groups indicate 16 to 70% of participants use leave-on hair care or hair styling products.^{1–3} Considering an average use frequency of HCPs between 2 and 5 times per week based on surveys on HCP usage patterns^{1,2} and assuming that 10% of HCPs are siloxane-based, the total indoor-to-outdoor emission of D5 could reach 0.4 to 6 tons per year in the U.S. With a box model, the outdoor D5 concentration in a specific city can be further estimated. Taking Chicago as an example, the outdoor D5 concentration attributed to residential hair care routines was estimated to be 0.07 to 0.8 ppt with the assumptions above. Coggon et al. (2021) reported an outdoor D5 concentration in Chicago of around 10 ppt.⁷³ Thus, D5 emissions from hair care routines may contribute 0.7 to 8% to outdoor D5 concentrations or even higher, considering that the assumptions for this estimation were conservative.

The estimation of indoor-to-outdoor emissions suggests that indoor human activities, such as hair care routines, can contribute to elevations in cVMS concentrations in urban atmospheres, especially D5 concentrations. cVMS oxidation

may not be substantial in an indoor environment due to low OH concentrations. However, once cVMS are transported to the outdoor atmosphere via ventilation, cVMS can react with the hydroxyl radical (OH) and produce oxidation products such as siloxanols, further contributing to the formation of SOA.^{36–38,74} Indoor-to-outdoor emissions of other VOCs, including monoterpenes and monoterpenoids, could potentially impact outdoor atmospheric chemistry as well.^{32,34,73}

Indoor hair care routines can have long-term impacts on inhalation exposures to VOCs and the urban atmospheric environment. However, there are several limitations to the inhalation and indoor-to-outdoor emission modeling in this study: (1) HCP use patterns (e.g., product selection, amount applied, hair care routines, and use frequency) vary from person to person, and studies on consumer behaviors are needed to improve this model; (2) variations in indoor surfaces in different indoor environments can impact surface absorption and desorption of VOCs, which has not been accounted for in this estimation; (3) exposure profiles would vary if one chose to stay in a different space after the use of HCPs and the continuing emissions of leave-on products on the hair after their application was not considered in this model; and (4) information on siloxane concentrations in the HCPs themselves is lacking, so this study could not quantitatively characterize the liquid-to-gas phase mass transfer processes for siloxanes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.3c05156>.

Description of the Purdue zEDGE Tiny House, operation and calibration of the PTR-TOF-MS, outdoor ACR calculation, material balance model descriptions, absorption/desorption analysis for cVMS, summary of the eight HCPs, details of all $n = 46$ emission experiments, average and peak VOC concentrations for each experiment, VOC EFs and ERs for each experiment, and EFs for the hot plate and surface area emission experiments (PDF)

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Notes

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