

ORIGINAL ARTICLE

Sources and dynamics of semivolatile organic compounds in a single-family residence in northern California

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Abstract

Semivolatile organic compounds (SVOCs) emitted from building materials, consumer products, and occupant activities alter the composition of air in residences where people spend most of their time. Exposures to specific SVOCs potentially pose risks to human health. However, little is known about the chemical complexity, total burden, and dynamic behavior of SVOCs in residential environments. Furthermore, little is known about the influence of human occupancy on the emissions and fates of SVOCs in residential air. Here, we present the first-ever hourly measurements of airborne SVOCs in a residence during normal occupancy. We employ state-of-the-art semivolatile thermal-desorption aerosol gas chromatography (SV-TAG). Indoor air is shown consistently to contain much higher levels of SVOCs than outdoors, in terms of both abundance and chemical complexity. Time-series data are characterized by temperature-dependent elevated background levels for a broad suite of chemicals, underlining the importance of continuous emissions from static indoor sources. Substantial increases in SVOC concentrations were associated with episodic occupant activities, especially cooking and cleaning. The number of occupants within the residence showed little influence on the total airborne SVOC concentration. Enhanced ventilation was effective in reducing SVOCs in indoor air, but only temporarily; SVOCs recovered to previous levels within hours.

KEYWORDS

cleaning, cooking, emissions, gas/particle partitioning, occupancy, ventilation

1 | INTRODUCTION

On average, humans spend 90% of their time indoors, including about 70% in their homes.^{1,2} Indoor air quality is an essential factor influencing healthy life and people's well-being.

Synthetic chemical compounds are ubiquitous in building materials and consumer products used in residential environments. Some chemicals in these materials have been reported to be in high abundance in indoor environmental compartments, including air and dust.^{3,4} Semivolatile organic compounds (SVOCs) constitute an

important yet understudied class of organic chemicals indoors.⁵ With wide-ranging applications of SVOCs as active substances or as additives in building materials and consumer products, indoor sources of SVOCs are numerous and include flooring, furniture, electronics, plastic items, textiles, cleaning, and cosmetic products.^{6,7} Owing to their semivolatile nature (vapor pressure and boiling point between 10^{-14} to 10^{-4} atm and ~240 to 400°C, respectively^{8,9}), SVOCs are present both as gaseous compounds and as condensed-phase components of particles, surface films, and settled dust. For this reason, once emitted from their original sources, SVOCs can become widely

distributed in multiple compartments of the indoor environment. Among the potentially important routes of exposure are inhalation of gases and airborne particles, ingestion of dust, and permeation of the skin following direct physical contact with surfaces or partitioning into skin oils from air.^{3,10,11} Certain SVOCs are linked with negative human health outcomes, such as reprotoxic and neurotoxic effects, thus motivating national and international control efforts.^{9,12-16} However, owing to their persistent nature, including wide distribution on indoor surfaces, occupant exposures to SVOCs may occur long after eliminating the original sources.⁹ For this reason, SVOCs that have not been routinely used indoors for many years may continue to exhibit measurable levels in air, in dust, and in body fluids.^{4,17}

Multiple studies have reported on the concentrations of SVOCs identified in the air and dust of diverse indoor environments.^{3,9,18-25} However, limited by analytical capabilities, the majority of published studies only report on small numbers of SVOCs, thus providing restricted insight into the chemical complexity and the total burden encountered in indoor environments. Historically, methods for analyzing SVOCs in both outdoor and indoor environments have relied on long time scale (days to weeks) collection of particulate matter and gases on filters and sorbents followed by offline analysis in the laboratory.²⁶ This approach provides little information on the temporal changes and dynamic behavior of SVOCs in indoor air, limiting the study of important processes and parameters that influence emissions, concentrations, exposures, and fates of SVOCs in the indoor environments, including gas/particle partitioning. As one example, environmental parameters such as indoor temperature might be particularly important because of the temperature-dependent vapor pressures of SVOCs and their rapid equilibration between surfaces and the gas phase. Some prior studies show that temperature may exert a large influence on the concentrations of SVOCs in indoor environments. Theory as well as laboratory-controlled studies predict increased emissions from indoor sources (eg, building materials) to indoor air at elevated temperatures.²⁷⁻³⁵ In addition, model simulation and chamber studies on specific SVOCs have shown that enhanced particle mass loading could facilitate partitioning of gaseous SVOCs in airborne particles, thus altering the SVOC distribution and exposure.³⁶⁻³⁹ Until now, however, no studies have documented the influence of temperature and particle mass loading on the indoor air SVOC concentrations in real indoor environments under normal occupancy, thus restricting efforts to validate models for indoor environmental emissions, fates, and gas/particle distributions of SVOCs and associated human exposures.^{35,36,40,41}

Furthermore, the influence of human occupants on the dynamic behavior and chemical composition of SVOCs indoors remains poorly characterized. The roles of human occupants influencing indoor chemistry have been reviewed by Weschler⁴², including information about direct emission of volatile organic compounds (VOCs) to the indoor air, occupant-influenced chemical transformation from reactions on human skin oils, and removal of SVOCs through dermal or clothing uptake and by means of inhaling gaseous and particle-bound species. However, little is known about occupant-related

Practical Implications

- This study contributes to a better understanding of the chemical composition of air in residential environments.
- Indoor temperature; occupants and occupant-related activities; and processes such as cleaning, cooking, and ventilation are shown to influence the chemistry of the air breathed within homes.
- The findings contribute insights into the factors controlling the sources and fates of chemical air pollutants in an occupied indoor environment and are therefore of value for accurately characterizing indoor exposures.

sources of SVOCs in indoor environments and their magnitudes relative to continuous sources such as indoor materials. Based on knowledge of VOC sources, one might anticipate that occupant activities such as cooking and cleaning could be important contributors to the pool of SVOCs in occupied residences.

To address these important gaps in knowledge, we report here the gas/particle distribution, dynamic behavior, and chemical composition of indoor air organic compounds in a San Francisco Bay Area residence during normal occupancy. The volatilities of the studied organic compounds range between those of tridecane and pentacosane, whose saturation concentrations (C^*) are on the order of 1×10^5 and $1 \mu\text{g m}^{-3}$, respectively. This range spans from intermediate volatility to semivolatile. For simplicity, we refer to the measured compounds as SVOCs throughout this article. Time-resolved measurements of the total (gas plus particle phase) SVOC concentrations are presented for the first time in an ordinarily occupied indoor environment using semivolatile thermal-desorption aerosol gas chromatography (SV-TAG). From hourly measurements of airborne SVOCs, we extract novel insights into the dynamic behavior of this important class of indoor pollutants. We explore here the influence of indoor temperature, occupancy, and occupant-related activities, including cooking and cleaning, on the SVOC-associated composition of residential indoor air.

2 | EXPERIMENTAL METHODS

2.1 | Observational campaign

This study was carried out in a single-story, ranch-style house (designated H2) situated in the East Bay of the San Francisco Bay Area, USA. The home was occupied by a family consisting of one male adult, one female adult, one teenager, and one dog. The 183-m² house built in 1951 contains three bedrooms, two bathrooms, a kitchen, family room, and living room. Indoor cooking was performed on a natural gas-fired cooktop and in an electric oven located in the kitchen. A floor plan of the house is recorded in Figure S1. Indoor samples reported in this work were drawn from the living room, a ~30-m² room, with hardwood flooring, separated from the adjacent kitchen by an open doorway.

Extensive observational monitoring was conducted over a 9-week period starting December 2017, including eight weeks of normal occupancy and one week of vacancy (vacant period: 22-28 December).

The house is equipped with a central forced-air heating system with supply registers in all rooms except the family room. The house temperature was controlled via a programmable thermostat that operated on a timed cycle to provide heating in the morning and evening of the winter months. The system operated consistently during the entire campaign with periodic heating occurring twice each day from 6:45 AM to 7:15 AM and again from 5:45 PM to 10:00 PM. Occasional variations occurred from manual override applied in the afternoon or evening by the occupants. In addition, a separate thermostat-controlled vented gas fireplace in the family room was used occasionally for supplemental heating during the occupied period.

An extensive set of time-resolved metadata was collected, including the utilization of more than 50 wireless sensors to monitor room occupancy, appliance use, door/window open status, temperature, and humidity.⁴³ Occupant-related activities such as cooking, cleaning, and candle burning were logged daily, with descriptions of type and duration. House-wide cleaning was performed on a biweekly basis by a professional cleaning crew. Cleaning products used by the cleaning crew are listed in Table S1.

A wooden shed was constructed and placed outside the house to contain most of the analytical instruments during the study. The shed was positioned with its nearest wall about 50 cm from the house exterior. Two stainless steel sample tubes (outer diameter 1.6 cm (5/8") and length ~2 m) were used for separate collection of outdoor and indoor air. Shed temperature was continuously monitored and regulated to ~20°C using a 1000 W (3500 BTU h⁻¹) portable air conditioning unit.

2.2 | Time-resolved measurements of SVOCs

Measurements of combined airborne particle-phase (PM_{2.5}) and gas-phase SVOCs were carried out using a semivolatiles thermal-desorption aerosol gas chromatography instrument (SV-TAG) developed by the Goldstein laboratory at UC Berkeley and Aerosol Dynamics Inc.⁴⁴⁻⁴⁷ Briefly, the instrument collects airborne organic compounds on two parallel sampling cells with a flow rate of 10 L min⁻¹ for each cell. The cells consist of high-surface area stainless steel fiber filters passivated with an Inertium® coating (Advanced Materials Components Express, Lemont, PA, USA) allowing for efficient adsorption of gas-phase SVOCs while particles are collected by filtration.⁴⁵ Following sampling (15 min), an internal standard (ISTD) is added and each cell is analyzed in series by thermal desorption into helium saturated with a derivatizing agent (n-methyl-n-(trimethylsilyl)trifluoroacetamide (MSTFA), Sigma) and then directed to a gas chromatograph (GC; Agilent model 7890A) with a quadrupole mass spectrometer using electron impact ionization at 70 eV (MS; Agilent 5970C). The ISTD solution consists of a mixture of deuterated organic compounds representative of a broad range of SVOCs commonly found in both indoor and outdoor environments. Gas chromatographic analysis

of each sample is performed in 14-min intervals using a non-polar GC column (Rtx-5Sil MS, 20 m × 0.18 mm × 0.18 μm; Restek) for chromatographic separation of SVOCs. The non-polar GC column in combination with applied derivatization allows for the analysis of compounds across wide ranges of volatilities and polarities, including alkanes, alcohols, and alkanic acids.

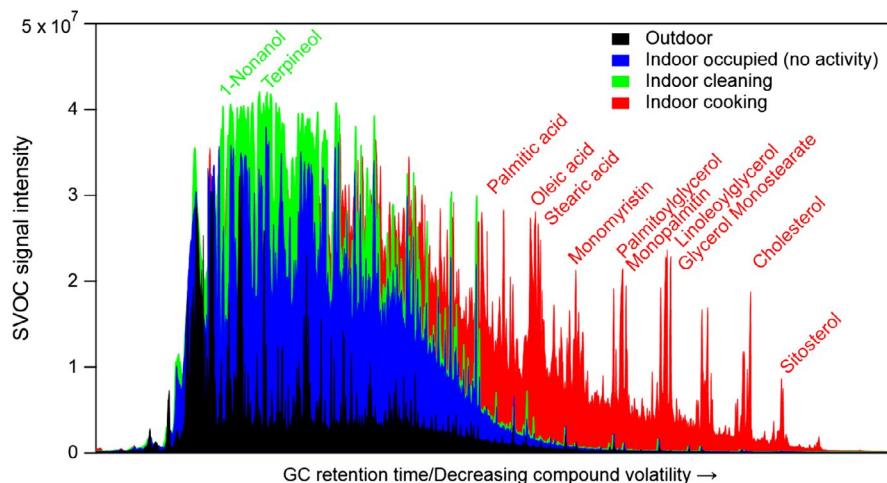
For each SV-TAG run (ie, GC analysis), a total ion chromatogram (TIC) is produced from the combined signal of all measured fragments of the ionized organics entering the MS from the GC. Mass-to-charge values associated with specific compounds or chemical functionality may be selected and extracted from the TIC providing information on the contribution of specific compounds or classes to the total analyzed organic material. In the current work, compound identification was achieved through matching the recorded compound-specific background-subtracted mass spectra with those of authentic standard runs on SV-TAG (when available) and with spectra available in the NIST/EPA/NIH Mass Spectral Library.^{45,48}

To study the gas/particle distribution of SVOCs, particle-only sampling is performed on one of the two sampling cells (Cell 2) by removing gaseous compounds from the sample airflow using a multichannel carbon monolith denuder (500 channels, 30 mm OD × 40.6 cm; MAST Carbon) before collection on the downstream cell. Thus, through simultaneous sampling and subsequent analysis of gas- plus particle-phase compounds on Cell 1 and particle-only compounds on Cell 2, the gas/particle phase distributions of the sampled SVOCs are determined.

Hourly indoor gas-plus-particle SVOC measurements were conducted continuously on Cell 1. A four-hour sampling sequence was utilized for Cell 2, with each interval comprising one indoor particle-plus-gas measurement, one indoor particle-only measurement, one outdoor gas-plus-particle measurement, and one outdoor particle-only measurement. Thus, measurement of indoor gas-plus-particle SVOCs was obtained with one-hour time resolution, and indoor vs outdoor SVOC comparisons, indoor gas/particle partitioning, and outdoor gas/particle partitioning were obtained every four hours. Indoor gas-plus-particle SVOCs measured on both cells simultaneously once every four hours were used to cross-calibrate the cells ensuring their comparability. Once per day, a known volume (4, 8, or 12 μL) of an SVOC standard solution, containing >120 different SVOCs, was injected onto both cells and analyzed, resulting in a three-point calibration curve every three days. A sample blank containing only the ISTD was analyzed at the beginning and end of the sampling campaign.

In the current work, we present the total gas-plus-particle SVOC signal recorded by the SV-TAG over a four-week period, from December 8, 2017, to January 5, 2018. The signal is quantified using calibration curves from twenty straight-chained alkanes (C₁₃-C₃₂) yielding the total alkane-equivalent SVOC mass concentration in units of μg m⁻³ of air. After subtracting the internal standard, the total chromatographic signal was integrated using the closest alkane standard calibration curve in retention time (Figure S2) to yield the total SVOC concentration in μg m⁻³ of air. The method details are described in the SI along with estimates of the associated uncertainties.

FIGURE 2 Total ion chromatograms from SV-TAG analysis of gas-plus-particle samples from outdoor (black), indoor occupied (no activity, blue), cleaning (green), and cooking (red). Compounds associated with the biweekly cleaning (1-nonanol, terpineol) are labeled as well as carboxylic acids (palmitic acid, oleic acid, steric acid), glycerols (linoleoyl glycerol, palmitoyl glycerol, monomyristin, monopalmitin, monostearin), and sterols (cholesterol and sitosterol) identified in the indoor air during cooking activities



by a single peak at a retention time in the TIC that generally increases with decreasing vapor pressure. The chromatograms reveal a complex mixture of hundreds to thousands of different organic compounds in the sampled indoor air. Highlighted peaks in Figure 1A represent a few of the many SVOCs detected by the SV-TAG. For example, 1-nonanol is a citrus fragrance molecule commonly found in washing and cleaning products and in personal care products. Phenoxy ethanol is a commonly used solvent found both in personal care products and in building and interior finishing materials, such as paints, glues, and carpets.⁴⁹ Tetradecamethylcycloheptasiloxane, also known as D7, is a cyclic siloxane found in personal care and other products.⁵⁰ Diethyl phthalate is a plasticizer additive in many consumer products and building materials. Galaxolide is a synthetic musk ingredient. Homosalate is an organic compound used in sunscreen lotions. To underline the high chemical complexity of the measured indoor air, Figure 1B shows extracted ion chromatograms related to different chemical functionalities, including alkanes ($-C-C-$), alcohols ($-OH$), aliphatic aromatics ($-C_6H_6$), and long-chain carboxylic acids ($-COOH$). Peaks related to select straight-chained alkanes, alcohols, and carboxylic acids are labeled according to their carbon-chain length and show how increasing GC retention times are associated with compounds of increasing size (and decreasing volatility), that is, C13-C21 alkanes (Figure 1B, top panel). From these chromatograms, it is clear that the measured indoor air contains a very large number of individual chemicals spanning a wide range of volatilities and chemical functionalities.

Figure 2 shows TIC chromatograms from typical SV-TAG gas-plus-particle sample analyses for several representative cases: outdoor air (black), indoor air during normal occupancy with no activity (blue), indoor air during cleaning (green), and indoor air during a cooking event (red). A large difference both in chemical complexity and in the abundance of SVOCs between indoor and outdoor air is consistently observed, even without contributions from occupant activities. In addition, relative to the baseline indoor condition, during biweekly cleaning, the SV-TAG TIC (Figure 2, green) is characterized by enhanced signal intensity associated with the application of cleaning products (see Table S1). Distinct organic compounds associated with the use of these cleaning products include 1-nonanol and terpineol,

fragrance additives often found in cleaning products.⁵¹ As indicated in Figure 2, signal peaks arising from the elevated concentration of both 1-nonanol and terpineol are found early in the SV-TAG TIC (ie, with shorter GC retention times) indicative of the more volatile nature of the compounds showing elevated signals during the cleaning event.

During the course of the campaign, the largest increases in the SV-TAG TIC were observed during cooking. As evident in Figure 2, cooking significantly changed the chemical composition of the indoor air with many new compounds appearing in the indoor SV-TAG measurements (Figure 2, red). In general, the most abundant compounds related to cooking events include straight-chained saturated and unsaturated fatty acids (palmitic, oleic, and stearic acids), mono-glycerides (monomyristin, palmitoyl glycerol, monopalmitin, linoleoyl glycerol, glycerol monostearate), and sterols (cholesterol and sitosterol). Such compounds have been identified as molecular tracers from cooking emissions.⁵² In contrast to the identified cleaning constituents (ie, 1-nonanol and terpineol), most chemical compounds arising from indoor cooking are significantly less volatile as evident from their longer GC retention time.

3.2 | SVOC dynamics

The time series of total indoor and outdoor alkane-equivalent SVOC concentrations (gas-plus-particle samples) measured by SV-TAG from December 8, 2017, to January 5, 2018, is shown in Figure 3. On average, the indoor total SVOC concentration was consistently significantly higher (by a factor of ~ 4) than measured in outdoor air, in broad agreement with previous studies of some specific chemicals.^{16,53-55} During occupancy, the average alkane-equivalent indoor SVOC concentration was $71 (\pm 16) \mu\text{g m}^{-3}$. The occupied period exhibits moderate-to-large fluctuations in the total indoor SVOC concentration, with episodic events producing concentrations in excess of $200 \mu\text{g m}^{-3}$. In contrast, during vacancy, the indoor total SVOC shows only small changes with an average alkane-equivalent concentration of $59 (\pm 7) \mu\text{g m}^{-3}$. Common to both occupied and vacant periods is the consistently elevated baseline concentration of indoor SVOCs, rarely dropping below

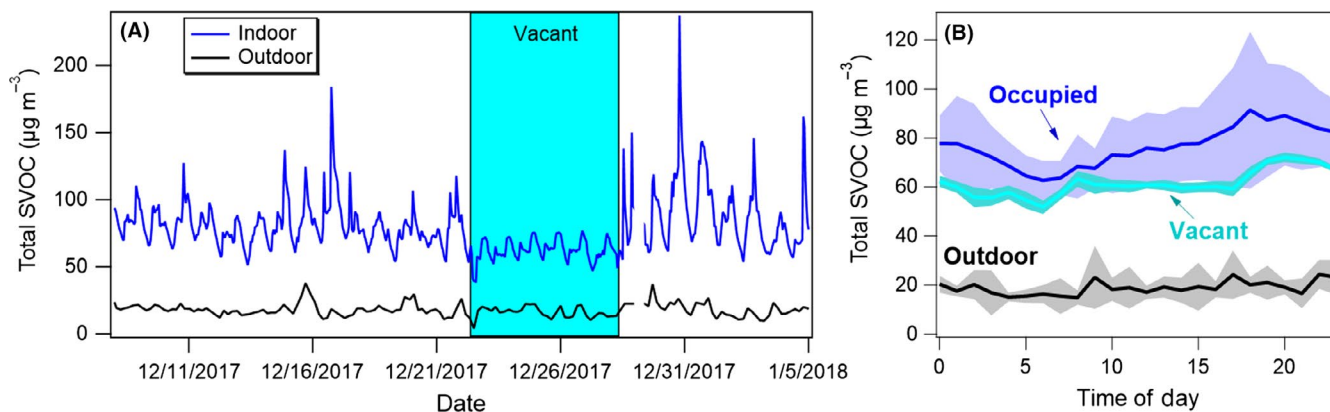


FIGURE 3 A, Total alkane-equivalent SVOC concentration ($\mu\text{g m}^{-3}$) in outdoor (black) and indoor (blue) gas-plus-particle samples as measured by the SV-TAG from December 8, 2017, to January 5, 2018. The vacant period is highlighted in teal. B, Average (\pm SD, shaded) total (gas-plus-particle) alkane-equivalent SVOC concentration ($\mu\text{g m}^{-3}$) as a function of time of day measured outdoors (black) and indoors during occupied (blue) and vacant (teal) period

$50 \mu\text{g m}^{-3}$, indicative of the importance of indoor sources other than occupant activities.

Figure 3B shows the average diurnal changes in the measured gas-plus-particle SVOC concentration outdoors (black) and indoors during the occupied (blue) and vacant (teal) periods. During occupancy, the indoor SVOC concentration is characterized by highest concentrations in the late afternoons and evenings (5 PM–11 PM) and lowest concentrations in the early morning hours (~6 AM). During the vacant periods, the SVOC concentration follows a strong diurnal pattern with rising concentrations observed every day at 6 AM and 6 PM (Figure 3). The diurnal changes in the total alkane-equivalent SVOC concentration closely correlate with indoor temperature. This feature is especially prominent during the vacant period, when the observed daily increases in SVOC concentration coincide with rising temperatures following the operation of the programmed central home heating system (Figure S4). The diurnal changes in total SVOC concentration during the vacant period are evident across all compounds in the recorded TIC (Figure S5) and thus are not controlled by large changes in the concentrations of only a few abundant species. In other words, the observed changes in the total SVOC concentration do not reflect large diurnal changes in the chemical composition with respect to the SVOCs measured by the SV-TAG. During occupancy, and in contrast to the vacant period, occasional spikes are apparent on top of the regular diel variation in the total SVOC concentration. These enhancements coincide with occupants' activities, especially cooking.

Figure 4 shows the total (gas-plus-particle) alkane-equivalent SVOC concentration plotted as a function of the indoor air temperature. Overall, the indoor SVOC concentration shows a positive dependence on indoor air temperature. In particular, a strong correlation between the total indoor SVOC concentration and temperature is observed in the vacant period ($R^2 = 0.88$, teal) showing a $6 \mu\text{g m}^{-3}$ (~10%) increase in the total indoor airborne SVOC concentration per $^{\circ}\text{C}$. A similar response to temperature is observed during the occupied period, but here the correlation is weaker ($R^2 = 0.34$) owing to episodic spikes in SVOC concentration attributable to occupant

activities that are not closely related to temperature (Figure 3). As is evident in Figure 4, the lower SVOC concentrations observed during vacancy are almost solely attributed to the lower temperatures during this period and not related to the absence of occupants. Accordingly, TICs recorded during the vacant period show a chemical composition of indoor SVOCs that is similar to that prior to the departure of the occupants (Figure S6). These findings indicate that the SVOCs in the studied residential environment are controlled to a large extent by emissions from building materials, household interior furnishings, and indoor surface reservoirs. Furthermore, the indoor SVOC concentrations are substantially related to indoor temperature suggesting a major influence on airborne SVOCs in this residence of temperature-driven emissions and/or temperature-modulated phase partitioning with materials and interiors.

Figure 4 displays evidence that all episodic enhancements of indoor SVOC concentrations during the occupied period (Figure 3A) coincide with specific occupant-related activities, mainly cooking,

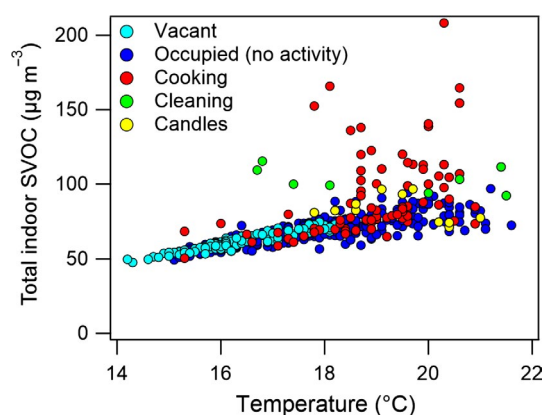


FIGURE 4 Total (gas-plus-particle) alkane-equivalent SVOC concentration ($\mu\text{g m}^{-3}$) vs indoor air temperature during vacant (teal) and occupied periods (blue, no associated emitting activities). Measured SVOC concentrations during indoor activities (cooking (red), cleaning (green) and candle burning (yellow)) are highlighted; some show elevated concentrations that are associated with emissions from occupant activities

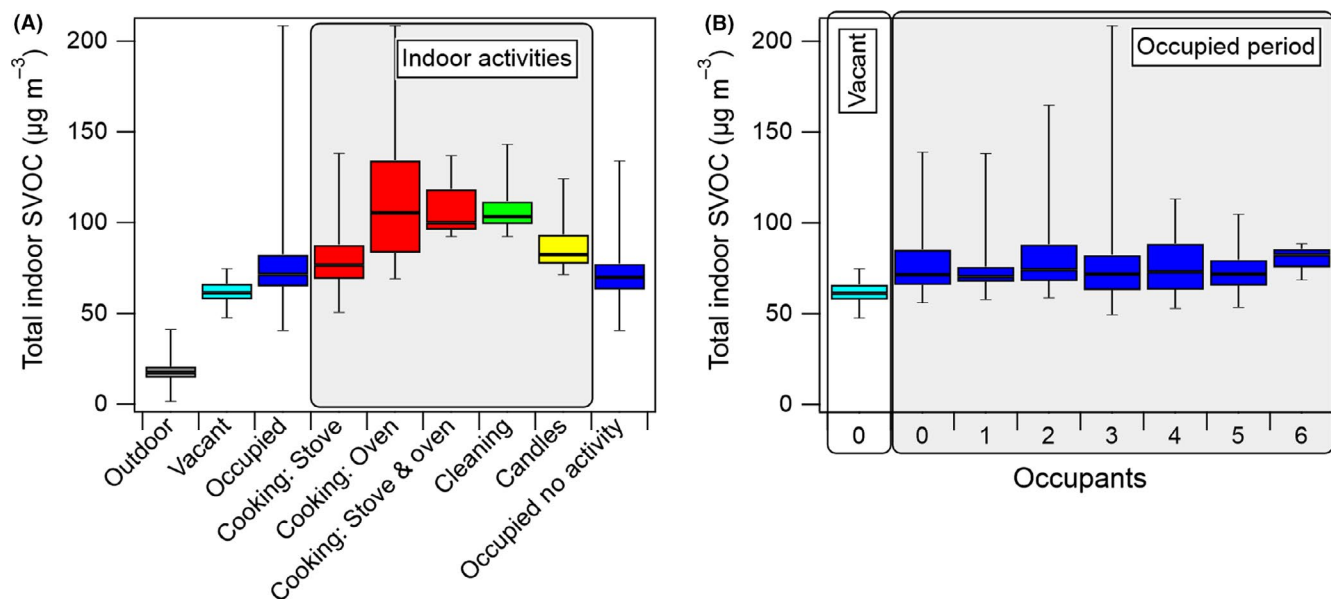


FIGURE 5 A, Box plot showing the outdoor and indoor gas- plus particle-phase SVOC concentrations ($\mu\text{g m}^{-3}$) during the vacant period and during the period of normal occupancy along with the total concentrations associated with indoor activities (stovetop and oven cooking, cleaning, and candle light burning). B, SVOC concentrations ($\mu\text{g m}^{-3}$) during different level of occupancy during vacant (teal) and occupied (blue) periods

cleaning, and candle use. With total SVOC concentrations exceeding $200 \mu\text{g m}^{-3}$, cooking is indicated as a major contributor to the indoor organic chemical burden. With respect to cooking, the largest increases in the airborne SVOC concentrations are observed with the use of the oven followed by stove-top frying (Figure 5A).

Cooking events that resulted in little or no increase in the total indoor SVOC concentration include boiling pasta, reheating leftovers in a microwave oven, and toasting bread. No significant effect of occupant number (0-6 occupants) on the total indoor SVOC concentration was observed during the monitoring campaign (Figure 5B), suggesting that the occupant-associated indoor airborne SVOC concentration is more influenced by specific activities rather than by occupant emissions per se. Although the influence of temperature on the total airborne SVOC concentrations is smaller (changing the indoor SVOC concentration between ~ 50 and $80 \mu\text{g m}^{-3}$) than the episodic increases associated with human activities, the influence of indoor temperature may be more important for governing overall airborne SVOCs because of the occasional nature and short duration of the indoor emitting activities.

3.3 | Gas- and particle-phase distribution of SVOCs

Figure 6 shows the recorded TIC representing the chemical composition along with particle fraction (0.0-1.0, color scale) of SVOCs measured in indoor air during periods with no occupant activities (indoor background), during cleaning, and during cooking. For the majority of the campaign, SVOCs in the indoor air were found primarily as gaseous species in the studied residence (Figure 6A). The average recorded gas/particle phase distributions of the total SVOC concentrations during the campaign (December

8, 2017, to January 5, 2018) are illustrated in Figure 7. During background measurements (ie, with no activities such as cooking and cleaning performed in the residence), <10% of the total measured indoor airborne SVOC concentration was particle-bound. In comparison, 22% of the total measured SVOC concentration was found in the particle phase of outdoor air. During the biweekly cleaning, elevated signal intensities of earlier eluting compounds were observed in the indoor TIC, indicating contributions of more volatile organics to the indoor air during cleaning. As no significant increase in particle-bound SVOCs was observed (Figure 6B) compared to background measurements, the addition of more volatile organics resulted in an overall lower SVOC particle fraction of around 4%. Conversely, cooking activities, especially when involving the use of the kitchen oven, were found to produce significant contributions of lower volatility organics to the indoor air. Consequently, and as highlighted in Figure 6C, many of the SVOCs from oven cooking predominantly exist as particle-bound compounds with particle fractions in excess of 50%. Accordingly, PM_{2.5} measurements show elevated particle mass concentrations during cooking events coinciding with TICs similar to that shown in Figure 6C. In general, the addition of the particle-bound SVOCs to the indoor air results in an overall 25% SVOC particle fraction during oven cooking events (Figure 7). Interestingly, compared to background measurements, cooking events such as that represented by Figure 6C reveal evidence of enhanced partitioning of many semivolatile species to the airborne particles. This inference is highlighted by an observed change of the particle fractions of compounds that, during background measurements, were almost exclusively found in the gas phase (ie, compounds with GC retention times of 400-500 seconds in Figure 6).

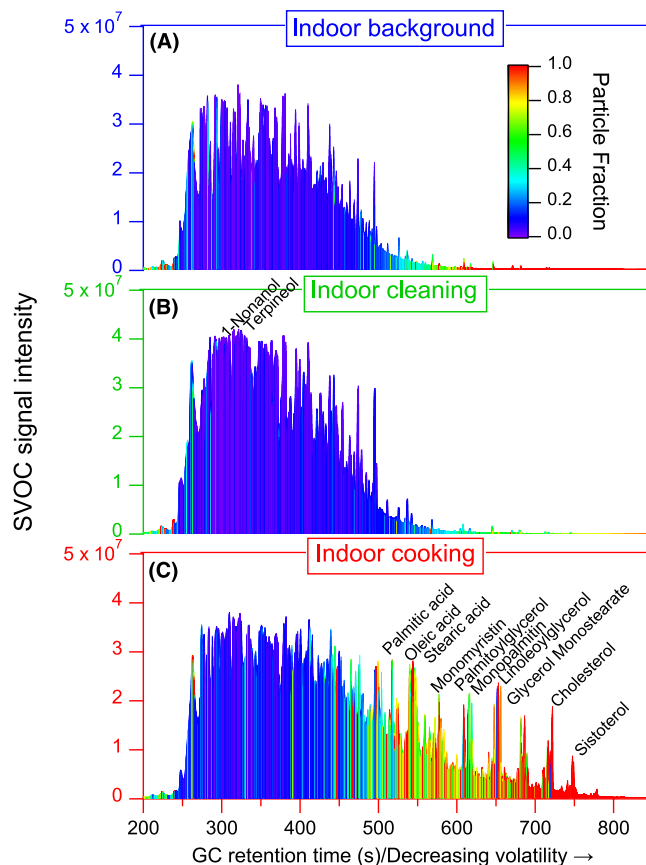


FIGURE 6 Total ion chromatograms (TIC) from SV-TAG analysis of gas-plus-particle samples from A, indoor background; B, cleaning; and C, cooking (oven). Particle fraction (0.0–1.0) of the organic compounds in the recorded TICs are calculated from simultaneous SV-TAG particle-only samples and indicated by the color scale

3.4 | Effect of ventilation on SVOC concentrations

During the vacant period, a mean air exchange rate of $0.46 (\pm 0.11) \text{ h}^{-1}$ was determined from the release and measurement of the inert molecular tracers (Figure S7). Using Equation 1, the mean emission rate of gas-phase SVOCs in the residence during vacancy is estimated to be $6.6 (\pm 2.4) \text{ mg h}^{-1}$. Interestingly, no discernible influence of the air exchange rate was found on the indoor concentration of airborne SVOCs during the vacant period (Figure S7). A possible explanation for this observation is that the time scale to attain steady state in indoor SVOC concentrations is faster than the ventilation time scale. That expectation was suggested by Weschler and Nazaroff, with more rapid sorptive partitioning between air and indoor surfaces accelerating the response time above that associated with air exchange alone.⁹ It seems likely that removal of SVOCs from the indoor air by means of the air exchange in this studied residence ($0.2\text{--}0.6 \text{ h}^{-1}$ during the vacant period, Figure S7) is slow compared to the influence of the temperature-modulated partitioning between the indoor air and surfaces.

Figure 8 shows total indoor and outdoor SVOC concentrations as measured by the SV-TAG during the enhanced-ventilation

experiment. House-wide venting was initiated at 10 AM. A significant drop in the total SVOC concentration is observed, reducing the indoor airborne SVOCs to levels comparable to those in outdoor air. Enhanced ventilation also resulted in a $\sim 1^\circ\text{C}$ drop in indoor air temperature. (The increase in SVOC concentration just before the ventilation was initiated is attributed to cooking activities inside the residence.) After one hour of enhanced ventilation, all windows and doors were closed, leading to a rapid increase in the SVOC concentration. In the hours following the house-wide enhanced ventilation, the indoor SVOC levels approach a steady-state concentration similar to that occurring before enhanced ventilation was initiated (disregarding the SVOC spike from cooking). Approximately six hours after venting, the indoor SVOC concentrations had effectively recovered. From the enhanced-ventilation experiment and the measured recovery of the indoor SVOC concentration, we derive an e-folding time for the total SVOCs (ie, the time required to return to within $1/e$ of the steady-state concentration) of 2.2 hours. (See Supporting Information for details about these calculations.) In comparison, the e-folding time of the added inert tracer was found to be 4.5 hours (Figure S8) corresponding to an air exchange rate of 0.22 h^{-1} , for the period immediately following enhanced ventilation. The tracer level is governed by a dynamic balance between controlled emissions and removal by means of ventilation. Following the enhanced ventilation, the e-folding time of the tracer relaxing back to its higher steady state value depends only on the removal rate (ie, the air exchange rate). Therefore, the lower e-folding time of the SVOCs compared to the inert tracer is indicative of additional SVOC removal (besides ventilation) by means of sorption to indoor surfaces. From the e-folding times of the inert tracers and the total SVOC concentration, we estimate the effective first-order sorption loss-rate coefficient (ie, for loss of SVOCs to surfaces) to be 0.23 h^{-1} (see Supporting Information) suggesting that sorptive uptake to indoor surfaces of the detected SVOCs is comparable to ventilation as a removal process in the studied residence. The estimated sorption loss-rate coefficient for the total SVOC is within the range of those of individual SVOCs reported in previous studies.^{56,57} Note that reported values for individual compounds vary by more than an order of magnitude.^{56,57} The reported sorptive uptake contributes evidence regarding the formation of SVOC reservoirs on indoor surface from which temperature-modulated emissions could contribute to the measured airborne SVOC concentrations in the studied residence.

4 | CONCLUSIONS

In this work, we have explored the chemical composition, dynamic behavior, and phase distribution of SVOCs in a normally occupied northern California residence. Using a dataset with hourly time resolution and extensive chemical speciation, we have assessed the influence of environmental parameters along with human occupancy and activities on the indoor concentrations of airborne SVOCs. The measurements and analysis reveal indoor air that contains a large

FIGURE 7 Gas/particle phase distribution of indoor and outdoor SVOCs measured by SV-TAG from December 10, 2017, to January 3, 2018, in a single-family residence in northern California during normal occupancy and during a vacant period (December 22-27, 2017). Gas/particle phase measurements were performed once every four hours; thus, not all cooking events are represented. (See Table S2 for overview of the cooking events.) The reported average total (gas-plus-particle) concentrations ($\mu\text{g m}^{-3}$ ($\pm\text{SD}$)) are related to the SV-TAG gas/particle phase measurements only. The indoor occupied gas/particle phase distribution and average SVOC concentration does not include cooking and cleaning events

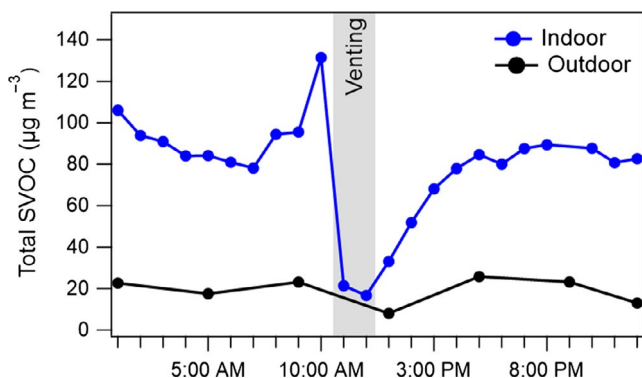
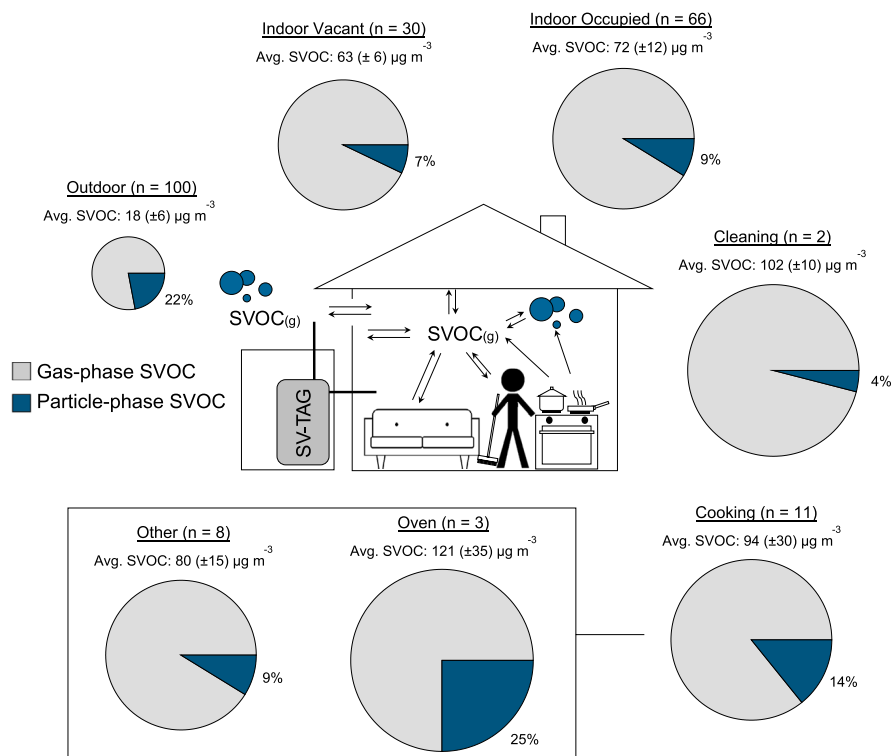


FIGURE 8 Gas-plus-particle SVOC concentrations in indoor (blue) and outdoor (black) air measured by the SV-TAG during enhanced ventilation experiment performed on February 1, 2018. Venting (opening of all doors and windows) was initiated at 10:25 AM. At 12:35 PM, all doors and windows were closed

number of SVOCs, spanning broad ranges of chemical functionalities and volatilities. Indoor air in the studied house is characterized by elevated baseline concentrations of SVOCs compared to outdoors, punctuated by episodic increases observed during occupancy that are related to indoor activities such as cooking and cleaning. During a one-week vacant period, little difference was observed in the total SVOC composition and concentration compared to the occupied period, indicating that SVOCs in the studied residence are controlled to a large extent by emissions from building materials, household interior furnishings, and indoor surface reservoirs. Supporting this inference, the total airborne SVOC concentration shows a positive temperature dependence during both occupied and vacant periods,

evidence that temperature-modulated emissions and/or partitioning with indoor surfaces is a key component of indoor SVOC dynamics.

Addressing the influence of human occupants on indoor air, the current work shows that occupant-related activities are important sources of SVOCs to the indoor environment. In particular, cooking and cleaning contribute to enhanced chemical complexity from the direct emissions of a wide range of distinct organic compounds. With total SVOC concentrations increasing by $>100 \mu\text{g m}^{-3}$ during some events, cooking in a normally occupied residence can be a major contributor to the indoor burden of SVOCs.

In general, we found that gas-phase SVOCs accounted for more than 90% of the total airborne (gas-plus-particle) SVOC concentrations in this residence. However, measurement of the SVOC gas/particle distributions revealed higher contributions of low volatility particle-bound organics during cooking events along with evidence of cooking-associated enhancement of the partitioning into the particle phase of many semivolatile species responding to the increased indoor particle mass concentrations. This finding illustrates how human activities that emit particles (ie, cooking) may alter the phase distribution of SVOCs in indoor environments and thus alter patterns and phases of occupant exposures.

Venting the indoor environment with less-polluted outdoor air significantly reduces the airborne concentrations of SVOCs. However, owing in part to reemission of SVOCs to the indoor air from abundant indoor sources and reservoirs, transitory enhanced ventilation, such as investigated here, results in only temporary improvement of indoor air quality, thus emphasizing the challenges to be overcome in efforts to reducing indoor exposure to SVOCs on a sustained basis.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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