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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 the majority of their time. Exposures to SVOCs potentially pose risks to human health. However, little is known about the chemical complexity, total burden, and dynamic behaviour 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.

Key words: emissions, cooking, cleaning, occupancy, ventilation, gas/particle phase distribution

Practical implications: This study contributes to a better understanding of the chemical composition of air in residential environments. The results illustrate how indoor temperature, occupants and occupant-related activities and processes such as cleaning, cooking, and ventilation may influence the chemistry of the air breathed within homes. The findings provide novel 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.

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.

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3 49 Synthetic chemical compounds are ubiquitous in building materials and consumer products used
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5 50 in residential environments. Some chemicals in these materials have been reported to be in high
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7 51 abundance in indoor environmental compartments, including air and dust.^{3,4} Semivolatile organic
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9 52 compounds (SVOCs) constitute an important yet understudied class of organic chemicals indoors.⁵
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11 53 With wide-ranging applications of SVOCs as active substances or as additives in building
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13 54 materials and consumer products, indoor sources of SVOCs are numerous and include flooring,
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15 55 furniture, electronics, plastic items, textiles, cleaning and cosmetic products.^{6,7} Owing to their
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17 56 semivolatile nature (vapour pressure and boiling point between 10^{-14} to 10^{-4} atm and ~ 240 to 400
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19 57 $^{\circ}\text{C}$, respectively ^{8,9}) SVOCs are present both as gaseous compounds and as condensed-phase
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21 58 components of particles, surface films, and settled dust. For this reason, once emitted from their
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23 59 original sources, SVOCs can become widely distributed in multiple compartments of the indoor
24
25 60 environment. Among the potentially important routes of exposure are inhalation of gases and
26
27 61 airborne particles, ingestion of dust, and permeation of the skin following direct physical contact
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29 62 with surfaces or partitioning into skin oils from air.^{3,10,11} Certain SVOCs are linked with negative
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31 63 human health outcomes, such as reprotoxic and neurotoxic effects, thus motivating national and
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33 64 international control efforts.^{9,12-16} However, owing to their persistent nature, including wide
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35 65 distribution on indoor surfaces, occupant exposures to SVOCs may occur long after eliminating
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37 66 the original sources.⁹ For this reason, SVOCs that have not been routinely used indoors for many
38
39 67 years may continue to exhibit measurable levels in air, in dust, and in body fluids.^{4,17}
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42 68 Multiple studies have reported on the concentrations of SVOCs identified in the air and dust of
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44 69 diverse indoor environments.^{3,9,18-25} However, limited by analytical capabilities, the majority of
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46 70 published studies only report on small numbers of SVOCs, thus providing restricted insight into
47
48 71 the chemical complexity and the total burden encountered in indoor environments. Historically,
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72 methods for analyzing SVOCs in both outdoor and indoor environments have often relied on long
73 timescale (days to weeks) collection of particulate matter and gases on filters and sorbents
74 followed by off-line analysis in the laboratory.²⁶ This approach provides little information on the
75 temporal changes and dynamic behavior of SVOCs in indoor air, limiting the study of important
76 processes and parameters that influence emissions, concentrations, exposures and fates of SVOCs
77 in the indoor environments, including gas/particle partitioning. As one example, environmental
78 parameters such as indoor temperature might be particularly important because of the temperature-
79 dependent vapor pressures of SVOCs and their rapid equilibration between surfaces and the gas
80 phase. Some prior studies show that temperature may exert a large influence on the concentrations
81 of SVOCs in indoor environments. Here, theory as well as laboratory-controlled studies predict
82 increased emissions from indoor sources (e.g., building materials) to indoor air at elevated
83 temperatures.^{27-30,31-35} In addition, model simulation and chamber studies on specific SVOCs have
84 shown that enhanced particle mass loading could facilitate partitioning of gaseous SVOCs in
85 airborne particles, thus altering the SVOC distribution and exposure.³⁶⁻³⁹ Until now, however, no
86 studies have documented the influence of temperature and particle mass loading on the indoor air
87 SVOC concentrations in real indoor environments under normal occupancy, thus restricting efforts
88 to validate models for the indoor environmental emissions, fates and gas/particle distributions of
89 SVOCs and associated human exposures.^{35,36,40,41}

90 Furthermore, the influence of human occupants on the dynamic behavior and chemical
91 composition of SVOCs indoors remains poorly characterized. The roles of human occupants
92 influencing indoor chemistry has been reviewed by Weschler et al.,⁴² including information about
93 direct emission of volatile organic compounds (VOCs) to the indoor air, occupant-influenced
94 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 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 SVOCs in a San Francisco Bay Area residence during normal occupancy. 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 1948 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 of the Supporting Information (SI). Indoor samples

117 reported in this work were drawn from the living room, a ~30 m² room, with hardwood flooring,
118 separated from the adjacent kitchen by an open doorway.

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

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

130 An extensive set of time-resolved metadata was collected, including the utilization of more than
131 50 wireless sensors to monitor room occupancy, appliance use, door/window open status,
132 temperature, and humidity.⁴³ Occupant-related activities such as cooking, cleaning, and candle
133 burning were logged daily, with descriptions of type and duration. House-wide cleaning was
134 performed on a biweekly basis by a professional cleaning crew. Cleaning products used by the
135 cleaning crew are listed in Table S1.

136 A wooden shed was constructed outside the house to contain most of the analytical instruments
137 during the study. The shed was positioned with one of its walls about 50 cm from the house
138 exterior. Two stainless steel sample tubes (outer diameter 1.6 cm (5/8") and length ~ 2 m) were

139 used for separate collection of outdoor and indoor air. Shed temperature was continuously
140 monitored and regulated to $\sim 20\text{ }^{\circ}\text{C}$ using a 1000 W (3500 BTU/h) portable air conditioning unit.

141 ***2.2 Time-resolved measurements of SVOCs***

142 Measurements of combined airborne particle-phase (PM_{2.5}) and gas-phase SVOCs were carried
143 out using a semivolatile thermal desorption aerosol gas chromatography instrument (SV-TAG)
144 developed by the Goldstein laboratory at UC Berkeley and Aerosol Dynamics Inc.⁴⁴⁻⁴⁷ Briefly, the
145 instrument collects airborne organic compounds on two parallel sampling cells with a flow rate of
146 10 L min^{-1} for each cell. Following sampling (15 min), an internal standard (ISTD) is added and
147 each cell is analyzed in series by thermal desorption into helium saturated with a derivatizing agent
148 (n-methyl-n-(trimethylsilyl)trifluoroacetamide (MSTFA), Sigma) and then directed to a gas
149 chromatograph (GC, Agilent model 7890A) with a quadrupole mass spectrometer using electron
150 impact ionization at 70 eV (MS, Agilent 5970C). The ISTD solution consists of a mixture of
151 deuterated organic compounds representative of a broad range of SVOCs commonly found in both
152 indoor and outdoor environments. Gas chromatographic analysis of each sample is performed in
153 14-min intervals using a non-polar GC column (Rtx-5Sil MS, $20\text{ m} \times 0.18\text{ mm} \times 0.18\text{ }\mu\text{m}$; Restek)
154 for chromatographic separation of SVOCs. For each SV-TAG run (i.e., GC analysis) a total ion
155 chromatogram, or TIC, is produced from the combined signal of all measured fragments of the
156 ionized organics entering the MS from the GC. Mass-to-charge values associated with specific
157 compounds or chemical functionality may be selected and extracted from the TIC providing
158 information on the contribution of specific compounds or classes to the total analyzed organic
159 material. In the current work, compound identification was achieved through matching the
160 recorded compound-specific background-subtracted mass spectra with those of authentic standard

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3 161 runs on SV-TAG (when available) and with spectra available in the NIST/EPA/NIH Mass Spectral
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9 163 To study the gas/particle distribution of SVOCs, particle-only sampling is performed on one of the
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11 164 two sampling cells (Cell 2) by removing gaseous compounds from the sample air flow using a
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13 165 multichannel carbon monolith denuder (500 channels, 30 mm OD × 40.6 cm; MAST Carbon)
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15 166 before collection on the downstream cell. Thus, through simultaneous sampling and subsequent
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17 167 analysis of gas-plus-particle-phase compounds on Cell 1 and particle-only compounds on Cell 2,
18
19 168 the gas/particle phase distributions of the sampled SVOCs are determined.
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23 169 Hourly indoor gas-plus-particle SVOC measurements were conducted continuously on Cell 1. A
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25 170 four-hour sampling sequence was conducted on Cell 2, with one indoor particle-plus-gas
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27 171 measurement, one indoor particle-only measurement, one outdoor gas-plus-particle measurement,
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29 172 and one outdoor particle-only measurement. Thus, measurement of indoor gas-plus-particle
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31 173 SVOCs was obtained with one-hour time resolution and indoor vs. outdoor SVOC comparisons,
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33 174 indoor gas/particle partitioning, outdoor gas/particle partitioning, were obtained every four hours.
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35 175 Indoor gas-plus-particle SVOCs measured on both cells simultaneously once every four hours was
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37 176 used to cross-calibrate the cells ensuring their comparability. Once per day, a known volume (4,
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39 177 8, or 12 µL) of an SVOC standard solution, containing >120 different SVOCs, was injected onto
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41 178 both cells and analyzed, resulting in a three-point calibration curve every three days. A sample
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43 179 blank containing only the ISTD was analyzed at the beginning and end of the sampling campaign.
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49 180 In the current work, we present the total gas-plus-particle SVOC signal recorded by the SV-TAG
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51 181 over a four-week period, from 8 December 2017 to 5 January 2018. The signal is quantified using
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53 182 calibration curves from twenty straight-chained alkanes (C13-C32) yielding the total alkane-
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equivalent SVOC concentration in $\mu\text{g m}^{-3}$ 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 $\mu\text{g m}^{-3}$ of air. The method details are described in the SI along with estimates of the associated uncertainties.

2.3 Air-exchange and SVOC emission rate

House air flows and air-exchange rates were acquired through high-time-resolution measurements of inert tracers continuously released inside the residence. The tracers were detected using proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF-MS) following previously reported methods.⁴³ Using the determined flowrates ($\text{m}^3 \text{h}^{-1}$) the effective emission rate (E , mg h^{-1}) of total SVOCs from indoor sources to the indoor air is estimated using the following equation:

$$E = \frac{dC_{\text{Indoor}}}{dt}V + \text{FlowRate}(C_{\text{Indoor}} - C_{\text{Outdoor}}) \quad \text{Equation (1)}$$

Here, C_{Indoor} and C_{Outdoor} refer to the SV-TAG measured indoor and outdoor SVOC concentrations, respectively (in mg m^{-3}). V is the house volume estimated to 380 m^3 . SVOC emissions are calculated only during the vacant period to eliminate uncertainties in effective house volume arising from occupants opening/closing of internal doors, or occupant activities that create emissions (e.g. cooking)) thus providing better estimates of the SVOC emissions from indoor static sources such as materials and surfaces. In this report, we do not attempt to describe quantitatively the SVOC emissions associated with occupants and their activities.

To investigate the effect of ventilation with outdoor air on the indoor concentrations of SVOCs, a house-wide venting experiment was conducted at the end of the campaign. Here, all windows and exterior doors were opened for one hour. After this venting period, all doors and windows were closed. The concentrations of the added inert tracer and the SVOCs was monitored by PTR-TOF-

MS and SV-TAG, respectively, throughout the venting experiment. Except for brief periods to open and close the windows and exterior doors, the house was unoccupied during this experiment.

3. Results

3.1 SVOCs in the indoor residence

The total ion chromatograms (TIC) representing typical gas-plus-particle SV-TAG measurements of indoor air during occupancy but with no cleaning or cooking activity are shown in Figure 1. The SV-TAG TICs show the total combined signal from all sampled organic compounds, each represented by a single signal 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 signal 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 in both personal care products and in building and interior finishing materials, such as paints, glues, and carpets.⁵⁰ Tetradecamethylcyclotrisiloxane, 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 (-C₆H₆), and long-chain carboxylic acids (-COOH). Peaks related to 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), i.e. C₁₃ to 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 in both 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 (i.e. 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 from 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 acid, oleic acid and stearic acid), monoglycerides (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 (i.e. 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 concentration (gas-plus-particle samples) measured by SV-TAG from 8 December 2017 to 5 January 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 $50 \mu\text{g m}^{-3}$, 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 to 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 $6 \mu\text{g m}^{-3}$ ($\sim 10\%$) 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 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, 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 to $80 \mu\text{g m}^{-3}$) 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 (8 December 2017 to 5 January 2018) are illustrated in Figure 7. During background measurements (i.e., with no activities such as cooking and cleaning performed in the residence) less than 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 gas-to-particle partitioning of many semivolatile species

to the airborne particles. This inference is highlighted by an observed change of particle fraction of compounds that, during background measurements, were almost exclusively found in the gas phase (i.e., compounds with GC retention times of 400 to 500 s in Figure 6).

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 SVOCs in the residence during vacancy is estimated to $6.3 (\pm 2.4) \text{ mg h}^{-1}$. 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 ($0.2 - 0.6 \text{ h}^{-1}$ 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 spike 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

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3 364 hours following the house-wide enhanced ventilation, the indoor SVOC levels approach a steady-
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5 365 state concentration similar to that occurring before enhanced ventilation was initiated (disregarding
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7 366 the SVOC spike from cooking). Approximately six hours after venting, the indoor SVOC
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9 367 concentrations had effectively recovered. From the enhanced-ventilation experiment and the
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11 368 measured recovery of the indoor SVOC concentration we derive an e-folding time for the total
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13 369 SVOCs (i.e., the time required to come back to within 1/e of the steady-state concentration) of 2.2
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15 370 hours (see Supporting Information for details about these calculations). In comparison, the e-
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17 371 folding time of the added inert tracer was found to be 4.5 hours (Figure S8) corresponding to an
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19 372 air-exchange rate of 0.22 h⁻¹, for the period immediately following enhanced ventilation. The tracer
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21 373 level is governed by a dynamic balance between controlled emissions and removal by means of
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23 374 ventilation. Following the enhanced ventilation, the e-folding time of the tracer relaxing back to
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25 375 its higher steady state value depends only on the removal rate (i.e. the air-exchange rate).
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27 376 Therefore, the lower e-folding time of the SVOCs compared to the inert tracer is indicative of
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29 377 additional SVOC removal (besides removal by ventilation) by means of adsorption onto the indoor
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31 378 surfaces. From the derived e-folding time of the inert tracers and the total SVOC concentration we
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33 379 estimate the effective first-order adsorption loss-rate coefficient (i.e. for loss of SVOCs to surfaces)
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35 380 to be 0.23 h⁻¹ (see Supporting Information) suggesting that sorptive uptake to indoor surfaces of
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37 381 the detected SVOCs is comparable to ventilation as a removal process in the studied residence.
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39 382 The estimated adsorption coefficient for the total SVOC is within the range of those of individual
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41 383 SVOCs reported in previous studies.^{56,57} (Note that reported values for individual compounds vary
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43 384 by more than an order of magnitude.^{56,57}). The reported sorptive uptake provides evidence for the
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45 385 formation of SVOC-reservoirs on indoor surface from which temperature-modulated emissions
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47 386 could contribute to the measured airborne SVOC concentrations in the studied residence.
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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 number of semivolatile organic compounds, 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 a major source 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 semivolatile organic compounds.

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 high 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 (i.e., cooking) may alter the phase distribution of SVOCs in indoor environments and thus consequently 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 performed 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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Figure 1. A) Total ion chromatogram (blue) from SV-TAG analysis of indoor gas-plus-particle sample during normal occupancy with no indoor activities. Signal contribution from selected compounds are highlighted in pink with corresponding compound information shown in the inset table. **B)** Extracted ion chromatograms of m/z -ratios associated with alkane (m/z 57, orange), alcohol (m/z 75, blue), aromatics (i.e. aliphatic benzenes, m/z 91, green), and acid (m/z 129, red) functionalities. Straight-chained alkanes, alcohols and acids are labelled according to their carbon chain length (e.g. tridecane, $C_{13}H_{28}$ is labelled as C13 alkane).

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 labelled 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.

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 8 December 2017 to 5 January 2018. The vacant period is highlighted in teal. **B)** Average ($\pm$ standard deviation, 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.

Figure 4. Total (gas-plus-particle) alkane-equivalent SVOC concentration ($\mu\text{g m}^{-3}$) versus 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.

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 colour scale.

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

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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 1 February 2018. Venting (opening of all doors and windows) was initiated at 10:25 AM. At 12:35 AM all doors and windows were closed.

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Figure 1.

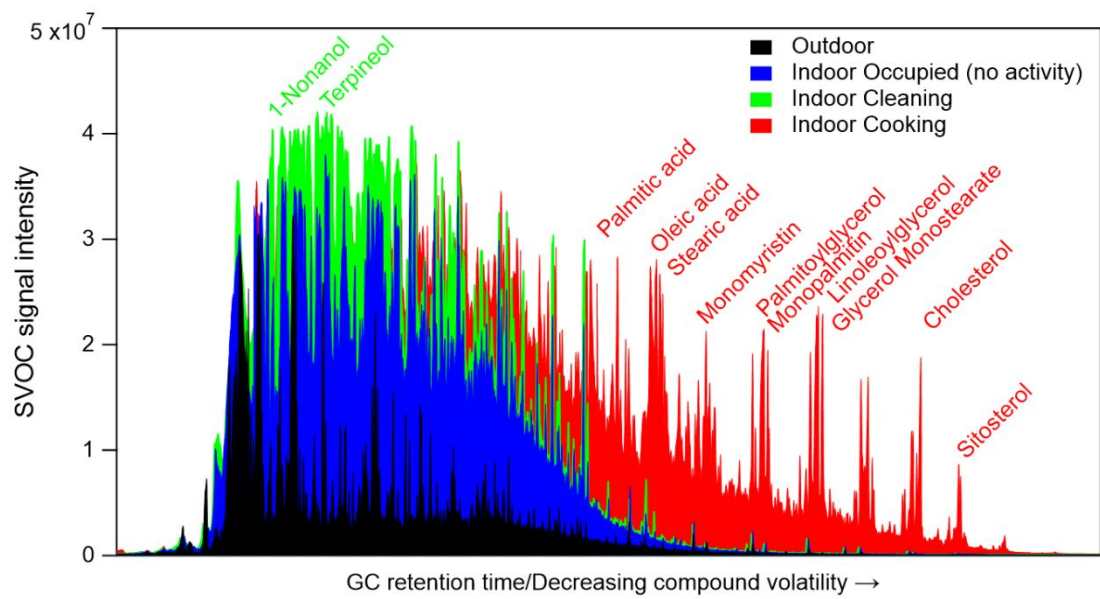


Figure 2.

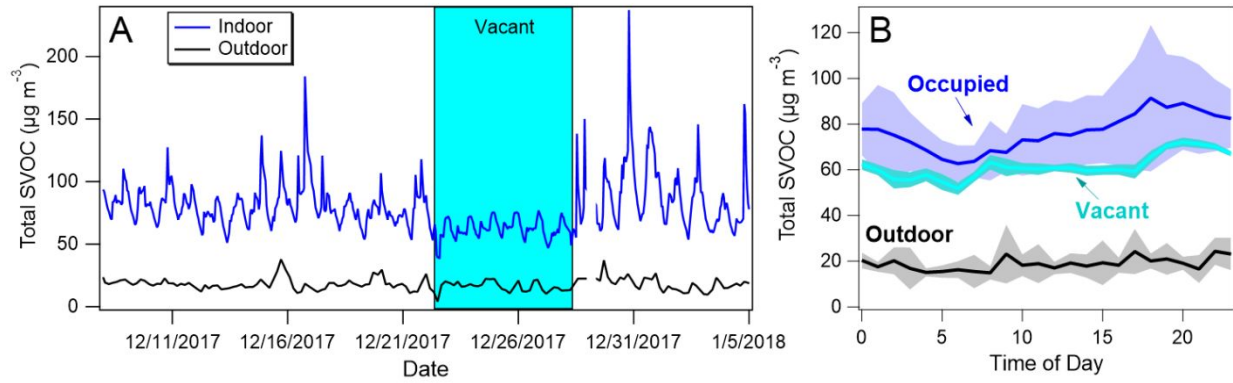


Figure 3.

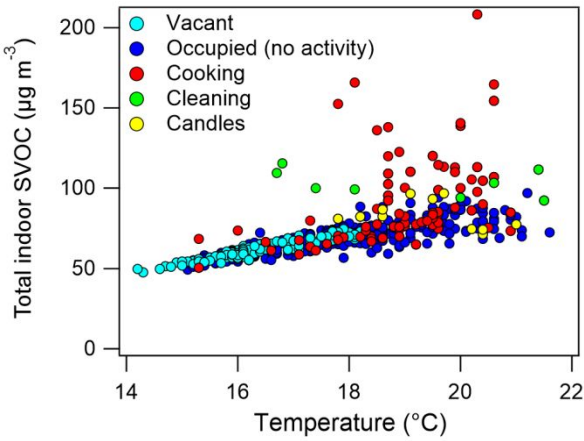


Figure 4.

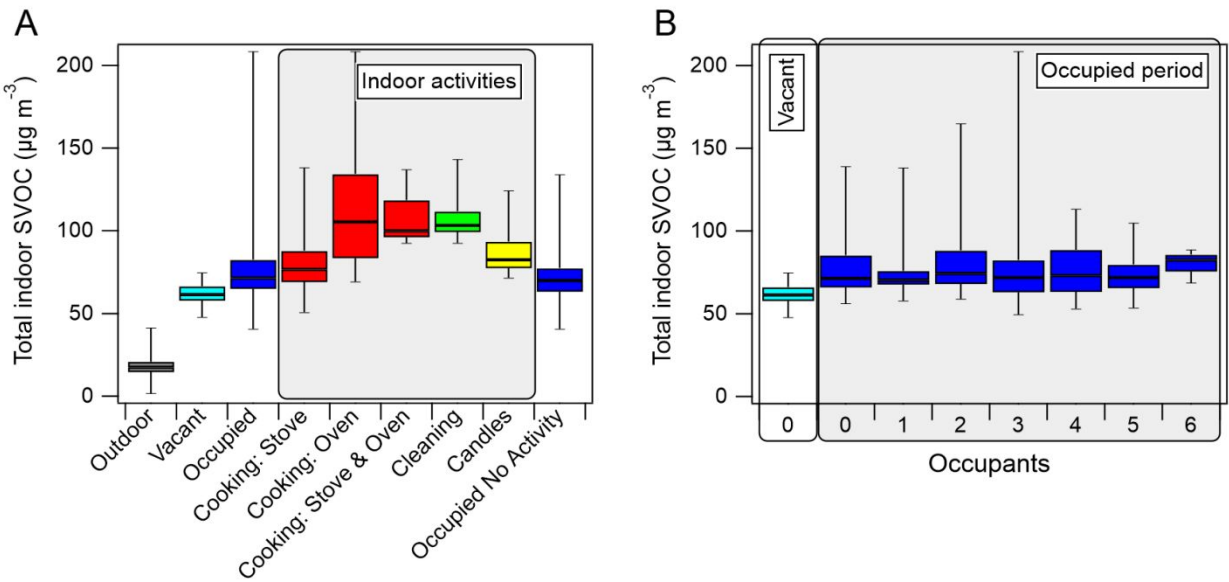


Figure 5.

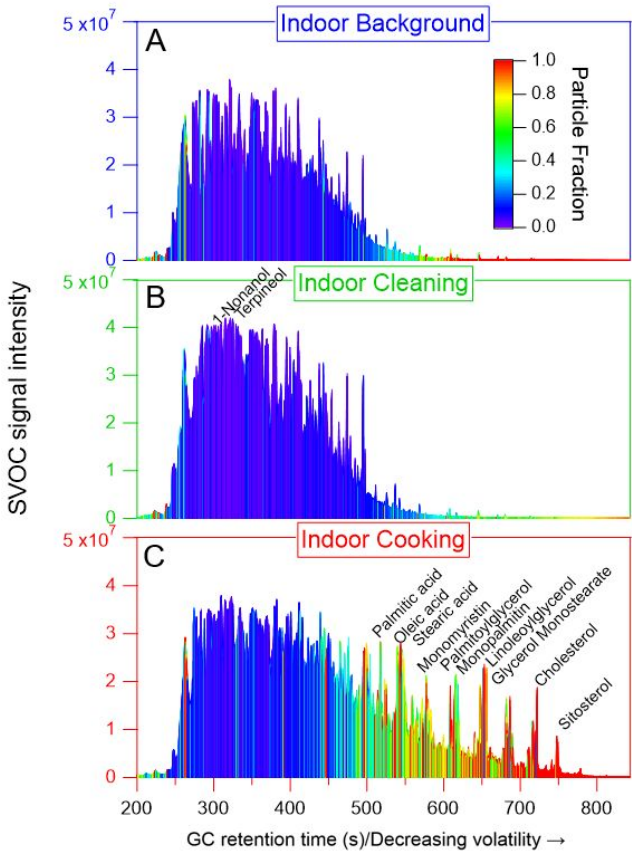


Figure 6.

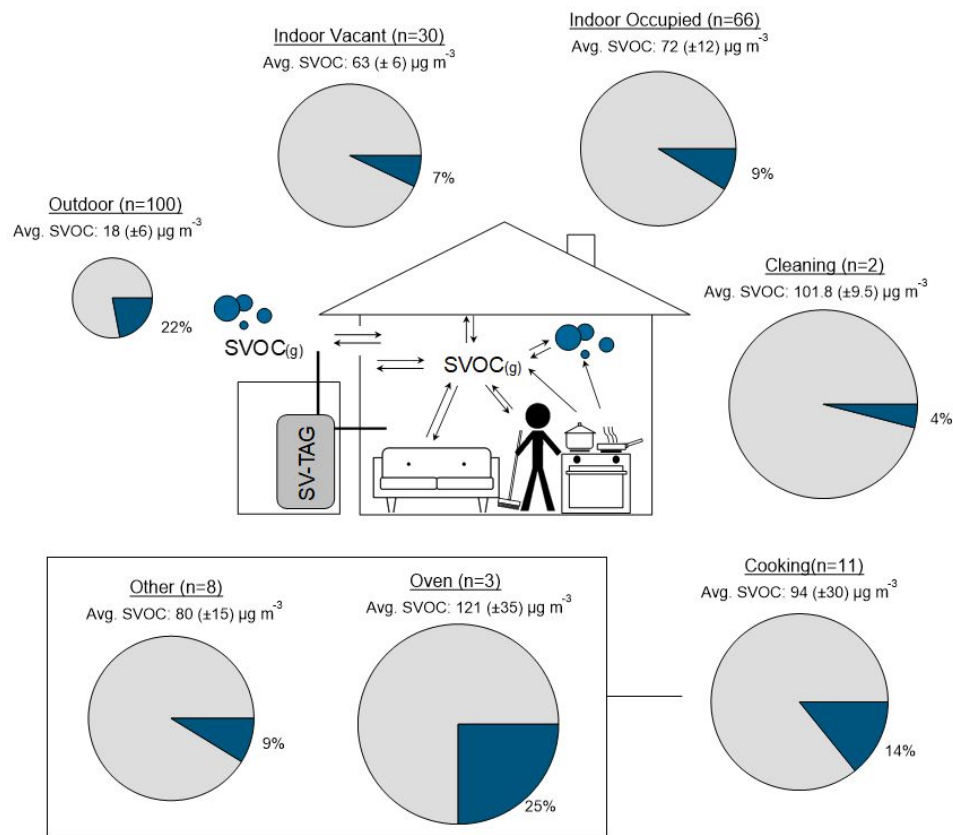


Figure 7.

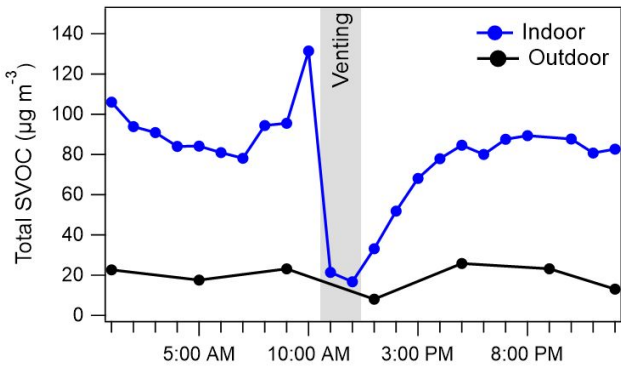


Figure 8.

Supporting Information for

“Sources and Dynamics of Semivolatile Organic Compounds in a Single-Family Residence in Northern California”

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Table S1. Products used by the cleaning crew during the biweekly cleaning of the studied residence.

Brand	Product
Dawn®	Antibacterial hand soap
Pledge®	Furniture spray (lemon scent)
Ajax®	Powder cleanser with bleach
Clorox®	Hard surface spray cleaner, with bleach
Windex®	Glass and multisurface cleaner

Table S2. Residence occupant activity log. Activities captured by the semivolatile thermal-desorption aerosol gas chromatography (SV-TAG) gas/particle distribution measurements are marked by “x”.

Date	Time		Location	Activity	SV-TAG gas/particle distribution measurement		Date	Time		Location	Activity	SV-TAG gas/particle distribution measurement
	From	To						From	To			
12/10/2017	16:30	18:15	kitchen	oven	x		12/17/2017	12:40		kitchen	cooking	
12/10/2017	20:30		kitchen	oven			12/17/2017	17:45		kitchen	cooking	x
12/11/2017	8:50	9:00	kitchen	cooking			12/18/2017	9:00		kitchen	cooking	
12/11/2017	17:50	18:30	kitchen	oven				12:00		kitchen	cooking	
12/12/2017	7:08	7:14	kitchen	cooking			12/18/2017				candles	
12/12/2017	8:45	8:55	kitchen	cooking	x		12/19/2017	23:20	23:46			
12/12/2017	19:00	19:10	kitchen	cooking			12/20/2017	7:16	7:20	kitchen	cooking	
12/12/2017	19:30	20:30		candles			12/20/2017	7:44	7:49	kitchen	cooking	
12/13/2017	16:33		kitchen	Tea			12/21/2017	11:25	11:45	kitchen	cooking	
12/13/2017	18:08	18:35	outdoor	cooking	x		12/21/2017	17:50	18:20	kitchen	cooking	
12/13/2017	18:08	18:35	kitchen	cooking			12/29/2017			house	cleaning	x
12/13/2017	18:03	18:10	kitchen	cooking			12/29/2017	20:30		kitchen	Tea	
12/13/2017	18:50			candles			12/30/2017	9:42	9:45	kitchen	cooking	
12/14/2017	12:12	12:20	kitchen	cooking	x		12/30/2017	10:20	10:26	kitchen	cooking	
12/14/2017	18:45		kitchen	oven			12/30/2017	13:00	13:10	kitchen	cooking	
12/14/2017	18:45	19:25	kitchen	cooking	x		12/30/2017	15:45	18:00	kitchen	cooking	x
12/14/2017	20:25	21:35		candles			12/30/2017	17:00	18:12	kitchen	oven	
12/15/2017	14:30	16:00	house	cleaning	x		12/31/2017	10:45	11:45	kitchen	cooking	
12/16/2017	9:00	9:19	kitchen	cooking	x		12/31/2017	12:10	13:00	kitchen	cooking	
12/16/2017	9:41		kitchen	cooking			1/1/2018	17:52		kitchen	Tea	
12/16/2017	13:23		kitchen	cooking			1/2/2018	10:02	10:16	kitchen	cooking	
12/16/2017	15:57	16:45	kitchen	oven	x		1/2/2018	14:21		kitchen	popcorn	
12/16/2017	22:45						1/2/2018	17:20	17:25	kitchen	cooking	
12/17/2017	10:27	10:56	kitchen	oven			1/2/2018	17:00	17:45	kitchen	oven	
12/17/2017	9:40		kitchen	cooking	x		1/3/2018	17:00	17:05	kitchen	cooking	x
12/17/2017	9:40		kitchen	cooking	x		1/3/2018	18:50	19:10	kitchen	cooking	

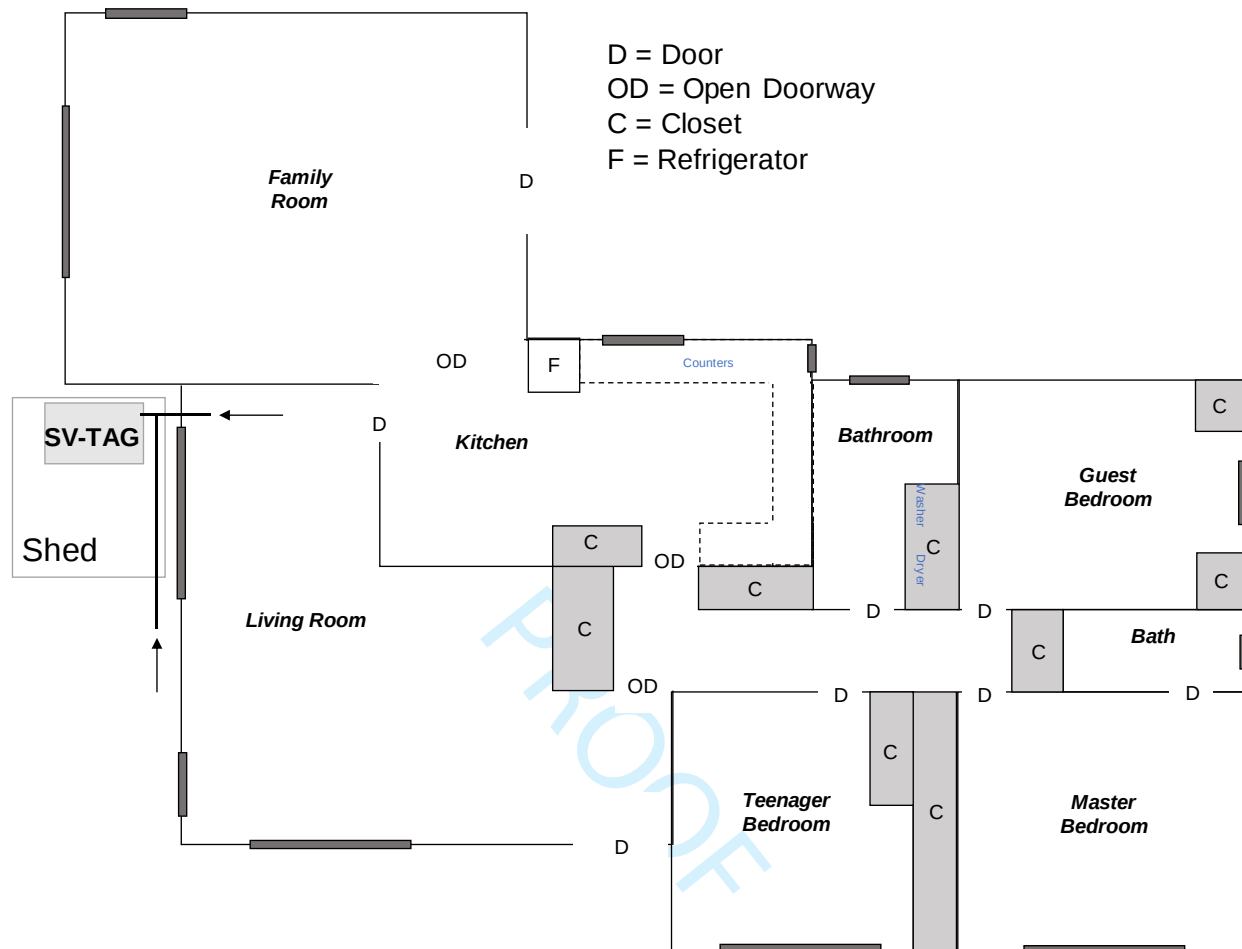


Figure S1. House floor plan at site House 2 (H2). Sampling for semivolatile organic compounds (SVOCs) was done through stainless steel tubes from the living room and from outside the instrument shed. The door between the kitchen and living room was open throughout the experimental monitoring period.

Total alkane-equivalent semivolatile organic compound (SVOC) concentration calibration

Figure S2 shows the total peak signals of the alkane standards (blue) used for the quantification of the recorded semivolatile thermal-desorption aerosol gas chromatography (SV-TAG) total ion chromatograms (TIC). The signal response of the alkane standard series is applied for the quantification of SVOCs with similar gas chromatography (GC) retention time/volatility (grey and white areas of the TIC) yielding total alkane-equivalent SVOC concentration. Changes in the overall performance of the mass spectrometer (MS) electron impact ionization source over the cause of the campaign was corrected for by normalization to the fitted signal of deuterated pentadecanol in the added internal standard (ISTD).

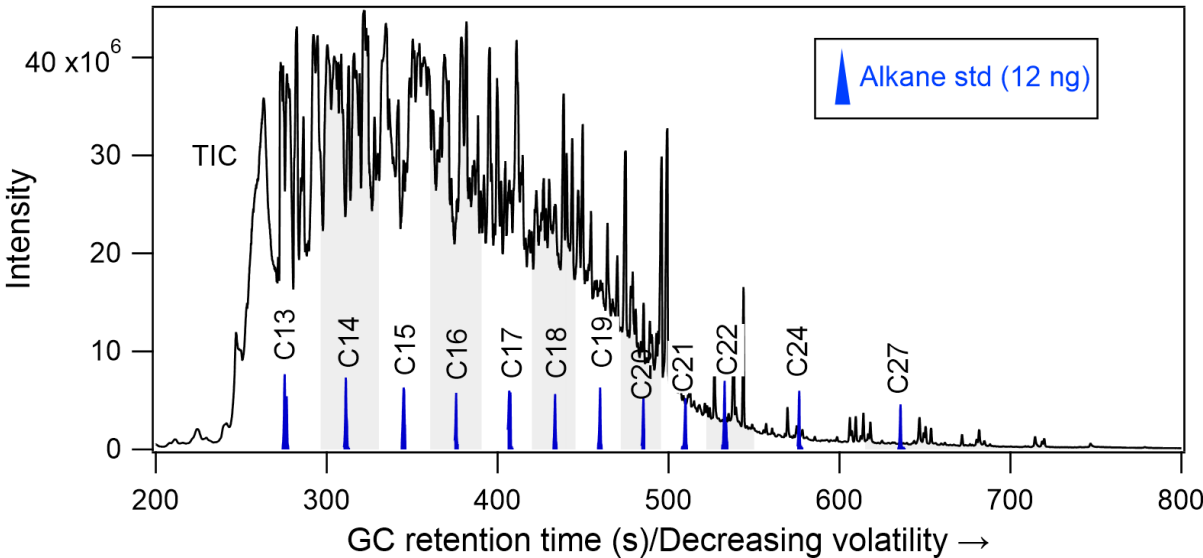


Figure S2. Total ion chromatogram (TIC) from typical gas-plus-particle SV-TAG measurement (black). Blue peaks represent overlaid signal from the non-deuterated straight-chained alkanes from separate SV-TAG measurement of standard solution (12 ng of each alkane) added to the sampling cells. The signal response of the alkane standard series is applied for the quantification of SVOCs with similar GC retention time/volatility (grey and white areas of the TIC) yielding total alkane-equivalent SVOC concentration.

To estimate the uncertainties associated with this method, the TICs recorded from internal and external standard runs are quantified and the resulting total alkane-equivalent concentrations are compared with the known amount of standard material added to the SV-TAG cell. The ISTD includes 44 different deuterated organic compounds covering the following chemical classes; alkanes (36%), alkanoic and benzoic acids (29%), alkenes and polyaromatic hydrocarbons (PAHs, 17%), alcohols and sterols (12%), aldehydes (5%), esters (2%) and sugars (2%). The external standard contains 133 compounds including lignins (13%), sterols (13%), alkanoic acids (13%), alkanes (12%), PAHs (11%), nitroaromatics (10%), pesticides (10%), phenols (4%), esters (4%), sesquiterpenes (2%), siloxanes (2%), alcohols (2%), and sugars (1%). The comparison between the derived alkane-equivalent concentrations and the known amounts added to the SV-TAG cell is shown in Figure S3A. In addition, we compare the total alkane-equivalent SVOC concentration of particle-only SV-TAG measurements with the total PM_{2.5} concentrations measured using a GRIMM Portable Aerosol Spectrometer (Model 1.1008, size range: 0.3 – 35 μm) and a scanning mobility particle sizer (SMPS) system including an electrostatic classifier (TSI 1080) coupled with a water-based condensation particle counter (CPC, TSI 3788). The SMPS system was optimized for measurements of particles in the range of 10 – 600 nm with a sampling time of 300 s (270 s upscan, 30 s downscan, aerosol flow rate = 0.6 L min⁻¹, sheath flow rate = 6 L min⁻¹). The comparison of the derived particle-phase (PM_{2.5}) total alkane-equivalent SVOC and the measured total PM_{2.5} particle mass is shown in Figure S3B. Based on the results shown in Figure S3 the uncertainty associated with the applied quantification method is estimated to < 30%.

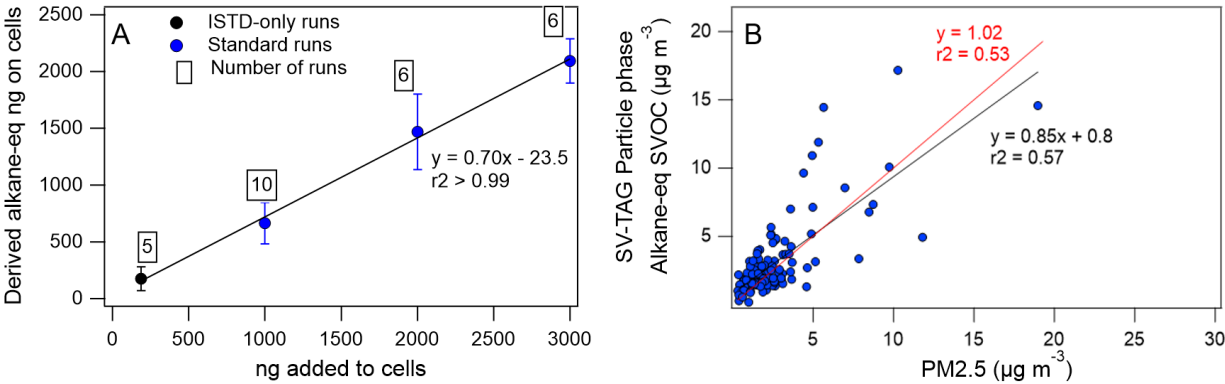


Figure S3. A) Comparison between derived alkane-equivalent mass and actual mass of standard material added to the SV-TAG cell during internal standard (ISTD, black) runs and external standard runs (blue). **B)** Comparison between derived alkane-equivalent SVOC concentration from SV-TAG particle-only measurements and PM2.5 mass measured by GRIMM Portable Aerosol Spectrometer and SMPS system.

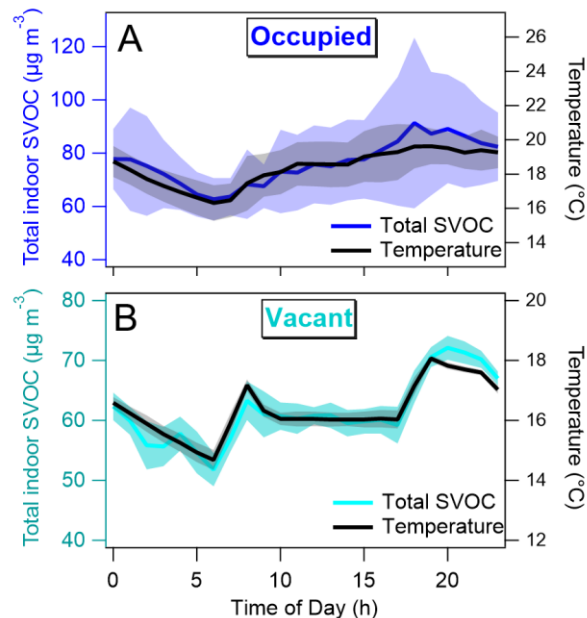


Figure S4. Average ($\pm$ standard deviation) total (gas plus particle) alkane-equivalent SVOC concentration ($\mu\text{g m}^{-3}$) and temperature (black) as a function of time of day measured in indoor air during occupied (blue) and vacant (teal) period. Sharp temperature increases during vacant period at 6 AM and 6 PM are caused by the central heating system, which was controlled by means of a programmable thermostat.

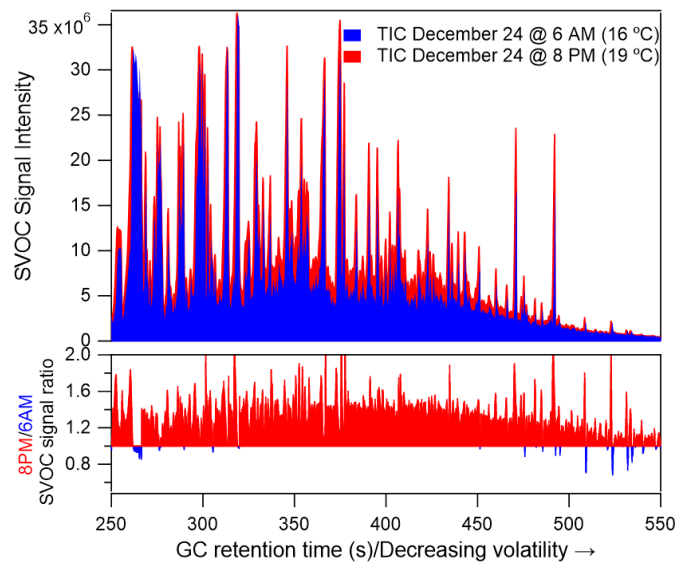


Figure S5. Total ion chromatogram (TIC) from gas-plus-particle SV-TAG measurement performed on 24 December (vacant period) at 6 AM (indoor temperature = 16 °C, blue) and 8 PM (indoor temperature = 19 °C, red). Bottom panel shows the 8 PM/6 AM ratio (i.e. 19 °C /16 °C-ratio) of the SVOC signals across the TIC.

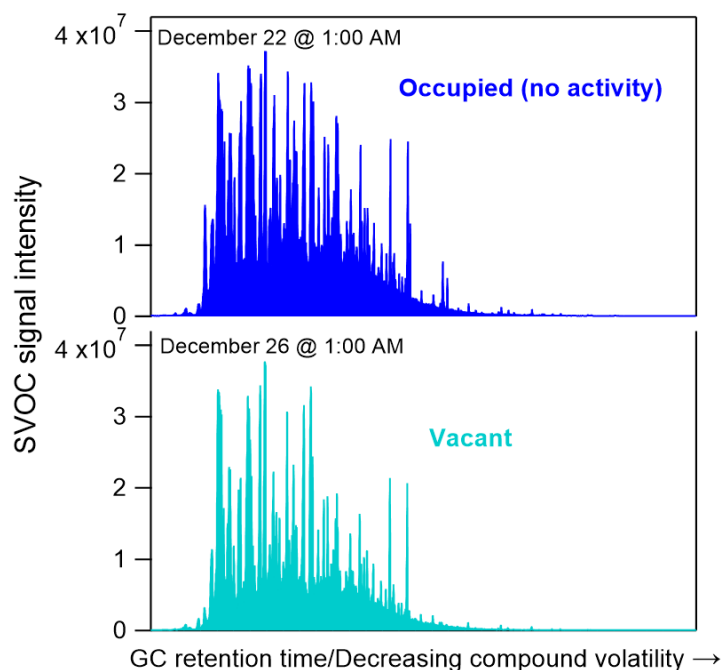


Figure S6. Total ion chromatogram (TIC) from gas-plus-particle SV-TAG measurement performed during the occupied period shortly before the occupants vacated the residence (blue) and during the vacant period (teal).

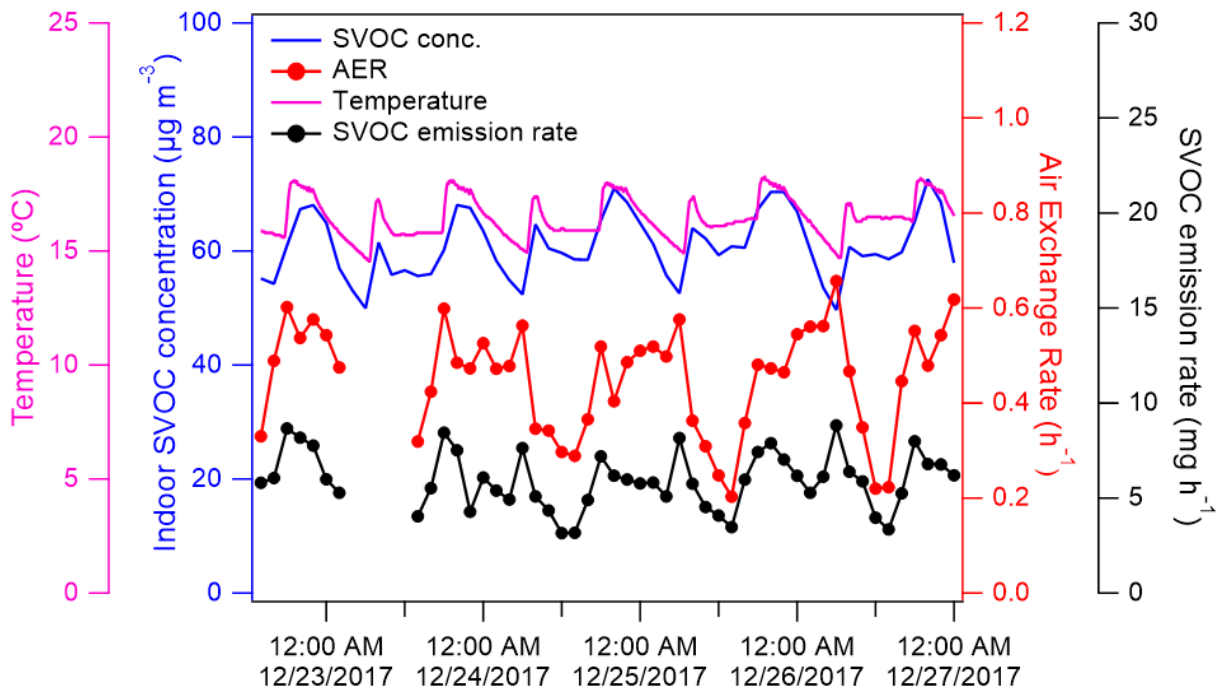


Figure S7. Indoor total airborne (gas-plus-particle phase) alkane-equivalent SVOC concentration ($\mu\text{g m}^{-3}$, blue), temperature ($^{\circ}\text{C}$, pink), air exchange rate (AER, h^{-1} , red) and the derived SVOC emission rate (mg h^{-1} , black) during the vacant period. SVOC emission rates are calculated using Equation (1) from the main article.

Calculation of e -folding time and the SVOC-surface sorption coefficient

Using the measured tracer and SVOC concentration rebound following venting we estimate the SVOC and tracer e -folding times, τ . For a step-change in conditions that would cause a transformation from steady concentration, C_1 , to a new steady concentration, C_2 , the e -folding time is defined as the time required for a fraction equal to $1-(1/e)$ ($= 63\%$) of the transformation to have occurred. For first-order removal processes, the e -folding times can be represented as

$$\tau_{\text{tracer}} = \frac{1}{k_{\text{tracer}}} \quad \& \quad \tau_{\text{SVOC}} = \frac{1}{k_{\text{SVOC}}} \quad \text{Equation (S1)}$$

where k_{tracer} and k_{SVOC} are the rate constants associated with tracer and SVOC removal processes, respectively, for the post-venting period. For SVOCs, the rate constant (k_{SVOC}) is derived by representing the SVOC concentration rebound after venting with the following equation, in which $k = k_{SVOC}$:

$$C(t) = C(0)e^{-kt} + \frac{S}{k}(1 - e^{-kt}) \quad \text{Equation (S2)}$$

Figure S8A shows the measured SVOC concentrations following the enhanced venting period along with the SVOC concentration as represented by Equation S2 ($C(t)$) consisting of the two terms: $C(0)e^{-kt}$ and $\frac{S}{k}(1 - e^{-kt})$; the latter is compared with that of the inert tracer in Figure S8B which also shows the derived e-folding times, τ .

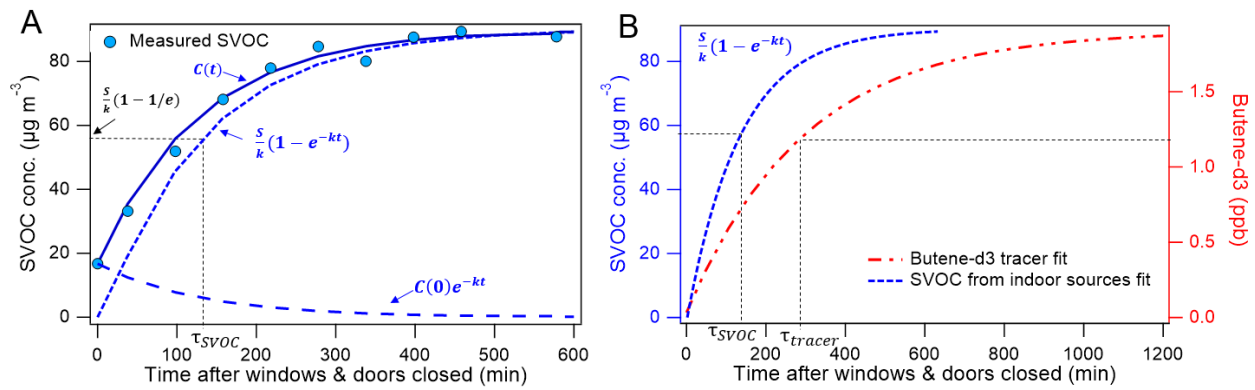


Figure S8. **A)** Indoor total airborne (gas-plus-particle phase) alkane-equivalent SVOC concentration as measured by SV-TAG ($\mu\text{g m}^{-3}$, markers) along with the SVOC concentration as represented by Equation 4 after all windows and doors were closed following the enhanced-venting experiment. **B)** Comparison of the increase in indoor concentrations following venting of SVOC as represented by $\frac{S}{k}(1 - e^{-kt})$ in Equation S2 and the added inert tracer (butane-d3) along with the derived e-folding times (τ_{tracer} and τ_{SVOC}).

To estimate λ_a , the first-order loss rate coefficient of SVOCs associated with sorption onto indoor surfaces, we adopt the following model from Singer et al.,¹

$$\frac{dC}{dt}V = -(\lambda_v + \lambda_a)CV + \lambda_d MA \quad \text{Equation (S3)}$$

Here, C is the airborne species concentration ($\mu\text{g m}^{-3}$), V is the house volume (m^3), A is the exposed interior surface area (m^2) and λ_v , λ_a , and λ_d are the rate coefficients (h^{-1}) describing the rates of removal by ventilation, sorptive uptake to surfaces and desorption from surfaces, respectively; M is the sorbed-phase species abundance ($\mu\text{g m}^{-2}$). For the purposes of the SVOC rebound in our study, i.e. over a short experimental period immediately after closing the windows and doors, we treat M as time invariant, specifically $dM/dt \sim 0$, which is justified by the expectation that the sorbed quantity of SVOCs is much greater than the amount that would be found in the house air at any time. In the case of $dM/dt \sim 0$, Equation S3 may be treated as a classic material balance of this form:

$$\frac{dC}{dt} = -LC + S \quad \text{Equation (S4)}$$

The characteristic time to respond to a step change in conditions in such a situation is $\tau \sim 1/L$. In this case, for the SVOC signal:

$$\tau_{SVOC} \sim \frac{1}{\lambda_a + \lambda_v} \quad \text{Equation (S5)}$$

In the case of the inert tracer, the removal only depends on ventilation. Consequently,

$$\tau_{tracer} \sim \frac{1}{\lambda_v} \quad \text{Equation (S6)}$$

From the evaluation of e-folding times for SVOC and for the tracer, we can estimate the SVOC sorption rate coefficient through application of Equations S5 and S6:

$$\lambda_a \sim \frac{1}{\tau_{SVOC}} - \frac{1}{\tau_{tracer}} \quad \text{Equation (S7)}$$

From the enhanced-venting experiment we find that: $\tau_{tracer} = 4.5$ h and $\tau_{SVOC} = 2.2$ h, and so:

$$\lambda_a \sim \frac{1}{2.2 \text{ h}} - \frac{1}{4.5 \text{ h}}$$

$$\lambda_a \sim 0.23 \text{ h}^{-1}$$

References

1. Singer BC, Hodgson AT, Hotchi T, et al. Sorption of organic gases in residential rooms. *Atmos Environ.* 2007;41:3251-3265.