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Characterizing sources and emissions of volatile organic compounds in a northern California residence using space- and time-resolved measurements

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Abstract

We investigate source characteristics and emission dynamics of volatile organic compounds (VOCs) in a single-family house in California utilizing time- and space-resolved measurements. About 200 VOC signals, corresponding to more than 200 species, were measured during 8 weeks in summer and five in winter. Spatially resolved measurements, along with tracer data, reveal that VOCs in the living space were mainly emitted directly into that space, with minor contributions from the crawlspace, attic, or outdoors. Time-resolved measurements in the living space exhibited baseline levels far above outdoor levels for most VOCs; many compounds also displayed patterns of intermittent short-term enhancements (spikes) well above the indoor baseline. Compounds were categorized as "high-baseline" or "spike-dominated" based on indoor-to-outdoor concentration ratio and indoor mean-to-median ratio. Short-term spikes were associated with occupants and their activities, especially cooking. High-baseline compounds indicate continuous indoor emissions from building materials and furnishings. Indoor emission rates for high-baseline species, quantified with 2-hour resolution, exhibited strong temperature dependence and were affected by air-change rates. Decomposition of wooden building materials is suggested as a major source for acetic acid, formic acid, and methanol, which together accounted for ~75% of the total continuous indoor emissions of high-baseline species.

KEYWORDS
air quality, cooking, material balance, occupancy, source apportionment, ventilation

1 | INTRODUCTION

Residential indoor air is an important contributor to pollutant exposure. The average American spends about two-thirds of their time in a residence.[1] More than half of the air breathed is residential indoor air. One major concern regarding residential indoor air quality is elevated concentrations of volatile organic compounds (VOCs).[2-6] Indoor VOCs encompass a broad range of chemical species, including saturated and unsaturated hydrocarbons, carbonyls, alcohols, organic acids, ethers, esters, furanoids, amines, siloxanes, sulfides, etc.[7,8] Some VOCs are known to pose health hazards, some may be important for indoor chemistry, and few have been well characterized.[8] Previous indoor VOC studies often focused on a small subset of compounds that are known to cause negative health effects, such

as aldehydes and aromatics. A key step toward improving knowledge about indoor VOC exposure and chemistry is to investigate a broader range of VOCs, with the goal to better understand the sources and respective emission characteristics.

VOCs in residences can arise from many sources, with potentially distinctive emission characteristics. They can be emitted from various building materials, furnishings, and household products inside the living space;[9] emitted from occupants and their regular and episodic activities (eg, cooking and cleaning);[10,11] produced from chemical processes taking place indoors (eg, reaction of ozone with skin oil);[12,13] emitted from indoor microbial communities;[14,15] and transported from outdoors or from other connected indoor spaces (eg, from attics, basements, and crawlspaces).[16,17] Dynamic processes affecting indoor-relevant VOC emissions have most commonly been studied in controlled laboratory settings, focusing on emissions from specific materials present indoors or from prescribed simulated activities.[11,18] Field observations in real indoor environments under normal occupancy constitute important complements to laboratory studies. Detailed field studies contribute information about the relative importance of various sources indoors and identify processes that merit further investigation in the laboratory. However, investigating VOC sources and emissions in field studies has been challenging, in large part because of limitations in analytical capabilities. Adding to the analytical challenge is that indoor environments contain many sources that emit the same VOC species.

One strategic approach to field studies characterizing VOC sources is to take advantage of patterns in the spatial and temporal variability of different emission sources and the resultant variability of VOC concentrations. Along this line of thinking, Seifert and Ullrich proposed to distinguish between continuous and intermittent sources with further subgroups of regular and irregular emissions.[19] Considering also the spatial patterns of sources, Levin divided sources using a two-by-three matrix (point and distributed; constant, periodic, and episodic).[20] A key to transform such concepts into reality is making spatially and temporally resolved VOC measurements in indoor field studies. The time resolution needs to be on the order of tens of minutes or better to capture some common sources (such as cooking) in the residential environment.[19] Such a measurement program would be demanding if undertaken using conventional VOC measurement techniques, that is, taking time-integrated or snapshot samples using sorbent tubes and then carrying out offline analysis of targeted compounds using gas chromatography with mass spectrometry.[21] Field measurements with lesser time resolution or conducted over short time spans focusing on targeted sources and dynamic processes have been undertaken. Examples include investigating the transport of VOCs from a garage or basement to the living zone using space-resolved measurement,[16,17] studying the impact of renovation on indoor VOC levels by taking samples at daily or monthly intervals,[22,23] and characterizing sorptive behavior of indoor VOCs using time-resolved measurements over periods of hours.[24] In addition, factor analysis has been applied to source apportionment studies, utilizing time-integrated VOC measurements in numerous residences.[2,25] However, in such investigations, attributing the statistically derived factors to different source classes is often ambiguous and sometimes speculative, owing in part to the variability of VOC sources and emissions across different residences.

Practical Implications

- This study advances knowledge about the relative contributions of three major categories of indoor air sources for VOCs: building materials and furnishings, occupants and their activities, and outdoor air.
- We find that in an 80-year-old, wood-framed single-family residence in California, the building materials and furnishings dominate for most measured VOCs, with a surprisingly large contribution from what appears to be wood decomposition.
- The building-associated emission rates increase with both increasing indoor temperature and increasing air-change rates.
- Among occupant activities, cooking is the most prominent indoor emission source.
- Outdoor air is relatively unimportant as a contributor to indoor air VOC levels at this site.

Recently, online chemical ionization mass spectrometry (CIMS) has begun to be used in field measurements of VOCs indoors. This analytical approach can measure speciated VOCs in real time, with second to minute resolution. Time-resolved observations of speciated VOCs have been made in classrooms, cinemas, and football stadiums under normal occupancy, using proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS),[10,26-29] as well as other types of CIMS instruments.[30] The high time resolution of this approach allows for exploring short–time-scale processes, which are difficult to investigate using time-integrated sampling. Among the findings to emerge from such studies is the importance of human occupants as VOC sources in densely populated indoor environments. For example, Tang et al[10] reported that siloxanes, emitted from personal care products used by students, were among the most abundant VOCs observed in a classroom.

Until now, measurements using CIMS-type instruments have not been reported for characterizing VOC concentrations and emission sources in residential environments during normal occupancy. Recognizing this gap, we report here on continuous VOC observations in a normally occupied single-family house in northern California using PTR-ToF-MS during two sampling seasons. The measurement approach was designed to provide time-resolved as well as space-resolved information, with the latter achieved by sequentially sampling from each of six locations in and near the house during each 30-minute interval. Indoor VOC emission rates were assessed with 2-hour resolution, utilizing simultaneous tracer-based determinations of air-change rates in the living space. Based on these VOC measurements, augmented by

extensive metadata on environmental and operational conditions of the household, the present study aims to characterize general features of emissions and source attributes of VOCs in the living space of the studied house.

2 | METHODS

2.1 | Observational campaign

Extensive observational monitoring was conducted in a single-family house (designated H1) in Oakland, California, during two seasons. The first observational period (summer campaign) was 8 weeks long from mid-August to early October 2016. The second period (winter campaign) spanned 5 weeks from late January to early March 2017. A detailed description of the studied house and of the two observational campaigns has been reported.[31,32] We provide a brief recap here of aspects essential for understanding and interpreting the VOC data.

The studied house is situated in the foothills of Oakland, in a lightly trafficked urban residential neighborhood. It was built in the 1930s of wood-frame construction. There had been no recent renovation or refurnishing of note. (For example, the most recent interior painting took place in 2011.) The house has a split-level floor plan for the main living space, with an unoccupied attic above, and a small basement and larger crawlspace below. In the living space, there are three bedrooms and two bathrooms on the upper level (volume ~150 m^3) and a kitchen, family room, and living room on the lower level (~200 m^3). Two adult occupants (ages in the range 55-65 years) live in the house. The house is equipped with central heating, but no air conditioning. A decades-old natural gas-fired gravity furnace (buoyancy-driven, with supply registers in each room and a single, centrally located return register, but no fan) is situated in the crawlspace; it operated intermittently during the winter campaign and was off during the summer. Except for the bathrooms, the interior doors in the living zone were normally kept open, including at night. The doors from the living zone to the substructure (basement and crawlspace) and to the attic were generally closed. The basement room, which was occasionally accessed, contained a washing machine, clothes dryer, and storage space. In addition to normal house operation (occupied periods), the occupants were deliberately away from the house for a few days for at least one time in each campaign. During these vacant periods, the house windows and doors were all closed and the furnace was off.

Temporally and spatially resolved measurements were made for a range of gases, including VOCs using a PTR-ToF-MS (Ionicon Analytik GmbH, Austria, PTRTOF 8000), ozone (O_3), and carbon dioxide (CO_2). The gas analysis instruments were situated in a detached garage about 5 m from the house. Air was continuously drawn through separate 30-meter-long 6.4-mm (¼″ OD) perfluoroalkyl (PFA) sampling tubes at a constant flow rate of ~2 L min^{-1} from six locations: outdoors, kitchen (representing the lower living zone), landing at the top of the half flight of stairs (with doors open to the bedrooms, representing the upper living zone), crawlspace, basement, and attic. A 2.0-μm-pore size PTFE filter was installed on the intake end of each sampling line to remove particles. From the house to the garage, the PFA sampling tubes were bundled together and heated by self-adjusting heating tape to reduce temperature-dependent wall effects in the tubes. The gas instruments regularly and automatically switched between subsampling from these lines through a 6-way manifold (NResearch, 648T091; PTFE inner contact surfaces). The total sampling rates of the gas instruments were ~1.4 L min^{-1}, which increased the flow rate through individual PFA tubes to ~3.4 L min^{-1} during measurement. As a reference point, the response delay due to the use of 30-meter-long tubes was estimated to be 0.8 minutes for nonanal ($C_9H_{18}O$) at this flow rate.[33]

Two different sampling sequences were employed for gas measurements during observational monitoring. During most periods, data were collected with spatial resolution emphasized, switching regularly at 5-minute intervals among each of the six inlets (ie, 30 minutes for one full cycle). Two weeks in summer and 1 week in winter were used to collect data with higher temporal resolution in the living zone; in this case, the 30-minute cycle involved only three locations: outdoors (5 minutes), kitchen (20 minutes), and bedroom area (5 minutes).

In addition, to facilitate compound assignment on PTR-ToF-MS, short-term VOC samples were collected using sorbent tubes in the studied house and then analyzed using 2-dimensional gas chromatography time-of-flight mass spectrometry (GC × GC-ToF-MS).

Extensive supporting data were acquired to characterize general environmental and operational conditions in the household. Three inert tracers, including deuterated propene (C_3D_6 and $C_3H_3D_3$) and deuterated butene ($C_4H_5D_3$), were steadily released in the house and measured by PTR-ToF-MS.[31] Using the tracer data, the airflow patterns between living space, attic, and crawlspace were characterized, and the time-varying air-change rate of the living space was determined with 2-hour time resolution.[31] More than 50 wireless sensors were used to monitor time-resolved room occupancy (motion), appliance use (on/off), door/window open status (open/closed), and indoor temperature and humidity. Occupants also maintained daily presence/absence and activity logs to complement the automatically acquired metadata.

2.2 | VOC measurement and data analysis

The PTR-ToF-MS uses soft chemical ionization, with hydronium ion (H_3O^+) serving as the primary reagent. The H_3O^+ ions can effectively protonate VOCs with proton affinities greater than that of water, allowing for detection of most unsaturated hydrocarbons (such as alkenes and aromatics), VOCs containing oxygen, nitrogen, sulfur, halogens, and silicon, among others.[34] Due to the low exothermicity of the proton transfer reaction, the extent of product ion fragmentation is limited and the accurate ion mass (mass resolution ~4000) can be used as the identifier for many important VOCs. Alkanes constitute a major class of VOCs that do not react with H_3O^+ and hence cannot generally be measured by PTR-ToF-MS. However, for some highly abundant alkanes, reactions with impurity reagent ions (ie, O_2^+ and NO^+; <5%) might also produce a high enough signal to allow for detection by the instrument.[35]

The instrument was operated at a drift-tube pressure of 2.3 mbar, a drift-tube temperature of 75°C, an *E/N* ratio of 120 Td, and an inlet temperature of 70°C. The instrument background was determined a few times per day using zero air generated by passing filtered ambient air through a platinum catalyst heated to 350°C. The humidity of generated zero air typically agreed with the level of ambient air within 10%. The instrument sensitivity was calibrated daily by diluting one of two multicomponent calibration gas standards with the zero air.

PTR-ToF-MS spectra were collected with 2-second time resolution. The recorded spectra were processed using PTRwid package under IDL,[36] to automatically detect mass peaks, to create a unified peak list for each campaign, and to provide signal output in counts per second. Given the sequential sampling scheme with 5-minute switching intervals, the peak signals were averaged over the last 3 minutes for each 5-minute period in analyzing the data; the first 2 minutes of data were excluded from the average to limit possible memory effects of the sampling system. As discussed in the supplement, the 2-minute trimming appeared sufficient to guarantee small influence by the previous sample, except for a small subset of ions that are denoted as sticky VOCs (cf. Table S1). Data from these sticky ions are not included in the quantitative analysis presented in this paper.

VOC speciation for each campaign was deciphered from the unified peak list and corresponding peak signals. In total, 656 mass peaks were detected in the summer campaign and 661 in the winter campaign, using consistent signal processing criteria. The mass peaks were first filtered to remove background ions predominantly arising from the instrument and from tubing. A best-guess ion formula was then assigned to each of the remaining peaks, utilizing the accurate mass determinations and the correlation of their signals with other peaks. The list of ion formulas was further reduced by combining isotopic ions and identified fragment ions; removing interference ions, tracer ions, sticky ions, and inorganic ions; and applying an abundance threshold. The inclusion criterion based on abundance was an average mixing ratio in the kitchen air >0.005 ppb and above the respective detection limit. Ion formula is a useful but by no means unique indicator of VOC identity (eg, it does not provide for discrimination among isomers, nor exclude the possibility of fragmentation). Some ion formulas can be confidently attributed by means of deductive reasoning to specific compounds or groups of compounds, such as $C_{10}H_{17}^+$ to monoterpenes, while other assignments are speculative or remain undetermined. In what follows, best-estimate compound assignments are indicated and reported together with the corresponding ion formula. In cases where the ion formula is uncertain, the exact ion mass is also reported. In addition to organic ions, two inorganic ions, attributable to chloramine and hydrogen sulfide, are also quantified and reported.

From the 656 ion peaks detected by PTR-ToF-MS across the summer campaign, 218 VOC signals (organic ion formulas) were extracted to represent measured VOC speciation. The corresponding procedure for the winter campaign yielded 171 VOC signals from among 661 ion peaks. Compared with previous full-spectra VOC analysis using PTR-ToF-MS for indoor and outdoor air,[26,37] here a lower fraction of ion peaks is selected for the analysis (25%-35% in this study vs >50% in previous studies), largely due to the extra step of combining isotopic and fragment ions. The reduced list of ions has minimum overlap in terms of parent compounds and serves as our best representation of VOC speciation measured using PTR-ToF-MS.

Airborne concentrations (in part per billion by volume, ppb) of parent VOCs were estimated from individual VOC signals by first adjusting for ion transmission, normalizing to the reagent ion signal (the summed signal of H_3O^+ and $H_3O^+{\cdot}H_2O$), and then applying a sensitivity factor. Mass-dependent ion transmission relative to H_3O^+ and its drift over each multiweek observational period was corrected utilizing daily calibrations with VOC gas standard mixtures.[38] For some major signals (such as acetic acid, formic acid, ethanol, furfural, and siloxane [D5]), the corresponding sensitivity factors were obtained from calibrations using authentic standard compounds during or after the campaign, and both the parent ion and major fragment ions were used for quantitation to account for humidity-dependent fragmentation. For other VOC signals, a default sensitivity factor was applied, assuming a constant rate coefficient at 2.5×10^9 cm^3 s^{-1} for the reactions of parent VOCs with H_3O^+ and with the water cluster $H_3O^+{\cdot}H_2O$. As a comparison point, estimated concentrations using this assumption would have an uncertainty of −40% to +60% for the range of compounds specially calibrated except ethanol. As previously reported, the sensitivity factor of ethanol was almost one-order-of-magnitude lower than other VOCs.[39]

A range of statistical parameters of measured VOC concentrations was calculated. Mean and median concentrations (C_{Avg} and C_{Med}) were determined for each VOC signal in each space for vacant and occupied periods in each campaign, serving as the basis of calculating more digested parameters. The C_{Avg} and C_{Med} values in the occupied periods were calculated based on measurements taken during space-resolved sampling to guarantee equivalent comparison across spaces. The C_{Avg} and C_{Med} in the vacant period were calculated only using measurements during the longer vacant periods (>2 days; in the beginning of winter campaign and at the end of summer campaign, respectively). Some VOC signals were above the detection limit in the kitchen, living, and attic spaces, but below the detection limit outdoors and in the subfloor spaces. In these cases, half of the detection limit was used to represent C_{Avg} or C_{Med} in below-detection-limit spaces. The detection limits varied by ions, with an interquartile range from 0.002 to 0.008 ppb. More digested parameters calculated using mean and median concentrations include indoor-to-outdoor (I/O) ratio of mean concentration for each indoor space, as well as mean-to-median concentration ratio in the kitchen, $(C_{Avg}/C_{Med})_{kitchen}$. In addition, the I/O ratio was calculated for the overall living zone; here, the indoor concentration was taken as the volume-weighted mean of the average concentration measured in the kitchen and bedroom area. (In contrast to absolute concentration, the ratios are not subject to uncertainties associated with instrument calibration.)

An automatic scheme was developed to identify transient indoor emission episodes, using steep increases in indoor concentration with

time (spikes in the time series) as the key criterion. The measured time series in the kitchen of each VOC signal during the whole campaign was first normalized to 30-minute resolution. Peak position of each spike was automatically identified on the times series using an optimized peak-detection algorithm. A manual check across a large range of VOC signals indicated that this algorithm had high fidelity, with few false identifications. Nevertheless, some small spikes might not have been detected owing to fast temporal variation in baseline concentrations, for example, associated with window opening (particularly during the summer). The total number of VOC signals which spiked within each hour (h^{-1}) was counted and used in some analyses.

2.3 | Determining indoor emission rates

Time-resolved emission rates in the living zone were determined for VOC signals using indoor air-change rates determined with 2-hour resolution.[31] Key approximations made in this calculation are (a) that the occupied internal volume of the house can be effectively considered as well-mixed and (b) that only indoor emissions and air change between indoor and outdoor air influence indoor-air concentrations. These approximations are supported by three important observations: (a) tracer results showed that air in the upper and lower living spaces mixed fairly well[31]; (b) the crawlspace and attic generally served as one-way paths for airflow into and out of living zone, respectively[31]; and (c) VOC composition in the crawlspace was similar to that outdoors. Under this approximation, the mass balance of a VOC in the living zone is given by the following equation:

$$\frac{dC_{in}}{dt}V = \frac{E}{\rho} - A\cdot(C_{in} - C_{out})\cdot V, \quad (1)$$

where $C_{in} = C_{in}(t)$ and $C_{out} = C_{out}(t)$ are the concentrations in the living zone and outdoors (ppb; part per billion by volume); V is the volume of the living zone (m^3); $E = E(t)$ is the emission rate in the living zone (mg h^{-1}); ρ is the gas density for the compound (mg mm^{-3}); and $A = A(t)$ is the living-space air-change rate (h^{-1}). Treating $A(t)$ and $E(t)$ as constant over each interval of Δt $[t, t + \Delta t]$, we obtain the following approximation for E by integrating Equation 1:

$$E = \rho V\left(\frac{C_{in}(t+\Delta t) - C_{in}(t)}{\Delta t} + A\cdot(\bar{C}_{in} - \bar{C}_{out})\right), \quad (2)$$

where $\bar{C}_{in}$ and $\bar{C}_{out}$ are the time averages over $[t, t + \Delta t]$ of C_{in} and C_{out}, respectively. In application, ρ is calculated based on molar mass of the compound (ion) at 20°C, V is the measured living-space volume (350 m^3), and Δt is 2 h. The time-dependent outdoor concentration, C_{out}, is directly measured. The time-dependent indoor concentration, C_{in}, is approximated as the weighted mean of VOC concentrations measured in the kitchen and bedroom area. The procedures to calculate values of $C_{in}(t+\Delta t) - C_{in}(t)$, $\bar{C}_{in}$, and $\bar{C}_{out}$ are described in the supplement and are consistent with the procedures to determine the air-change rate using measured tracer concentrations.[31]

3 | RESULTS AND DISCUSSION

Figure 1 presents an overview of the measurement results, displaying a full time series of the summed concentrations of VOCs (∑VOCs) measured by PTR-ToF-MS at each of the six measurement locations in the summer (Figure 1A, for 8 weeks) and winter (Figure 1B, for 5 weeks) campaigns. Note that ∑VOCs is not equal to the total VOC concentration, given that a major class of VOCs, alkanes, was not measurable by PTR-ToF-MS. Two prominent features of the time series are highlighted. First, ∑VOCs in the living zone (bedroom and kitchen) and in the attic were of similar scale and were an order of magnitude higher than those in subfloor spaces (basement and crawlspace), which were close to the outdoor level. This feature was exhibited consistently for both occupied and vacant periods in both seasons. Secondly, for ∑VOCs measured in the living zone, the vacant periods were characterized by consistently high background levels, while the occupied periods displayed frequent short-term increases on top of these levels. The implication of this observation is that occupants and their activities influenced the temporal pattern of VOC concentrations. Utilizing the observed spatial and temporal variation in VOC concentrations, the following analysis aims to characterize generic features of indoor VOC emissions and sources, in particular focusing on VOCs measured in the living zone where human exposure occurs.

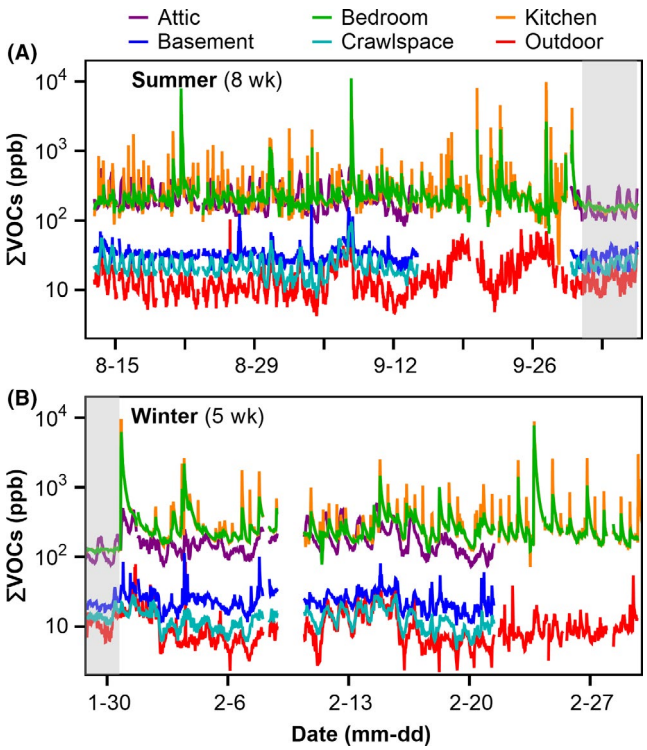

FIGURE 1 Time series of summed VOC concentration (∑VOCs) during (A) summer and (B) winter campaigns. The gray shaded region represents the longer vacant periods (≥2 days) in each campaign. Traces in purple, green, orange, blue, cyan, and red represent measurements in the attic, bedroom area, kitchen, basement, crawlspace, and outdoors, respectively

3.1 | VOC composition in the living zone

Figure 2A presents the average VOC mass spectrum measured by PTR-ToF-MS for kitchen air. Mass-to-charge ratio of detected ions (m/z, with implicit units of the atomic mass unit normalized by the charge number), which is a proxy of molecular mass ($m/z = m + 1$ in typical case of the proton transfer reaction) of the corresponding compound, ranged from 25 to 450. Most ions (N = 167) were detected in both campaigns. Some were detected only in summer (N = 51) and a few only in winter (N = 4). For PTR-ToF-MS analysis, the signal of many ions can have contributions by multiple isomeric organic species, so the 222 ions correspond to at least 222 VOCs. The following statistical analysis is based on the number of measured VOC signals (detected organic ions), which is a proxy for (but not equal to) the number of measured VOCs. Table S1 presents the complete list of detected ions, along with the respective compound assignments and key measurement parameters in each season.

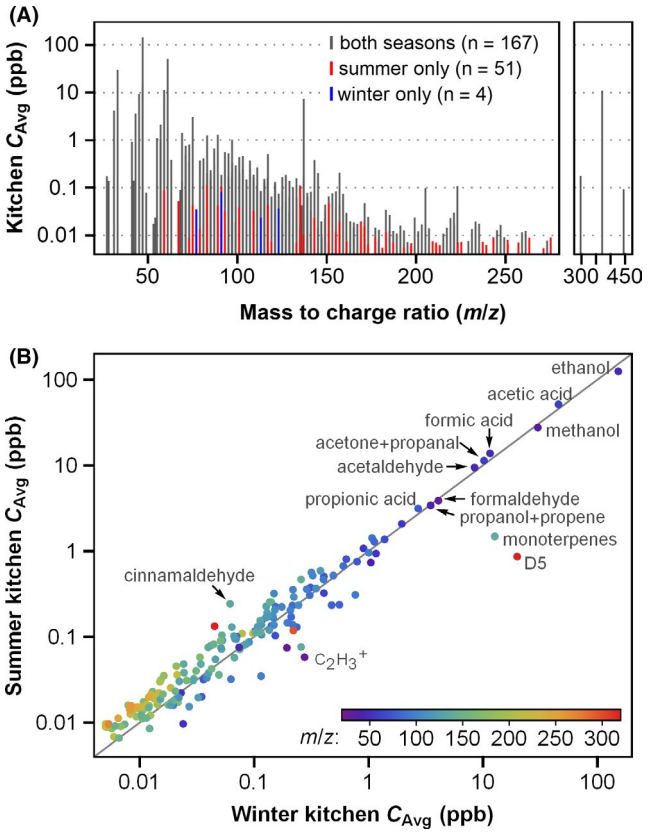

FIGURE 2 VOC composition in the kitchen air measured using PTR-ToF-MS under normal occupancy: (A) averaged VOC mass spectrum and (B) scatter plot of averaged concentrations (C_{Avg}) of VOC signals in the summer against those in the winter. In Panel (A), the dark gray vertical lines represent C_{Avg} of individual ions which are detected in both seasons. The red and blue lines represent ions detected only in the summer and only in the winter, respectively, with C_{Avg} shown for only that season. The mass spectrum has been filtered to remove internal, isotopic, and fragment ions. Please note that ions at the same nominal masses overlap due to limited resolution in the figure, but their abundances are determined separately at their accurate masses. In Panel (B), the data are shown for ions detected in both seasons, colored by ion masses. For some prominent ions, parent VOC compounds or ion formulas are labeled. The solid gray line denotes a 1:1 relationship

For more than half of the VOC signals only detected in the summer, the mass-to-charge ratios were >120 and the signals were just above the respective detection limits. The lower prevalence of these VOC signals in the winter campaign might be attributed to the lower wintertime indoor air temperature (16-18°C) than in the summer (20-23°C), driving more massive (and usually less volatile) organic molecules to partition more onto surfaces than into the air. As shown in Figure 2A, the measured average concentrations of individual VOCs spanned over four orders of magnitude from 0.005 ppb to 100 ppb, exhibiting a generally decreasing trend with increasing ion mass. A noteworthy exception to this trend was high signals of cyclic siloxanes (D4, D5, and D6) at m/z > 290, attributable to their exceptionally high volatilities relative to their molecular masses combined with their widespread use in consumer products.[10]

Figure 2B presents scatter plots of averaged concentrations in kitchen air of the 167 VOC signals detected in the two seasons, colored according to ion mass. In general, the data points cluster close to the 1:1 line, suggesting an overall similarity of VOC composition in the two seasons. Signals corresponding to small alcohols, carboxylic acids, and carbonyls were among the most abundant observed across the two seasons. Examples include (ordered by the abundance) ethanol ($C_2H_7O^+$), acetic acid ($C_2H_5O_2^+$), methanol (CH_5O^+), formic acid ($CH_3O_2^+$), acetone + propanal ($C_3H_7O^+$), and acetaldehyde ($C_2H_5O^+$).

Despite overall similarity, Figure 2B also shows some clear seasonal differences in the VOC composition between the two seasons. For VOC signals at higher masses, the concentrations were generally higher in the summer than in the winter (above the 1:1 line), suggesting an effect of temperature and volatility. In addition, clear exceptions to the near 1:1 relationship are evident and are generally attributable to variation in occupant activities. For example, the winter concentration of siloxane D5 and monoterpenes were more than 5 times higher than those in the summer. Their enhancements in winter were probably associated with increases in the use of skin care products and in the consumption of wintertime citrus fruits (such as oranges), respectively.

3.2 | Spatial distribution of VOC emission sources

In theory, VOCs in the living-zone air could be transported from outdoors, transported from coupled spaces (attic, crawlspace, and basement), or emitted directly into the living zone itself. Space-resolved VOC measurements, combined with the house airflow pattern as characterized using tracers, is used herein to evaluate the relative importance of each of these possible pathways. Tracer release observations demonstrated there were substantial *upward* interzonal airflows with negligible *downward* airflows among the living zone, attic, and crawlspace in the studied house.[31] The implication is that VOC emissions in the crawlspace, if present, could influence concentrations in the living zone. Conversely, emissions into the attic would not materially contribute to living zone concentrations.

Figure 3 presents histograms of the indoor-to-outdoor concentration ratios (I/O) of measured VOC signals for each indoor space in each season. As described in Section 3.2, the I/O ratios of individual VOC signals were calculated using the mean concentration in each space. An underlying assumption of space-resolved analysis herein, including I/O ratios, is that the same compound assignment can hold for an ion measured in different spaces. The I/O ratios for the crawlspace had a narrow distribution of values centered around 1 in both seasons, indicating that VOC composition in the crawlspace was close to that outdoors. By comparison, the distributions of I/O ratios measured in the living zone, including both the kitchen and bedroom area, were broader with many substantially higher values. For >75% of ions, the average living-zone concentrations were more than 5 times higher than outdoors (I/O > 5). For about half of the ions, the difference was at least one order of magnitude (I/O > 10). These results demonstrate that for most VOCs measured in the living zone, neither outdoor air nor the crawlspace was a major source.

For a few VOCs observed in the living zone, transport from outdoors or from the crawlspace did, however, make considerable and

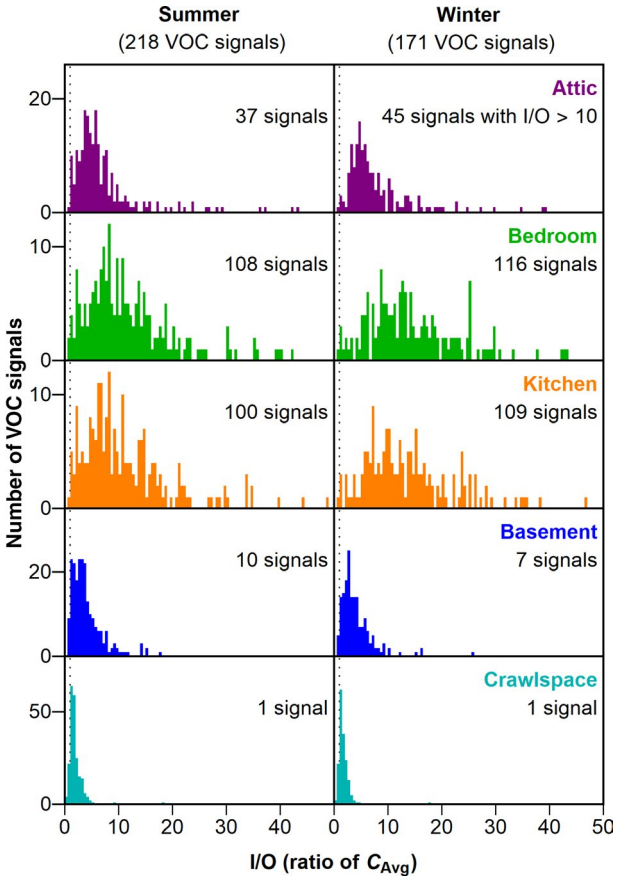

FIGURE 3 Histogram of the indoor-to-outdoor ratios (I/O) of averaged concentrations (C_{Avg}) of the VOC signals for each indoor space. Data are presented from the top to bottom for the attic, bedroom area, kitchen, basement, and crawlspace, in summer (left) and winter (right) campaigns, respectively. Dotted lines indicate equal indoor and outdoor concentrations (I/O = 1). Number of signals with I/O > 10 is listed for each indoor space. Data are not shown for I/O > 50

even dominant contributions. For example, a few halogen-containing ions, including CCl_3^+ (likely from $CHCl_3$ based on GC × GC-ToF-MS analysis of VOC samples), CCl_2F^+ (only detected in summer), and $C_7H_4F_2Cl^+$(likely from parachlorobenzotrifluoride $C_7H_4F_3Cl$ based on GC × GC-ToF-MS), had I/O ratios close to 1 in all the measured indoor spaces, suggesting a dominant contribution from outdoors. The $C_2H_4^+$ ion exhibited a consistently high I/O ratio (18) in the crawlspace in both seasons and lower ratios in the living zone (11 in summer and 15 in winter). This ion may correspond to a product of natural gas leakage from the furnace or water heater in the crawlspace, ionized via reactions other than proton transfer. The ratio of I/O values of $C_2H_4^+$ ion in the two indoor spaces is consistent with the fraction of air entering into the living zone from the crawlspace (ie, on average ~60% in summer and ~80% in winter), suggesting that the $C_2H_4^+$ signal observed in the living zone was predominantly attributable to transport from the crawlspace.

Contributions from the attic and basement to the living zone also appear to be minor overall. Although high I/O ratios were observed in the attic for many VOC signals, air rarely flowed downwards from the attic to the living zone.[31] To the contrary, some of the high I/O ratios in the attic can, at least in part, be due to upward transport from the living zone. The distribution of I/O ratios in the basement was similar to that in the crawlspace, and values were much lower than in the living zone. No single VOC signal exhibited higher I/O ratios in the basement than in the living zone, suggesting that emissions into the basement did not make important contributions for any VOC signals observed in the living zone. For example, the highest I/O ratio observed in the basement (28) was for $C_{10}H_{21}O^+$, but the corresponding I/O ratios in the kitchen and bedroom area were much higher (>80).

Since transport from outdoors and from coupled spaces in the house cannot explain the concentration levels observed in the living zone for most VOC signals, the clear implication is that the major sources of VOCs in the living zone were emissions directly into the living zone. Such emissions can originate from the building envelope, from the static contents (such as furniture) inside the space, from bioeffluents of the human occupants, and from occupants' activities. The next two sections will discuss features regarding occupant-related emissions and building-related emissions (including furnishings and household products), respectively, as interpreted from time-resolved measurements.

3.3 | Intermittent emissions from occupants and their activities

The time series of observed VOCs in the living zone was generally characterized by clear short-term enhancements (spikes) on top of more slowly variable baseline levels. For some compounds, the baseline level was relatively low, and the presence of strong spikes was the major feature of the concentration time series. The spikes for some compounds were episodic; for others, the pattern was more nearly periodic. Ethanol, the most abundant VOC observed in the living zone, is an example of a species whose time pattern

is dominated by spiky behavior. (The summer time series for ethanol is shown in Figure S1A.) In contrast, for some other compounds, such as acetic acid (the second most abundant VOC observed; Figure S1B), the most prominent feature of the time series is a consistently elevated baseline concentration. There were some spikes in acetic acid concentration above the baseline, but their contribution to the average concentration over the whole campaign was small. Other compounds fell in between such that their concentration time series showed considerable influence from both spikes and the high baseline level. (One example is acetaldehyde as displayed in Figure S1C.) These distinct features serve as the basis of analysis in this and the following sections to distinguish intermittent occupant-related emissions from continuous building-related emissions.

Figure 4 shows the time series of kitchen concentrations for selected compounds on one particular day along with recorded occupant activities. When the occupants were asleep (0-6 AM), concentrations of all the compounds were relatively steady. At breakfast time, pyridine concentration ($C_5H_6N^+$) spiked from 0.06 ppb to at least 1.7 ppb and ethanol concentration increased from 80 ppb to 420 ppb, attributable to making coffee and toasting bread (which, as a fermented product, contains ethanol), respectively. In the morning when occupants did some house cleaning, concentrations of solvents, such as ethanol and acetone, increased by factors of 6-7. In the afternoon, when occupants prepared ratatouille using a frying pan at high temperature, concentrations of many compounds became elevated. Some were elevated persistently (eg, $C_2H_7S^+$ attributable to enthanethiol and dimethyl sulfide),[11] and others were elevated only for a short period (eg, $C_5H_9^+$ likely attributable to isoprene). A party was hosted in the evening with about a dozen guests. Ethanol concentration rose strongly to 4.3 ppm (50 times higher than the overnight level). Elevated concentrations were also observed for ethanethiol + dimethyl sulfide from ratatouille being reheated and served, for isoprene mainly attributable to human breath, and for D5 from personal care products such as antiperspirants. After the party, another large ethanol spike was observed, coincident with a spike of chloramine (H_3NCl^+; inorganic compound; disinfectant in tap water),[40] likely associated with cleaning up after the party. At the end of the day, occupants left the kitchen with the dishwasher running, and another spike of chloramine was observed attributable to dishwasher operation. The examples displayed in Figure 4 illustrate that occupants and their activities can emit many VOCs and greatly enhance their indoor concentrations in a temporally specific manner. The effect is seen in the concentration time series as short-term elevations (spikes) above the respective baseline concentrations. In the next few paragraphs, we describe how we utilize the spikiness feature of the time series to gain greater understanding of occupant-related emissions.

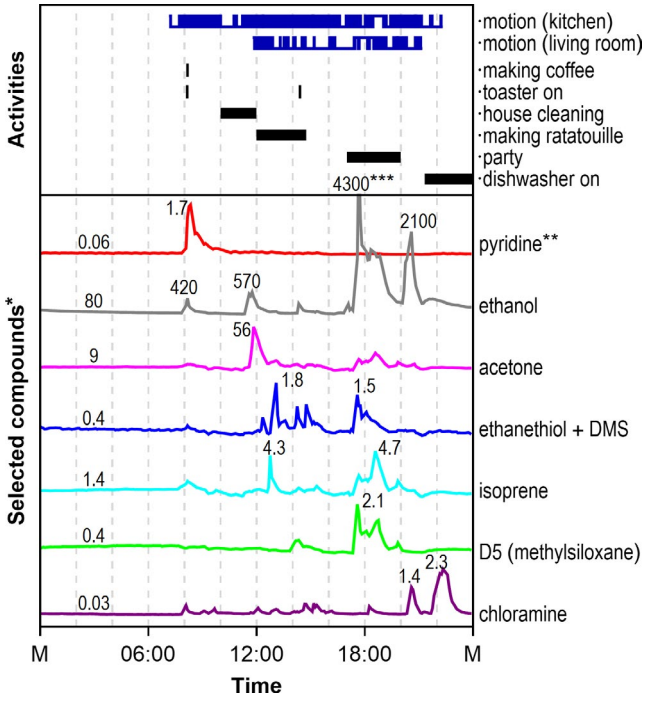

FIGURE 4 Time series on a selected day (September 22, 2016) of (top) activities recorded by sensors and occupants and (bottom) kitchen concentrations of selected compounds. Selected compounds (associated major ions) include pyridine ($C_5H_6N^+$), ethanol ($C_2H_7O^+$), acetone ($C_3H_7O^+$), ethanethiol + dimethyl sulfide (DMS; $C_2H_7S^+$), isoprene ($C_5H_9^+$), methylsiloxane D5 ($C_{10}H_{31}O_5Si_5^+$), and chloramine (H_3NCl^+). *Background and peak concentrations (in ppb) of each compound are noted. **Pyridine appeared sticky in our inlet system and consequently the peak signal represents a lower-bound estimate (cf. Supplement). ***Peak value out of plot range

No VOC signals were observed to spike during vacant periods in either campaign, but spikes frequently occurred during periods when occupants were home and awake. We used spike statistics to identify prominent VOC-emitting activities. Figure 5 shows averaged hourly occurrence of the number of spiked VOC signals (h^{-1}) in the summer and winter occupied periods. Diel variation in the number of spiked signals peaked at breakfast and at dinner time. The diel pattern resembles remarkably the variation in the frequency of stove burner use, which serves as a proxy indicator for cooking activities. This spike analysis strongly suggests that cooking activities were the dominant contributor to occupant-associated intermittent VOC emissions. As a reference point, some recent laboratory studies demonstrate that cooking can emit a large variety of VOCs.[11,41]

The presence of spikes in a concentration time series can increase the mean concentration across the whole observational period, but will have less effect on the median. Herein, we used the mean-to-median concentration ratio (C_{Avg}/C_{Med}) as a quantitative indicator of the relative importance of occupant-related emissions. Figure 6 presents histograms of C_{Avg}/C_{Med} for all VOC signals during the occupied and vacant periods in each season, respectively. For vacant periods, values of C_{Avg}/C_{Med} tightly clustered around 1.0 and rarely went above 1.1, with mean values of 1.02 in the summer and 1.01 in the winter. For occupied periods, the C_{Avg}/C_{Med} distribution broadened and extended more toward higher values. For ethanol, acetic acid, and acetaldehyde (Figure S1), the summer C_{Avg}/C_{Med} ratios were 2.3, 1.0, and 1.3, respectively. In total, there were 7 VOC signals in the summer and 6 in the winter with $C_{Avg}/C_{Med} > 1.5$. For

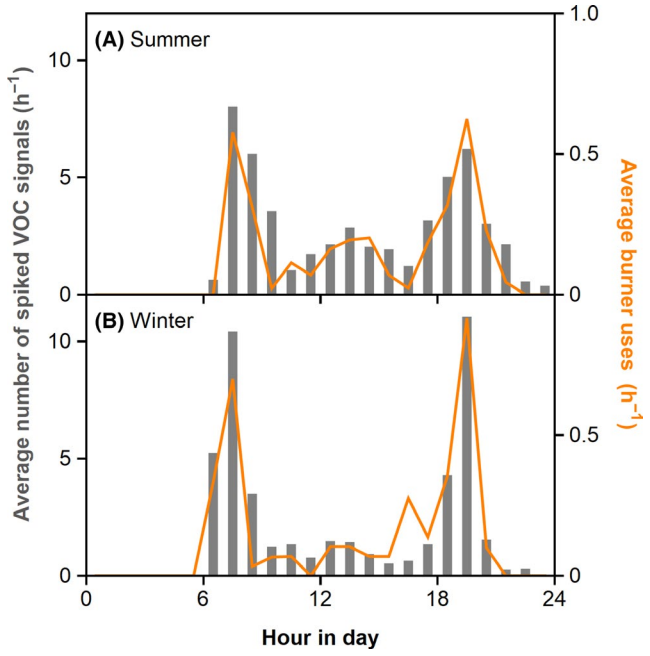

FIGURE 5 Hourly variation in the average number of spiked VOC signals measured in the kitchen (gray bars; left axis) and burner uses (orange lines; right axis) in (A) summer and (B) winter campaigns during normal occupancy

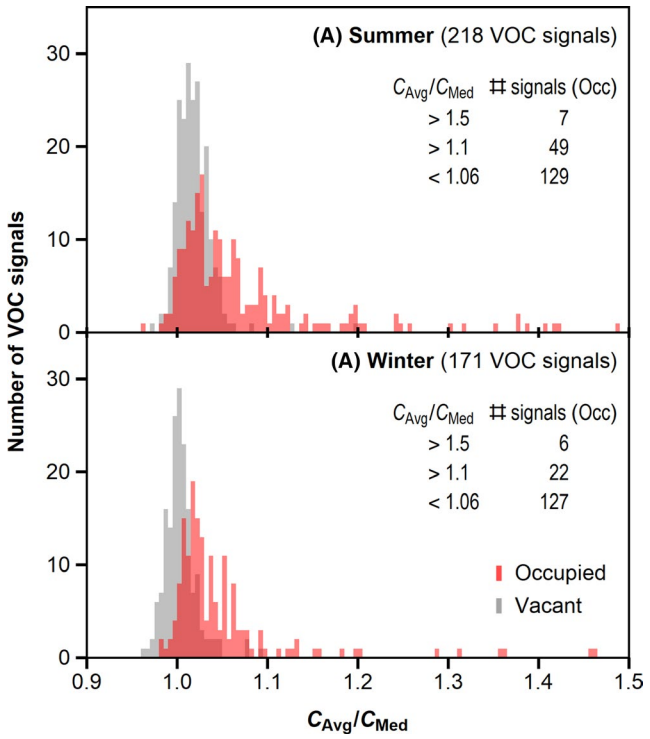

FIGURE 6 Histogram of kitchen mean-to-median concentration ratios (C_{Avg}/C_{Med}) for VOC signals in (A) summer and (B) winter campaigns. Data are presented for vacant and occupied periods in gray and red colors, respectively. Signal count is listed for C_{Avg}/C_{Med} > 1.5, > 1.1, and < 1.06, respectively, for the occupied periods

C_{Avg}/C_{Med} > 1.1, the respective numbers of VOC signals were 49 for summer and 22 for winter.

Table 1 lists a subset of 11 VOC signals for which the C_{Avg}/C_{Med} values were >1.5 during at least one season; these represent compounds with major (dominant) contributions from occupant-related emissions. Emission sources of the individual compounds were further constrained by associating the respective spikes with event records. Emissions of the siloxanes D5 and D6 can be attributed to the use of personal care products (for both species) and cleaning products (for D6). Each of the other occupancy-dominated species was predominantly associated with cooking. For example, ion $C_5H_5O^+$ (likely a fragment ion) typically spiked when making coffee. (The $C_5H_6N^+$ ion, which can be attributed to pyridine, was removed from the analysis due to stickiness in the sampling system, but it also spiked when making coffee.) Ion $C_9H_9O^+$ (cinnamaldehyde) was particularly abundant when making applesauce (a frequent activity within this home during summer but never in winter). Large spikes of $C_6H_9O_4^+$ ion (tentatively attributed to 3-deoxyglucosone; see Table 1 notation) occurred when baking granola. Spikes of $C_2H_3O_4^+$ (likely attributable to oxalic acid) were observed during some occasions of sautéing in the summer. A few other ions spiked during a wider variety of cooking events, including $C_2H_7O^+$ (ethanol), $C_4H_6N^+$ (pyrrole), and $C_{10}H_{17}^+$ (monoterpenes; consumption of citrus fruits led to a particularly high C_{Avg}/C_{Med} in winter). In addition, two inorganic ions, attributable to chloramine and H_2S, also had high C_{Avg}/C_{Med} values associated with use of tap water and cooking (especially melting butter), respectively.

3.4 | Continuous building-related emissions

Figure 6 shows that, for the majority of VOCs, intermittent event emissions were not their major source, with $(C_{Avg}/C_{Med})_{kitchen}$ < 1.06 for 59% of measured VOC signals in summer and for 74% in winter. A few additional criteria were applied to further select signals whose time series were characterized by elevated baseline levels in the living zone, indicating that the dominant sources were continuous building material- and furnishing-associated emissions into the living space. These specific selection criteria included the following: $(I/O)_{kitchen}$ > 10, $(C_{Avg}/C_{Med})_{kitchen}$ < 1.06, and $(I/O)_{kitchen}$ > 2 $(I/O)_{crawlspace}$ during both monitoring campaigns. This selection process yielded 54 VOC signals. The analysis in this section focuses on indoor emissions of these 54 signals.

Figure 7A shows a pie chart of mean indoor emission rates of the 54 VOC signals for the summer occupied period. The mean summed emission rate of the 54 VOC signals was 37.3 mg h^{-1} during summer (average temperature 22°C), as compared to 23.3 mg h^{-1} during winter (average temperature 17°C). The top six most highly emitted VOC signals were acetic acid, methanol, formic acid, formaldehyde, $C_6H_{11}^+$ (likely an alcohol fragment, such as *cis*-3-hexen-1-ol),[42] and furfural. Acetic acid alone accounted for half of the summed VOC emission rate; methanol and formic acid together accounted for a quarter. In addition, signals attributable to a homologue of saturated carbonyls (C_6-C_{12}) and saturated

TABLE 1 List of signals with dominant contributions from occupants and their activities[a]

Ions (species)[b]	Summer[c]			Winter[c]			Major intermittent sources
	C_{Avg} (ppb)	I/O	C_{Avg}/C_{Med}	C_{Avg} (ppb)	I/O	C_{Avg}/C_{Med}	
$C_{10}H_{17}^+$ (monoterpenes)	1.5	13	1.4	13	100	2.3	Citrus fruits (winter), cooking, cleaning
$C_2H_7O^+$ (ethanol)	130	44	2.3	150	63	1.9	Beer and wine, toasting bread, other cooking, cleaning
$C_5H_5O^+$ (unknown[d])	0.24	22	1.4	0.56	80	1.6	Coffee[e]
$C_9H_9O^+$ (cinnamaldehyde)	0.24	21	1.6	0.062	25	1.07	Making applesauce (summer), other cooking
$C_2H_3O_4^+$ (oxalic acid)	0.016	2.3	1.8	NA[f]	NA	NA	Sautéing certain vegetables
$C_6H_9O_4^+$ (3DG[g])	0.015	2.5	2.5	0.012	10	1.3	Baking granola, other cooking
$C_4H_6N^+$ (pyrrole)	0.10	100	2.6	0.070	35	1.6	Sautéing (sometimes), coffee, other cooking
$C_{10}H_{31}O_5Si_5^+$ (D5)	0.87	34	2.0	20	280	6.0	Use of personal care products
$C_{12}H_{37}O_6Si_6^+$ (D6)	0.13	130	1.6	0.05	67	1.5	Use of personal care and cleaning products
H_3NCl^+ (chloramine)	0.088	13	1.5	0.031	14	2.6	Use of tap water
H_3S^+ (hydrogen sulfide)	0.007	2.0	1.7	0.012	3.3	1.6	Cooking (esp. melting butter)

[a]Selection criteria: $(C_{Avg}/C_{Med})_{kitchen} > 1.5$ in at least one season, where C_{Avg} is the mean concentration and C_{Med} is the median.
[b]Ions are sorted by formula family ($C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$, $C_xH_yN_z^+$, siloxane ions, inorganic ions).
[c]Presented indoor data are for measurements in the kitchen during occupied periods.
[d]$C_5H_5O^+$ might be is a fragment of certain furanoids.[55]
[e]Another compound dominated by coffee emission is pyridine ($C_5H_6N^+$). However, this ion appeared sticky and was therefore not included in quantitative analysis (cf. Supplement).
[f]Ion was not detected in winter.
[g]Tentative assignment to 3-deoxyglucosone (3DG; $C_6H_{10}O_5$), a dicarbonyl sugar that is synthesized through the Maillard reaction; $C_6H_9O_4^+$ can be a dehydrated ion of $C_6H_{10}O_5$.

fatty acids (C_6-C_8) accounted for 10% and 12% of the emissions, respectively. The remaining signals, for which an ion formula could be confidently assigned, were summarized according to ion formula family ($C_xH_y^+$, $C_xH_yO^+$, and $C_xH_yO_2^+$). VOC signals for which empirical ion formulas could not be confidently assigned were summed and reported as "others"; these account for <0.5% of the building-associated emissions. The full list of 54 VOC signals and their respective average emission rates in each season are reported in Table S1.

A key feature of the VOC species that are dominated by building-related emissions is a strong temperature dependence. Figure 7B illustrates this point, displaying the dependence of indoor emission rates on indoor temperature. In this analysis, the determined 2-hour average emission rates were sorted according to indoor temperature, binned with 1°C resolution. The mean was taken for each one-degree temperature interval containing at least 50 data points. Indoor temperature was primarily in the distinct ranges 16-18°C in winter and 20-23°C in summer. As shown in Figure 7B, summed emission rates increased with temperature in each season as well as across the two seasons. Comparing 23°C to 16°C, an overall doubling of building-associated VOC emission rate was observed. Similar trends were evident for most individual ions/groups of ions, such as acetic acid (Figure 7B).

The temperature dependence of indoor concentration of these continuously emitted VOCs is seen to be less pronounced than the emission rates. As shown in Figure 8A, the summed concentration of 54 VOC signals did increase with temperature in the winter as the corresponding emission rates increased. The increase of concentration with temperature was modest in the summer (Figure 8A), despite the strong dependence of emission rates on temperature. These features can be resolved when taking account of temperature-dependent air-change rates in this naturally ventilated house. In the summer, occupants used window opening as a means to regulate indoor temperature. A higher air-change rate was generally observed at higher temperatures, with an average 50% increase from 20 to 23°C (Figure 8B). The observation of a smaller temperature effect on VOC concentrations in summer is hence associated with the combination of enhanced emissions at higher indoor temperature and enhanced removal via elevated air-change rates. The implication is that higher indoor emission rates do not always lead to correspondingly higher indoor concentration levels, since the concentrations and therefore exposures are also modulated by air change.

We also infer from the observations that variation in air-change rate affects VOC emission rates by altering indoor concentrations. From a mass-transfer perspective, the VOC emission rate from indoor materials varies with the difference between the airborne VOC concentration near material surfaces and the concentration in the core indoor space. The gas-phase VOC concentration near the material surface is regulated by the air-material partition coefficient, which is a function of temperature.[43] For the selected

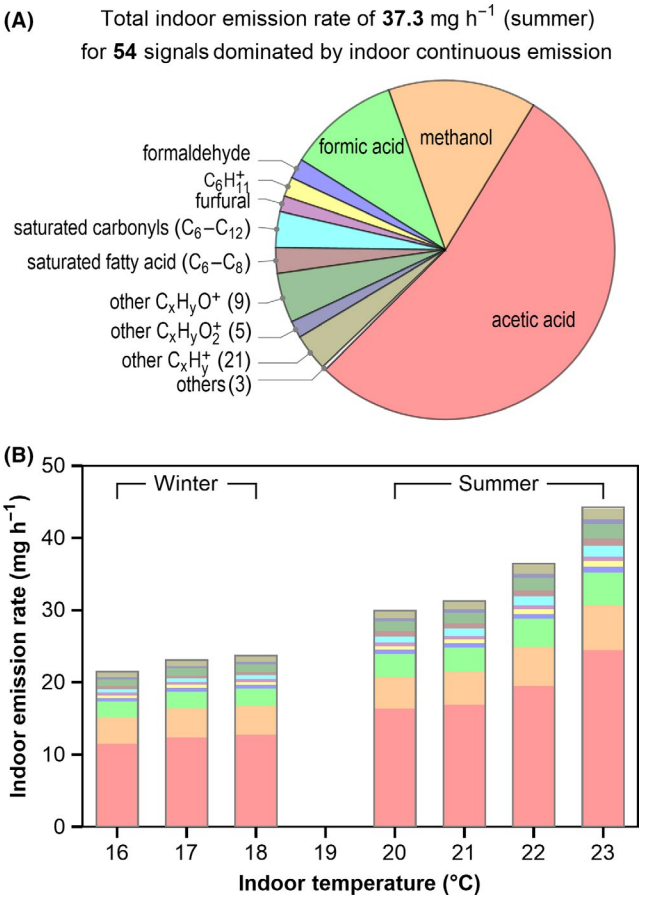

FIGURE 7 Indoor emission rates for VOC signals that are dominated by continuous indoor emissions: (A) pie chart of averaged emission rate in summer and (B) stacked bar chart of emission rates by indoor temperature across two seasons. Selection criteria for included ions are provided in the text. Both pie and bars are colored by VOC speciation. Emission rates in mg h^{-1} were determined for each ion with 2-hour resolution. In Panel (B), an average is shown for each integer temperature at which more than 50 emission rates were measured

54 VOC signals, the observed relations of emission rate, concentration, and temperature were generally in line with theory (ie, at fixed indoor concentration, the emission rate was higher at higher temperature, and at a fixed temperature, it was higher when the measured concentration was lower). Figure S2 shows the data (after filtering spikes) for acetic acid as an example. An increase in air-change rate lowers the corresponding indoor VOC concentration, making the concentration gradient larger than it would be otherwise, and thereby enhancing the emission rate. For this particular house, the apparent temperature dependence of VOC emissions (Figure 7B) is a combined effect of more partitioning into the air at higher temperature and a larger concentration gradient associated with enhanced air change at higher temperatures. In particular, the stronger dependence of emission rates on temperature in the summer than in the winter, as shown in Figure 7B, can result from larger increase of air-change rates with higher temperatures in the summer (Figure 8B).

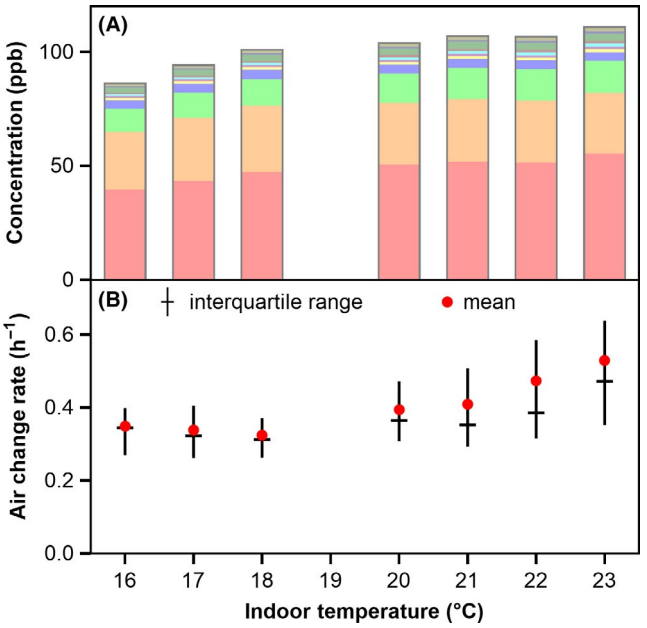

FIGURE 8 Variation with indoor temperature: (A) stacked concentration for VOCs that have indoor continuous emissions as their dominant source and (B) air-change rate. Data are shown for each integer temperature bin for which more than 50 measurements were recorded. In Panel (A), stacked bars represent averaged summed concentrations in ppb at individual integer temperature, colored by VOC speciation. The color code is the same as the pie chart in Figure 7A. In Panel (B), vertical lines, horizontal lines, and points represent interquartile ranges, medians, and means of measured air-change rates within 1°C temperature intervals

We also used the empirical evidence in this study to seek out clues about the major building-associated VOC emission sources. One set of clues emerges from measured VOC concentrations in the attic. Figure 9 plots the I/O ratio in the attic vs that in the living zone for all the VOC signals measured during the summer campaign. The size and color of each data point is respectively scaled by C_{Avg} and C_{Avg}/C_{Med} of the corresponding VOC signal measured in the kitchen. The dashed line represents the lower limit of attic I/O ratio predicted solely by transport from the living zone and from outdoors, as given by this expression:

$$(I/O)_{attic,predicted} = (1-\chi) + (I/O)_{living}\chi, \quad (3)$$

where χ is the fraction of air entering attic from living zone, estimated to be 0.22 using the attic-to-living-zone ratio of average concentration of the tracer released in the living zone; $(1-\chi)$ is the fraction of air entering attic directly from outdoors, assuming that the air transported directly from the crawlspace to the attic is negligible.[31] The light gray band in Figure 9 represents the confidence interval for estimated attic I/O ratio, assuming a 40% uncertainty for χ.

As shown in Figure 9, some data points lie within the gray band, indicating that the attic concentrations of the corresponding compounds could be primarily a consequence of transport from the living zone and from outdoors. For these compounds, direct emissions into the attic

appear relatively unimportant as a source. Most species with dominant emissions from occupant-associated activity in the living zone (in red), such as ethanol and the siloxanes (D5 and D6), belong to this category. By contrast, the attic I/O ratio of some VOC signals can be 4-10 times higher than the transport-focused predictions of Equation 3, suggesting strong direct emission sources into the attic for these species. These species include small carboxylic acids, aldehydes and alcohols (eg, acetic acid, formic acid, methanol, acetaldehyde), some furanoids (eg, furfural and dimethylfuran), and some aromatics ($C_7H_9O^+$, $C_9H_{11}O^+$, and $C_8H_{11}^+$).

The unoccupied and unfinished attic is framed with redwood lumber from the original construction (~ 80 years old) and also has exposed plywood sheathing from reroofing that was completed more than a decade before the measurement campaign. The attic contains fiberglass insulation, decades old, above the ceiling of the living zone. It also contains some stored personal items of the occupants, such as cardboard boxes with books, seasonal decorations, children's playthings, and luggage. The contents, present at much lower densities than in the living zone, did not appear to be prominent VOC sources based on a focused "sniffing" experiment using the PTR-ToF-MS with a moveable sampling probe. It seems, therefore, that the direct VOC emissions inferred to occur in the attic are largely attributable to emissions from wooden building materials. Since the same wooden building materials also envelop the living space and a large fraction of air flowing into the living space was by infiltration (flowing through the building envelope),[31] emissions from wood is also likely an important

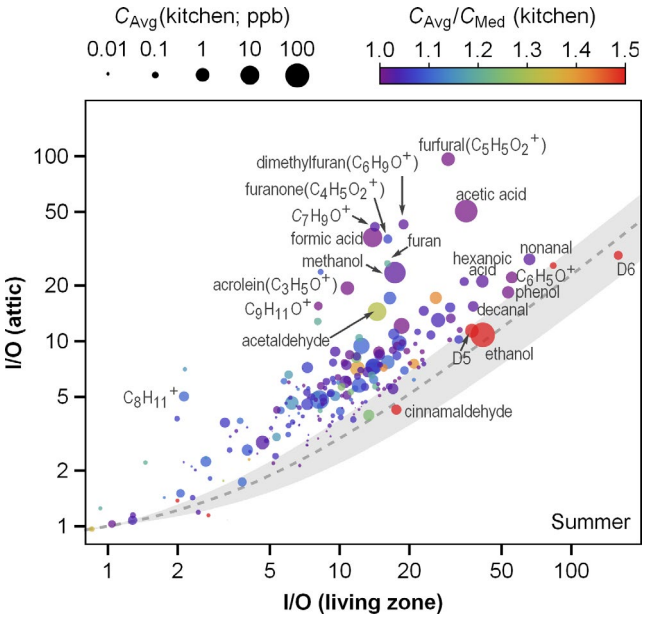

FIGURE 9 Scatter plot of indoor-to-outdoor (I/O) ratios in the attic vs those in the living zone for all the organic signals observed in the summer campaign. The size and color of each data point are respectively scaled by average concentration (C_{Avg}) and mean-to-median concentration ratio (C_{Avg}/C_{Med}) measured in the kitchen. The dashed gray line represents the predicted lower limit of attic I/O ratios, assuming that the attic concentration is solely determined by transport from the living zone and from outdoors. The light gray band shows uncertainty of the prediction. Ion and compound assignments are noted for some prominent species

VOC source for the living zone. Consistent with this hypothesis, the VOCs exhibiting the strongest building-associated emissions into the living space (large purple points in Figure 9; eg, acetic acid, formic acid, and methanol) are among those exhibiting the strongest emissions into the attic (ie, points well above the gray band).

Detailed mechanisms resulting in emissions of the small-molecule organic compounds from the wooden building materials of this 80-year-old house remain to be better understood. One plausible hypothesis is decomposition of wood, which is mainly composed of celluloses, hemicelluloses, and lignin. The suite of organic compounds elevated in the attic closely resembles the volatile degradation products of heat-treated wood as reported in laboratory-based measurements.[44,45] With heat treatment, the reactions are believed to start with deacetylation of hemicelluloses, and the released acetic acid further catalyzes the decomposition of polysaccharides and reduces their degree of polymerization.[46,47] Commonly reported volatile products are acetic acid and furfural;[44,45,48-50] the latter compound is a degradation product of some pentoses.[47] Production of formic acid, methanol, small aldehydes, other furanoids, and some phenolic compounds (lignin decomposition products) is also reported.[44] The timber used to build this house was unlikely heat treated prior to construction, based on the wood color and building age. We suspect that similar degradation processes might have taken place over the near century time scale since house construction. High abundance of acetic acid and furfural both in the attic and in the living zone, along with high abundance of other compounds associated with wood degradation, is consistent with the hypothesis of wood decomposition being their major source.

As a further note, the high detection frequency and high abundance of acetic acid, formic acid, and furfural have been reported for residential air in places where wood-framed houses are common. Mixing ratios of acetic acid and formic acid were measured in residences in New Jersey and in the greater Boston area at levels comparable to the current study and also more than an order of magnitude higher than outdoors.[51,52] An indoor air survey of ~3800 homes in Canada showed that furfural was detected in 98% of homes (acetic acid was not a target compound in that study).[7] Another study in Finland showed that furfural was detected in 21 out of 26 houses.[53] Although further investigation is warranted, emissions from wood construction materials might have been important sources of these VOCs among others for the residences in previous studies.

Emissions from the wooden building envelope are prominent in this studied house. Yet, the building envelope cannot explain the whole story of material-associated emissions into the living zone. As shown in Figure 9, for some VOCs such as nonanal, phenol, and decanal, high I/O ratios were observed in the living zone, but their attic I/O ratios were just slightly above what is predicted by transport. For these VOCs, continuous emission sources other than the wood building envelope were present in the living zone. Specific sources for these compounds were not isolated. While there are multiple possible sources, we suspect phenol could have been emitted from plastic products, and nonanal and decanal could be emitted from ozone reactions with various indoor surfaces (eg, with surface oil films originating from cooking).[13,54]

4 | CONCLUSION

We have characterized the sources and emissions of VOCs in the living space of a normally occupied single-family house in northern California. The analysis is based on space- and time-resolved measurement of a full spectrum of VOCs observable by PTR-ToF-MS throughout two multiweek, continuous monitoring campaigns. In total, about 200 VOC ion signals were measured, corresponding to more than 200 chemical compounds. For the studied house, most VOCs observed in the living space were primarily emitted from sources directly into the living space. Transport from outdoors and from coupled spaces such as the crawlspace, basement, and attic was overall minor for a large majority of VOCs. For many VOCs observed in the living space, continuous temperature-dependent emissions were prominent, characterized in the time series by indoor concentrations consistently elevated above outdoor levels. These emissions come from building materials, furnishings, and other static contents of the household. In particular, slow decomposition of the wooden building envelope is suggested as a major source for acetic acid, formic acid, and methanol, which together accounted for approximately 75% of the total continuous indoor emissions, as well as for some other abundant VOCs. Intermittent emissions from occupants and their activities produced short-term enhancements (spikes) in the VOC concentration time series. The diel pattern of the number of spiked ions indicates that cooking activities were the major occupancy-associated VOC emission sources.

Much of the concern about indoor air VOCs in the past has focused on primary emissions from new building materials and furnishings. There is ample evidence that these emissions decline over time.[22,23] To our surprise, notwithstanding that the residence studied here is old and has not been remodeled or refurbished recently, the overall spectrum of VOCs measured is still dominated by continuous emissions from the building and its contents. The distinction is that the emissions in this house seem to be largely secondary in nature. The dominance of small oxygenated compounds (small carboxylic acids, alcohols, and carbonyls) in the spectrum of measured VOCs and the continuous emission pattern for many of them indicate they likely result from ongoing chemical processes, such as decomposition and oxidation. Slow decomposition of wooden building materials is suggested as a potentially important pathway, but other unidentified chemical pathways might also exist. These results call attention to the possible importance of indoor chemistry as a source for indoor VOCs, even in older structures. Further studies are warranted to investigate whether wood decomposition is a general secondary VOC source common to wood-structured houses.

Our team's first indoor study using PTR-ToF-MS revealed that in a university classroom, the occupants themselves were the primary source of indoor VOCs, including the noteworthy prominence of cyclic siloxanes from personal care products.[10,26] Relative to a classroom, the typical single-family dwelling in the United States has more ventilation per person, more frequent high-emitting activities (such as cooking), and more emissions from objects in the building materials and furnishings. In both the university classroom setting and the residential environment, we found the contribution of outdoor air to indoor VOC levels to be modest. The combination of much higher VOC levels indoors than outside and the high proportion of time spent indoors, especially in residences, points to the need for a shift in overall air quality research emphasis toward the indoor environment to more thoroughly understand the species and concentrations of VOCs that dominate indoor chemistry and human exposure.

From a technical perspective, this study demonstrates how continuous time- and space-resolved VOC observations can contribute toward understanding the source characteristics and emission dynamics of VOCs in occupied buildings. Space-resolved measurements in this 80-year-old wood-framed house have led to the discovery of a previously unreported major VOC source, slow decomposition of aged wooden building materials. Looking to the future, similar measurements in other types of residences might help identify additional interesting and important VOC sources that are currently not well understood or potentially not recognized. The use of time-resolved measurements in this occupied residence allowed identification of cooking as the major source coming directly from occupants and their activities. Even though the two occupants had relatively simple indoor lifestyles (eg, having no evident emissions-associated hobbies, rarely cooking meat, and spare use of personal care or commercial cleaning products) in this moderately large house, emissions from occupants and their activities still made considerable contributions to tens of indoor VOC signals. In residences with higher occupant density and more VOC-emitting activities, occupants' contribution could be even more important.

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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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