High-resolution exposure assessment for volatile organic compounds in two California residences

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0 ABSTRACT

Time spent in residences substantially contributes to human exposure to volatile organic compounds (VOC). Such exposures have been difficult to study deeply, in part because VOC concentrations and indoor occupancy vary rapidly. Using a fast-response online mass spectrometer, we report time-resolved exposures from multi-season sampling of more than 200 VOC species in two California residences. Chemical-specific source apportionment revealed that time-averaged exposures for most VOCs were mainly attributable to continuous indoor emissions from buildings and their static contents. Also contributing to exposures are occupant-related activities, such as cooking, and outdoor-to-indoor transport. Health-risk assessments are possible for a subset of observed VOCs. Acrolein, acetaldehyde, and acrylic acid concentrations were above chronic advisory health guidelines, whereas exposures for other assessable species were typically well below guideline levels. Studied residences were built in the mid-20th century, indicating that VOC emissions even from older buildings and their contents can substantially contribute to occupant exposures.

KEYWORDS:

source apportionment, time-activity patterns, air pollution, indoor, health risk assessment, cooking, building-material emissions

1 INTRODUCTION

Exposures to volatile organic compounds (VOCs) can be associated with adverse health outcomes (1–5). Considering that modern populations spend most of their time in residences and that most VOC concentrations and associated exposures are substantially higher indoors than outdoors (6–8), evaluating the residential component is critical for understanding total VOC exposures. Certain VOCs and very volatile organic compounds (henceforth bundled as VOCs for brevity), such as formaldehyde, some halogenated solvents, and BTEX (benzene, toluene, ethyl benzene, xylene), among others, have been the subject of substantial attention (9–11). However, for many VOCs, the levels of exposure, the controlling physical processes, and the consequent health risks remain understudied (12, 13).

Residential VOC abundances are attributable to multiple sources, which vary among compounds. Potential sources include building materials (14), outdoor-to-indoor transport (8), indoor chemistry (15), consumer products (16), activities such as cooking (17, 18), and the human occupants themselves (19, 20). For most VOCs and in most buildings, the relative contributions from each source to indoor concentrations are not known. In addition, indoor VOC abundances are modulated by physicochemical parameters, such as the ventilation rate (21), temperature (through sorptive interactions with interior surfaces (22) and temperature-dependent material emissions (18)), humidity (23) and both seasonal and diel variations in outdoor VOC concentrations (18). Some studies have suggested that VOC emissions from building materials are most important immediately after construction or renovation and can decline by orders of magnitude within a few years (24–26).

Time-resolved measurements of VOCs in residences and associated exposures are scarce. Time-averaged VOC measurements, either actively collected on sorbent tubes or passively collected on diffusive samplers over fixed intervals, have been used to characterize VOC exposures in cross-sectional studies (7, 8, 27, 28). Samples are sometimes collected in multiple locations specific to each research participant, including direct monitoring of air immediately proximate to study subjects using personal samplers. In many cases, studies implement a targeted screening approach where analysis is restricted to a subset of chemicals of relevant health interest.

Typically, source apportionment has not been conducted via intensive study of individual residences. Studies focusing on source apportionment of indoor VOCs may collect time-averaged samples and conduct source apportionment via multivariate receptor models. These analyses typically use data reduction techniques such as principal component analysis (PCA) or positive matrix factorization (PMF) on population-level data acquired in survey studies (8, 29–31). In one such study of Canadian residences, Bari et al. reported that a majority of indoor VOCs were attributable to indoor sources with household products being the largest contributor and off-gassing of building materials the smallest (31).

Personal exposures measured by portable samplers are often greater than those predicted by stationary monitoring of outdoor, home, and occupational environments (7, 32). Predictions based on stationary monitoring often assume a well-mixed single-zone space, an assumption which may not be fully justified for strongly localized source events that create spatial

71 heterogeneities (33, 34). Proximity of occupants to source events has been used to explain the
72 discrepancy between personal monitoring and stationary monitoring for particles (35–37). This
73 effect may partially explain the discrepancy between microenvironmental monitoring and
74 personal monitoring when assessing exposures to VOCs released by occupant activities, such as
75 cooking, cleaning or application of personal care products. Another important point is that
76 stationary exposure estimates using time-integrated sampling rest on the assumption that average
77 measured VOC concentrations are representative of average VOC concentrations during
78 occupancy. For VOCs with significant contributions from occupant-related episodic sources,
79 such as cooking or use of personal care products, concentrations may be elevated during
80 occupancy and so occupant exposures would be underestimated if based on time-average
81 concentration measurements that include periods of vacancy. Sporadic, high-concentration
82 events might produce significant temporal variability in VOC abundances and, if so, would
83 necessitate the acquisition of time-resolved VOC measurements and occupant activity data for
84 estimating VOC exposures and apportioning exposure sources. Owing to advances in analytical
85 capabilities, such measurements have begun to be acquired in recent years in several field
86 monitoring campaigns (17–20, 22).

87 In this work, we discuss the first broad-scale application of time-resolved VOC measurements
88 coupled with a) occupant time budgets to assess residential exposures to VOCs and b) occupant
89 time-activity budgets to attribute exposures to source categories. The 250 monitored analytes in
90 this work span a broad range of volatilities, chemical functionalities, and toxicities (Tables S1–
91 S3). Among the characterized analytes are aromatics (including benzene, toluene, xylene),
92 carbonyls (including acetaldehyde and acrolein), furanoids, halogenates, organosulfur
93 compounds, carboxylic acids, alcohols and alkenes, siloxanes, and other compounds of potential
94 health interest (acetonitrile, acrylic acid, acrylonitrile).

95 In total, we assess residential VOC exposures for more than 200 VOCs sampled with high time
96 resolution over three multiweek monitoring campaigns conducted in two California households.
97 We implement a source apportionment model for VOCs to attribute exposures to four broad
98 source categories: continuous indoor sources, outdoor origin, cooking, and other. We
99 contextualize our observations by utilizing information that relates exposure to health risk, as
100 reported by two U.S. governmental agencies and one California state agency. Lastly, we assess
101 the performance of stationary time-averaged exposure estimates relative to time-resolved best
102 estimates of exposure.

2 EXPERIMENTAL METHODS

Site information. This work utilizes measurements from three field campaigns conducted at two normally occupied California residences in the East Bay region of the San Francisco Bay Area in summer and winter seasons (H1 summer, H1 winter, H2 winter). The monitoring campaigns in these residences have been described elsewhere in detail (18, 38, 39, 40). This paper represents a continuation of prior analyses describing indoor ventilation patterns (38) and VOC emissions (18) at the H1 residence. It also represents the first reporting of VOC data acquired at the H2 residence. Briefly, the H1 site is a single-family, split-level wood-frame residence, constructed in the 1930s, with two adult occupants designated here as "H1M1" and "H1F1." Measurements were made for 8 weeks in 2016 from mid-August to early October (H1 summer) and for 5 weeks in 2017 from late January to early March (H1 winter). The house did not have air conditioning. During (mild) winter, the residence was sometimes heated by a gas furnace. The H2 site consisted of a single-family, single-story wood-frame residence, constructed in the 1950s, with two adult occupants designated "H2M1" and "H2F1", a teenager, and a dog. A third adult occupant designated "H2M2" was present for approximately half of the measurement period. Measurements were made for an 8-week campaign in 2017-18, from early December to early February. The H2 site was heated by a forced-air gas-fired furnace operating twice a day, in morning and evening.

At each residence, occupants maintained daily logs describing their temporal presence and activity. Occupant presence data was recorded with approximately 5-min resolution and coded as "indoors," "indoors sleeping," and "away." Time-resolved activities, including cooking, cleaning, candle combustion, and some use of personal care products, were also recorded by the occupants. A network of >50 wireless sensors collected metadata during each measurement period, including temperature, humidity, motion, appliance use, and door/window status.

Chemical measurements. A proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS, Ionicon Analytik GmbH, Austria, PTRTOF 8000) was used to measure VOCs during each campaign. The PTR-ToF-MS was located in an external garage (H1 summer, H1 winter) or an external shed (H2 winter). The PTR-ToF-MS uses soft ionization with H_3O^+ as the primary reagent ion, yielding parent masses (1.000 amu – 500.00 amu) of gaseous species whose proton affinities are greater than the proton affinity of water. Most unsaturated hydrocarbons and compounds with heteroatoms are quantifiable with detection limits on the order of 0.005 ppb and time-resolution on the order of minutes. PTR-ToF-MS operating parameters and quantification during the H1 summer and winter campaigns have been described elsewhere (18, 38) and are summarized in the supporting information (SI, Section 1).

Exposure Analysis. Time-integrated exposures (hereafter "exposures") were calculated as the integral of time-instantaneous exposures over the time period of exposure. Daily occupant exposures in units of ppb-hours per day (ppb-h d^{-1}) were calculated by integrating ion formula concentrations for each day during periods when each occupant was present. Measurement periods with major interferences from researcher activities were excluded from all analyses. The kitchen concentration was used at H1 as the best-estimate for calculating occupant exposures and the living room concentration was used at H2. VOC concentrations throughout the living spaces

144 and kitchen in both residences were well-coupled. During sleeping hours at H2, the
145 concentration in the kitchen may not be fully representative of occupant exposures as each closed
146 bedroom is partially decoupled from the main living space. In this condition, occupant exposures
147 to bioeffluents emitted during sleeping periods may be underestimated. At H1, the bedroom
148 doors were left open throughout the sampling campaign and so the sleeping environment is
149 expected to be well-coupled to the kitchen, although biogenic emissions may still be higher
150 within the bedroom. Simulated distributions of time-averaged exposures were constructed by
151 random sampling. These distributions may be biased by 1-2 data gaps (<2 days) in concentration
152 time series related to instrumental down time or intentional manipulation experiments conducted
153 by researchers. Data gaps encountered during random selection were treated by using the next
154 available measurement in the "time-averaged" sample.

155 **Source Apportionment.** VOC time series were typically characterized by a persistent
156 background modulated by regular changes in temperature in association with the diurnal
157 temperature cycle (H1 summer) or house heating cycle (H2 winter) and punctuated by rapid
158 concentration spikes related to specific events. The temperature-dependent background was
159 clearly identified during periods of vacancy when occupant-related events did not occur.
160 Concentration spikes and associated peak boundaries were manually identified for each ion
161 formula and assigned to specific source categories based on coincident events during the growth
162 phase of the peak. The peak baseline was determined by a linear regression between the
163 concentrations observed at peak boundaries. Net peak areas were defined as the total integrated
164 area above the peak baseline. Event peaks were excluded if at least 50% of the event by peak-
165 height was attributable to outdoor infiltration. More detailed information about the peak selection
166 process is available in the SI (Section 1b). Outdoor VOC concentrations were assumed to enter
167 the indoors without attenuation, allowing for outdoor VOC concentrations to be used as a proxy
168 for the indoor VOC concentrations of outdoor origin. On the rare circumstance that outdoor
169 concentrations were greater than indoor concentrations, the indoor concentration was assumed to
170 be derived wholly from outdoor-to-indoor transport. The integrated areal remainder after
171 subtracting contributions from events and from outdoor transport was defined as "continuous
172 indoor sources." In total, more than 12,000 peaks were identified from among the 594 chemical
173 concentration time series acquired during the three campaigns.

174 **Risk-Based Prioritization.** Advisory health guidelines for acute and chronic exposures to VOCs
175 were acquired from three organizations: the U.S. Environmental Protection Agency (USEPA)
176 Integrated Risk Information System (IRIS, chronic only),[41] the California Environmental
177 Protection Agency Office of Environmental Health Hazard Assessment (OEHHA),[42] and the
178 Agency for Toxic Substances and Disease Registry (ATSDR).[43] Each organization has
179 independently developed concentration guidelines for chronic VOC exposures. The IRIS
180 database reports reference concentrations (RfCs), "an estimate (with uncertainty spanning
181 perhaps an order of magnitude) of a continuous inhalation exposure to the human population
182 (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious
183 effects during a lifetime." OEHHA reports reference exposure levels (RELs), an estimate of
184 concentrations for inhalation exposure "at or below which no adverse health effects are

185 anticipated following long-term exposure." ATSDR reports minimal risk levels (MRLs), "an
186 estimate of the amount of a chemical a person can eat, drink, or breathe each day without a
187 detectable risk to health." These health guidelines were selected as three major guidelines from
188 state and federal agencies in the United States that are relevant to the location of the studied
189 residences. Other international guidelines have also been developed.[44-48]

3 RESULTS AND DISCUSSION

191 **Time-resolved exposures.** Indoor VOC concentrations and occupant time-activity budgets were
192 acquired at two normally occupied California residences in the summer and winter seasons over
193 three monitoring periods: the H1 summer campaign (8 weeks), the H1 winter campaign (5
194 weeks), and the H2 winter campaign (8 weeks). In total, 250 ion masses corresponding to
195 molecular formulas of VOCs were identified (H1 summer: 217 ions; H1 winter: 170 ions; H2
196 winter: 205 ions), with substantial overlap among campaigns. Of these ions, 115 were assigned
197 to specific chemical structures based on site-specific knowledge, fragmentation patterns, and
198 supporting measurements using thermal desorption two-dimensional gas chromatography time-
199 of-flight mass spectrometry (TD-GC×GC-ToF-MS). Paired indoor/outdoor VOC concentrations
200 were acquired every 30 minutes. Figure 1 displays occupant time-budgets and activities for the
201 H2 winter campaign. During each campaign, VOC concentrations generally increased with
202 increasing temperature or specific occupant activities and decreased with increasing ventilation.
203 Concentrations were higher indoors when compared to outdoors (> 2×) for most VOCs (~95%)
204 at the H1 (18) and H2 sites, consistent with past field studies. Moreover, for about half of the
205 observed VOCs, concentrations were substantially higher (> 10×) indoors than outdoors.

206 Source apportionment in this study attributed the residential VOC exposures to four source
207 categories: "continuous indoor sources," "outdoor origin," "cooking," and "other." Time-
208 resolved exposures and associated source apportionments are displayed in Figure 1 for site H2
209 and subject H2M1 for the case of acrolein, an illustrative compound of health interest with prior
210 evidence of both continuous indoor sources (lumber) and episodic sources (combustion, cooking)
211 (48–52). We note that acrolein has been previously measured in outdoor ambient air and retail
212 stores near the H1 and H2 residences (53, 54). In the present study, daily occupant exposures to
213 acrolein were mainly attributable to continuous indoor sources, with a median exposure of ~ 4.6
214 ppb-hours per day (ppb-h d^{-1}). Substantial variation was observed in daily exposures, principally
215 due to variations in the fraction of time that occupants spent indoors combined with the effects of
216 event-specific sources. Certain days with cooking events doubled the daily occupant acrolein
217 exposures. Due to the infrequency of cooking events that emitted acrolein at H2, exposures
218 attributable to continuous indoor sources accounted for ~65% of cumulative occupant acrolein
219 exposures, with cooking contributing 25-30% and outdoor-to-indoor transport the small
220 remainder. Most episodic enhancements in acrolein concentrations were specifically attributed to
221 cooking. Only two episodic enhancements remained unassociated with any reported events.
222 (These enhancements did not significantly influence cumulative occupant acrolein exposures,
223 indicating that episodic contributors to acrolein exposures are well understood at this site and are
224 principally derived from cooking.) At H2, oven cooking produced the largest enhancements in
225 acrolein concentrations. At H1, stovetop cooking produced the largest acrolein enhancements.
226 Both the H2 oven and the H1 stovetop were electric, suggesting that heated food (rather than
227 natural gas combustion) was the largest episodic contributor to acrolein emissions in agreement

228 with past studies observing no differences between types of cooking appliances (48). While
229 enhancements in acrolein concentrations at H2 were also observed in association with use of a
230 natural gas stove-top, these enhancements were much smaller in abundance than those from the
231 electric oven. Most acrolein enhancements at H2 were observed in association with the use of
232 cooking oil. This finding aligns with previous reports that heated cooking oil is a primary source
233 of acrolein during cooking (50–52).
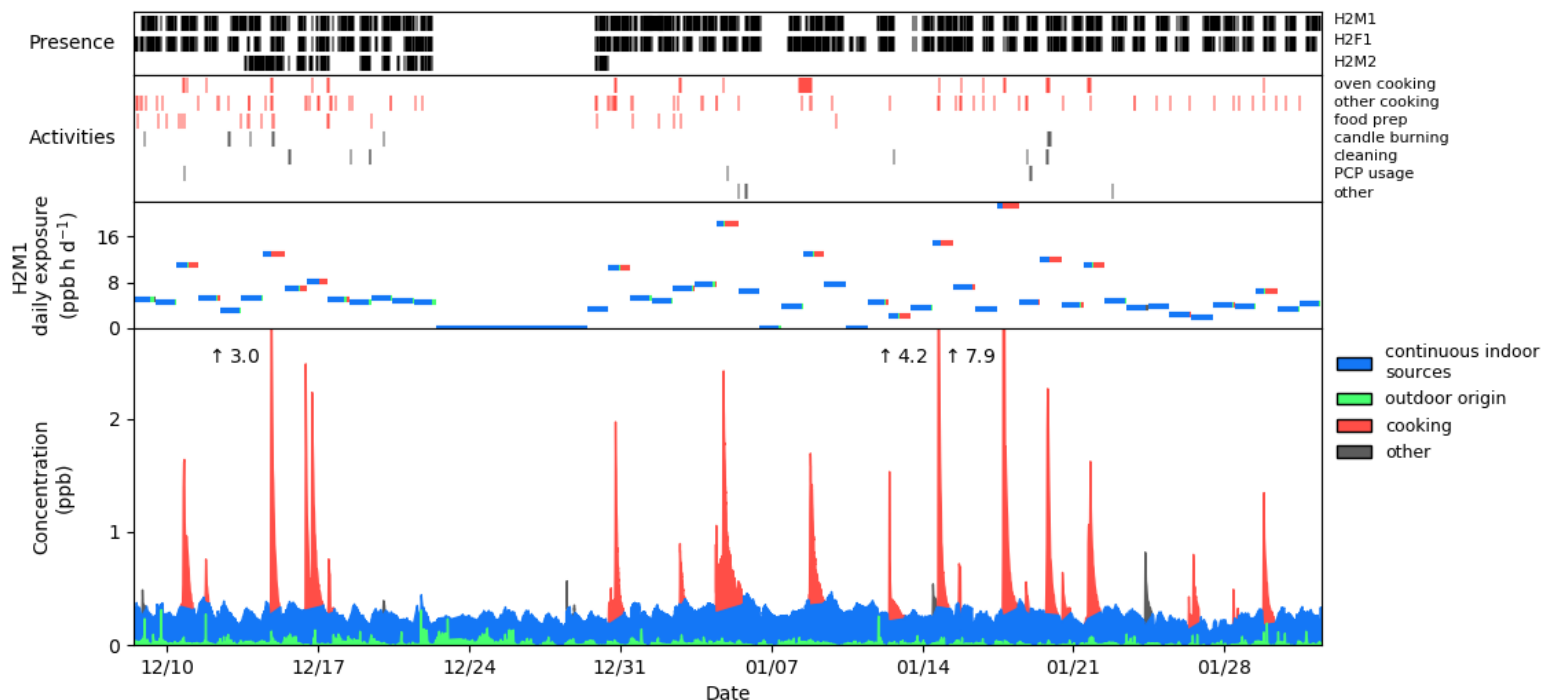
235 **Fig. 1. Acrolein exposure data at H2.** In the two uppermost panels, occupant presence
236 and activity data are displayed during the H2 campaign. In the bottommost panel, the
237 time series and associated source apportionment of indoor acrolein ($C_3H_5O^+$) is
238 displayed, with colors corresponding to the relative contribution from each source
239 category. Integrated daily exposures are shown in the second panel from the bottom for
240 occupant H2M1. The shading of the horizontal bar is colored according to the proportion
241 of exposure attributable to each source category.

242 **Source apportionment.** Source apportionment of occupant VOC exposures was performed for
243 all VOCs observed in the H1 winter, H1 summer, and H2 winter campaigns following the
244 method shown in Figure 1. At each site, exposures are assessed separately for each of the
245 primary adult occupants. The relative contributions to the total exposure from each source
246 category were identified for each VOC and are reported on a percentage basis. Source
247 apportionment of residential exposures to 205 VOCs for occupant H2M1 is shown in Figure 2.
248 Approximately 90% of observed VOCs produced time-averaged exposures that were primarily
249 attributable to continuous indoor sources during all three monitoring campaigns at these two
250 residences. Compounds with predominantly indoor continuous sources spanned diverse ranges of
251 volatilities and chemical functionalities, including carboxylic acids (octanoic acid – 95% of
252 exposure from indoor continuous emissions), siloxanes (caprylyl methicone – 95%), aromatics

253   (phenol – 93%), carbonyls (C9 carbonyl – 92%), among others, and were not easily
254   generalizable to specific categories. Caprylyl methicone is a trisiloxane commonly used in
255   cosmetics; surprisingly, its presence was dominated by continuous emissions with the exception
256   of two short-term concentration spikes in the evening. Cooking was the most important episodic
257   source of indoor VOC exposures (18); however, only eight specific VOCs had exposures that
258   were principally attributable to cooking during any of the campaigns for any occupant: ethanol,
259   methanethiol, pyrrole, dimethyl sulfide, $C_6H_9O_4^+$, D4 siloxane, L5 siloxane, and
260   dimethoxysilane. The latter three compounds were emitted synchronously with cooking events,
261   but it is not certain that they originated directly from the food, cookware or cooking appliances.
262   Apart from cooking, exposures of only three volatile compounds—acetone, an unidentified
263   siloxane ($C_7H_{21}O_3Si_3^+$), and the inorganic gas dichloramine—were otherwise largely attributable
264   to episodic indoor emission events for any occupant. Acetone was identified as originating from
265   the indoor use of nail polish remover during the H2 winter campaign. Dichloramine was
266   identified as originating from episodic cleaning events. Cyclic siloxanes are known additives to
267   consumer personal care products. Noting that three of five concentration spikes of the
268   unidentified siloxane over the H2 winter campaign occurred immediately following sleeping
269   periods when a personal care product might have been applied as part of a morning routine, it is
270   suspected that the unidentified siloxane is a component of a personal care product. Only ten
271   specific VOCs had exposures that were primarily attributable to outdoor-to-indoor transport for
272   any occupant. Four of these compounds were observed in all campaigns (chloroform,
273   acetonitrile, parachlorobenzotrifluoride, $C_4H_3O_3^+$), four compounds were unique to the H1
274   summer campaign ($C_{10}H_9O_3^+$, $C_2H_5O_3^+$, $C_5H_5O_3^+$, CCl_2F^+), and two compounds were unique to
275   the H2 winter campaign (ethane thiol + DMS and $C_{10}H_{15}O^+$). We also highlight $C_8H_9O_2^+$
276   (anisaldehyde, a floral fragrance) and $C_{10}H_{17}^+$ (monoterpenes, emitted during citrus
277   consumption) as compounds of interest. In addition to cooking, we observed large contributions
278   from episodic events unrelated to cooking (31% and 36%, respectively during the H1 winter
279   campaign), expected to partially originate from personal care product use and citrus
280   consumption.
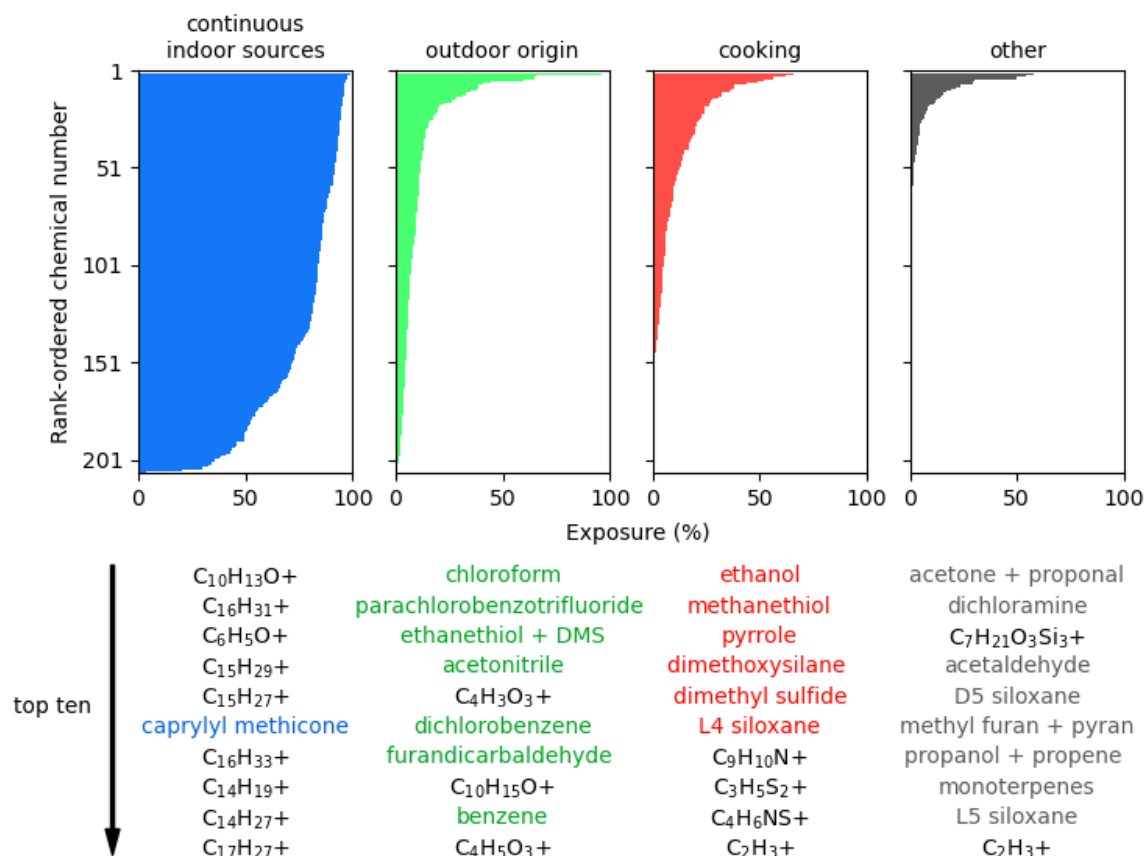
Fig. 2. Rank-ordered VOC exposures by source category for occupant H2M1 during the winter campaign at H2. Residential VOC exposures to 205 VOCs were calculated for occupant H2M1. The contributions from each source category to the total exposure of each VOC were identified and are reported on a percentage basis. The relative contributions from each VOC were then rank-ordered from greatest-to-least for each source category. Source categories include continuous indoor sources (blue), outdoor-origin (green), cooking (red), and other (gray). The unique rank-orderings for each source category are displayed in the upper panel and the top ten VOCs in each rank-ordered source category are identified in the lower section of the figure.

Relative contributions for each source category were calculated for all observed VOCs and for each occupant during each campaign (Figure 3). Absolute daily exposures and relative source apportionments can be found in the SI (Figure S1, Tables S1-S3). Time-activity budgets exhibit some differences (Figure S2); however, source apportionments for each occupant were qualitatively and quantitatively similar. For the H1 campaigns, relative contributions from source categories for occupant exposures were within 15 absolute percentage points of relative source apportionments derived from concentration time series for all but $C_6H_9O_4^+$. (Source apportionments from concentration time series are equivalent to relative source apportionments of exposures for an occupant who is always present.)
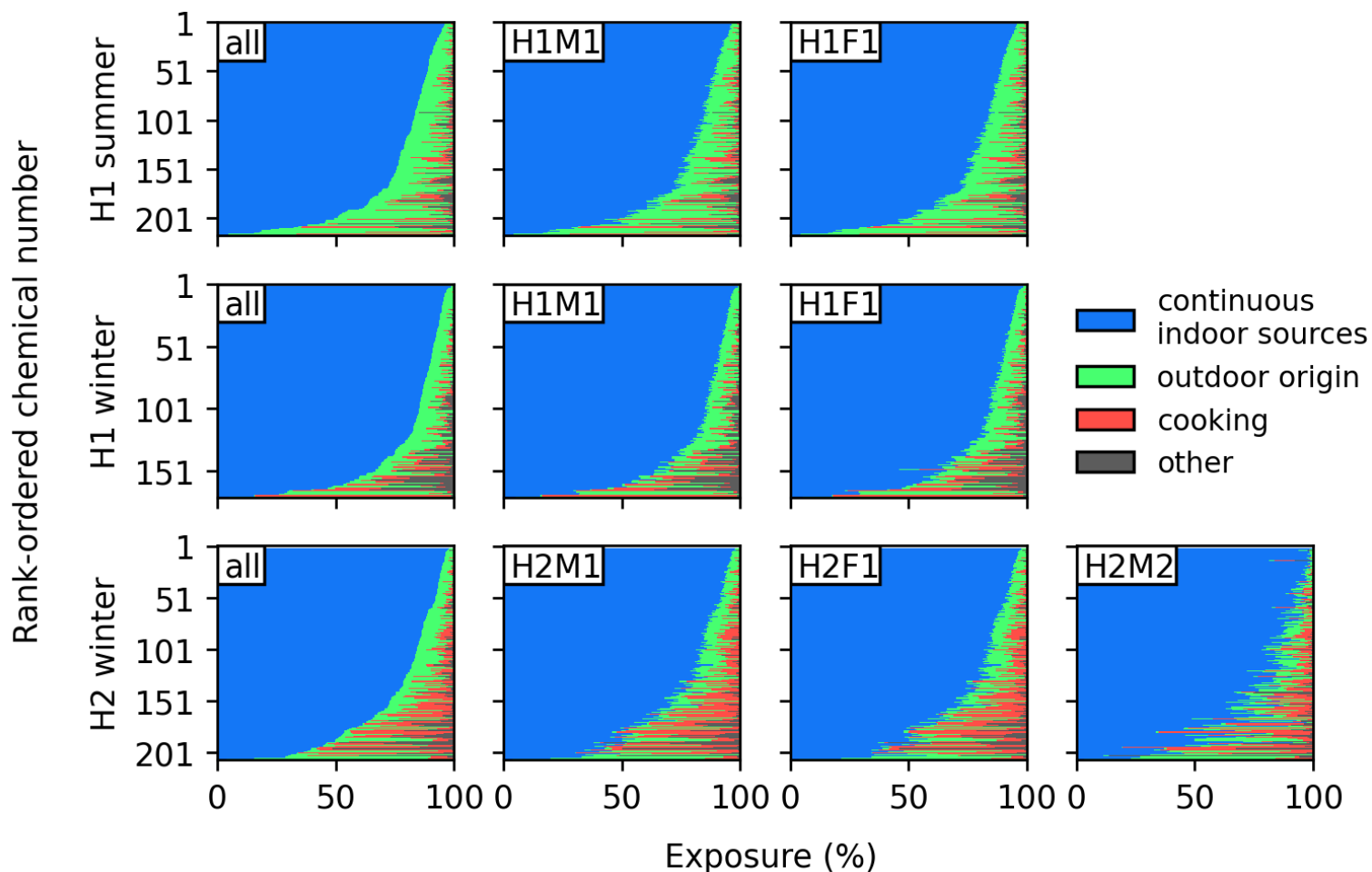
Fig. 3. Relative source apportionment of VOC exposures. Residential exposures to (217, 170, 205) detected VOC ions were calculated for each occupant during the (H1 summer, H1 winter, H2 winter) monitoring campaigns and were apportioned into specific source categories. Subpanels display relative VOC exposures for individual occupants; the heading 'all' refers to a hypothetical occupant who is present for all of the measurement period. In subpanels, each horizontal bar corresponds to a single VOC and is colored according to the relative contribution from each source category (continuous indoor sources [blue], outdoor-origin [green], cooking [red], and other [gray]). Each row of panels uses the same rank-ordering defined by the first 'all' subpanel, which has VOCs rank-ordered from greatest-to-least by the relative contribution from "continuous indoor sources." The top, middle, and bottom rows correspond to the H1 summer, H1 winter, and H2 winter campaigns, respectively.

In contrast, deviations were observed between source apportionments for a substantial subset of VOCs that were dominantly event-driven during the H2 winter campaign (19 of 205 ions). These mainly occurred for the H2M2 occupant, who was present for only part of the measurement campaign. If the H2M2 occupant is excluded, only two exceptions are observed, the inorganic gas dichloramine (related to cleaning) and the $C_3H_6^+$ ion. Generally,

318   if an occupant was absent for a large emission event, as in the case of H2M2 for much of the
319   measurement campaign, discrepancies were observed.

320   Absolute exposures were comparable between the H1 summer and winter seasons for most
321   VOCs. Of 166 ions concurrent to both seasons, absolute mean concentrations for 66% (97%) of
322   VOCs differed by no more than 50% (factor of 2) between seasons (Figure S3). Large exceptions
323   (> 2× difference) were observed for D5 siloxane, monoterpenes, $C_2H_3^+$, and methane sulfonic
324   acid (greater during the H1 winter season) and for cinnamaldehyde (greater during the H1
325   summer season). During the H1 summer season, 47 more compounds were observed above the
326   detection threshold than during the H1 winter season. These compounds are chemically diverse,
327   including halogens, aromatics, oxygenates, and organosulfurs. We are unable to assign most of
328   these ions to specific chemical structures. While only four VOCs were principally attributable to
329   outdoor-to-indoor transport during the H1 winter season, the same four plus four additional
330   VOCs were attributable to outdoor-to-indoor transport during the H1 summer season, of which
331   three were highly oxygenated species ($C_2H_5O_3^+$, $C_5H_5O_3^+$, $C_{10}H_9O_3^+$). The highly oxygenated
332   species had cyclical outdoor fluctuations with afternoon peaks, suggesting that these compounds
333   may be arising as secondary VOCs produced through summertime enhanced outdoor
334   photochemistry or as biogenic emissions. In general, outdoor-to-indoor transport was more
335   important during the summer season as opposed to the winter season. Indoor concentrations
336   attributable to outdoor-to-indoor transport were greater on an absolute basis for 147 compounds
337   concurrent to both the H1 summer and H1 winter campaigns (88%). However, contributions for
338   these compounds remained low, accounting, on average, for 16% and 11% of total indoor
339   concentrations in summer and winter, respectively.

340   A recent review of longitudinal studies measuring total volatile organic compound (TVOC)
341   levels asserts that emissions from buildings and their contents are a "new building" phenomenon
342   that is most important only soon after construction, renovation, or refurbishing as new materials
343   off-gas. After an initial 1-2 year off-gassing period, TVOC emissions from building materials
344   decline such that they are assumed to be unimportant relative to VOC emissions related to
345   occupants and their activities (26). However, measurements of TVOC levels are not
346   generalizable to specific VOCs that may be of interest to public health. One longitudinal study of
347   25 speciated VOCs including alkanes, aromatics, and aldehydes in 251 Japanese residences
348   similarly found that VOC concentrations in wood-framed housing will generally decrease over a
349   1-2 year off-gassing period before stabilizing at levels consistent with much older residences
350   (24). In contrast, homes with ferroconcrete or light-steel frames, regardless of age, produced
351   VOC profiles consistent with aged-wood frames. The present study focused on measurements
352   acquired at two houses of wood-frame construction, as is common in the US housing stock. We
353   caution that certain features of wood-framed houses, such as temperature-dependent emissions
354   originating from wood and substantial buffering of indoor humidity (55), may not be fully
355   generalizable to other construction types.

356   While it may be true for some chemicals that VOC emissions from buildings are less important
357   in older residences, observations at the H1 and H2 sites indicate that continuous indoor sources
358   were the largest contributors to VOC exposures for more than 90% of observed species, even
359   though the residences were many decades old and had not been recently remodeled or
360   refurnished. Plausible sources might include continued material off-gassing as deeply bound

VOCs migrate to surfaces; oxidative, thermal or microbial decomposition of building materials yielding decomposition products; or sorptive interactions as VOCs related to occupant events deposit on surfaces and then slowly off-gas. The last mechanism has been traditionally understood to apply to semivolatile organic compounds (SVOCs), but recent studies suggest that sorption in surface reservoirs is also important for VOCs (22). That phenomenon may cause primary emissions from episodic sources to be interpreted as originating from building materials.

Source control efforts prioritize building materials and furnishings with the specific goal of encouraging use of materials with low short-term VOC emissions. Unified regulatory limits are generally not available, but some countries have implemented product certification and voluntary emissions testing programs. The H1 and H2 sites suggest that ongoing VOC emissions can be expected to occur from building materials long after any short-term VOC reservoirs are depleted. While we expect that these sites are ordinary for their age and location, further study is warranted to see if these findings generalize to other sites, especially those with higher concentrations of airborne VOCs. If exposures associated with long-term VOC emissions from building materials prove to be significant for occupant health and well-being, current control strategies may need augmentation. Some compounds associated with wood degradation, such as carboxylic acids, furanoids and acetaldehyde, may prove particularly challenging to address via source-control strategies of the type currently employed.

Past source apportionment studies using multivariate receptor models of population-level data have diverged on the relative importance of off-gassing from building materials (29–31). For instance, Bari et al. noted that off-gassing from building materials contributed only 6% of measured total VOCs ($n = 119$ analytes; alkanes, alkenes, aromatics, halogens, carbonyls, alcohols, terpenes, others) in Canadian residences (31). Conversely, Guo reported that 77% of measured VOCs in Hong Kong residences were attributable to emissions from building materials ($n = 16$ representative analytes; alkanes, aromatics, carbonyls, terpenes, acids, others) (30). Such differences between studies may reflect the choice of studied analytes rather than differences in building age and composition. Furthermore, dimensionality reduction techniques, such as positive matrix factorization (PMF) and principal component analysis (PCA), reduce complex datasets to specific factors or components unique to each dataset that must be interpreted and assigned to specific source categories. While such source apportionment studies yield qualitatively similar results reflecting commonalities in residential VOC sources, it is difficult, and often unjustifiable, to generalize quantitatively between different source apportionment analyses. Contrasting findings between the present study, indicating substantial contributions from continuous indoor sources, and past studies, indicating that off-gassing from aged building materials is less important, may be related to subjective choices for source assignment in multivariate receptor models. This observation emphasizes that detailed characterizations of single-residences are needed to complement and justify inferences from population-level surveys.

Risk-based prioritization. Chronic advisory health guidelines from at least one agency were acquired for 31 VOCs consistent with chemical formulas identified at the H1 and H2 field sites. Of these 31 VOCs, 18 were specifically identified at the H1 and H2 field sites with high degrees of confidence (Table 1). Considering residential exposures at these two study sites, three compounds exceeded a health-risk guideline given by IRIS, OEHHA, or ATSDR. Acrolein

404 concentrations were 1-2 orders of magnitude higher than the health-risk guidelines of IRIS and
405 ATSDR, and ~3–4 times higher than the OEHHA guideline, for each occupant during all three
406 campaigns. Acetaldehyde concentrations were above the USEPA IRIS health guideline and
407 within an order of magnitude of the OEHHA health guideline for all occupants during all three
408 campaigns. Acrylic acid concentrations were comparable to the USEPA IRIS health guideline
409 for all occupants during all three campaigns. Health guidelines for acrylic acid were not available
410 from OEHHA and ATSDR. Acrolein and acetaldehyde have already been identified as two of
411 nine "priority hazards based on the robustness of measured concentration data and the fraction of
412 residences that appear to be impacted." (3)

413 We also consider acute advisory health guidelines from OEHHA and ATSDR for 15 VOCs
414 consistent with chemical formulas identified at the H1 and H2 fields sites, all of which were
415 identified with high confidence (Table S4). Acrolein concentrations exceeded acute
416 concentration guidelines 1–2 times each week during the H1 summer and H2 winter campaigns,
417 often in association with cooking. Exceedances were less common during the H1 winter
418 campaign, occurring only twice over the five-week monitoring period. Three events during the
419 H2 winter campaign produced acetaldehyde concentrations that exceeded OEHHA acute
420 concentration guidelines. Benzene concentration spikes reached concentrations roughly one third
421 that of the acute guideline value. A short-term spike in acetone concentration associated with the
422 use of nail polish remover reached 20% of the acute guideline value during the H2 winter
423 campaign. All other compounds with available acute concentration guidelines were typically 2–3
424 orders lower than the guideline value.

425 Public health guidelines often incorporate large uncertainty factors to account for limitations
426 in the available toxicological data. In some cases, this may lead to uncertainties "spanning
427 perhaps an order of magnitude" as explicitly stated by USEPA IRIS. In the event that
428 USEPA guidelines are an order-of-magnitude overestimate, several of the flagged VOCs
429 would no longer be expected to be of health interest at observed levels. If guidelines are an-
430 order-of-magnitude underestimate, additional compounds may be of health interest at
431 observed levels.

432   **Table 1.** Chronic hazard assessment of select VOCs. Indoor concentrations are presented as
433   time averages of measured living space concentrations for the periods that individual
434   occupants are indoors at home.[a]

435   [see table on following page]

436   [a] Reference concentrations (USEPA IRIS), reference exposure levels (OEHHA), and
437   minimal risk levels (ATSDR) are presented for chronic and intermediate (int.) VOC
438   exposures. Ion formulas with uncertain confidence in compound assignment are
439   designated with an asterisk. All other compounds are possible assignments. OEHHA and
440   IRIS values were converted from mass per volume concentrations to mixing ratios by
441   applying the ideal gas law and assuming standard conditions (298 K, 1 atm). The
442   "Concentration-to-Guideline Ratio" is defined as the ratio between the greatest mean
443   occupant exposure concentration among the campaigns and the smallest health guideline
444   concentration. All concentrations are reported in ppb. Values marked with "#" are
445   uncertain ion formula assignments that, if assigned correctly, may be exceeding health
446   advisory guidelines or warrant additional interest.

VOC	Mean Abundance (ppb)										Compound Assignment			Health Guideline (ppb)		
	H1 summer			H1 winter			H2 winter									
Ion Formula	all	H1M1	H1F1	all	H1M1	H1F1	all	H2M1	H2F1	H2M2	Name	Confidence	Concentration Guideline Ratio	OEHHA REL	USEPA IRIS RfC	ATSDR MRL
$C_3H_5O^+$	0.57	0.56	0.57	0.44	0.44	0.45	0.36	0.39	0.39	0.38	acrolein		66	0.15	0.0087	0.04 (int.)
$C_2H_5O^+$	9.3	9.7	9.5	8.3	8.2	9.1	24	28	26	14	acetaldehyde		5.6	78	5	
$C_3H_5O_2^+$	0.37	0.37	0.37	0.29	0.29	0.31	0.27	0.29	0.29	0.27	acrylic acid		1.1		0.34	
$C_6H_7^+$	0.24	0.24	0.24	0.46	0.46	0.46	0.31	0.33	0.33	0.27	benzene		0.15	94	9.4	3
$C_8H_{11}^+$	0.25	0.24	0.25	0.25	0.24	0.24	0.33	0.34	0.34	0.31	xylene		0.15#	160	2.3	50 (int)
											ethyl benzene		0.0057	460		60
CH_5O^+	28	27	27	28	28	28	45	50	50	42	methanol		0.033	3100	1500	
$C_3H_7O^+$	11	11	11	9.9	10	10	30	39	39	19	acetone		0.03			1300
											propionaldehyde	*	11		3.4	
$C_7H_9^+$	0.36	0.34	0.35	0.75	0.76	0.75	1.3	1.3	1.3	1	toluene		0.016	80	1300	1000
$C_6H_7O^+$	0.52	0.52	0.52	0.48	0.48	0.48	0.34	0.36	0.36	0.31	phenol		0.001	52		
CCl_3^+	0.17	0.17	0.17	0.13	0.13	0.13	0.14	0.13	0.13	0.14	chloroform		0.0085			20
$C_2H_4N^+$	0.16	0.16	0.16	0.11	0.11	0.11	0.14	0.14	0.14	0.14	acetonitrile		0.0044		36	
$C_6H_{15}O_2^+$	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.05	0.053	0.053	0.043	2-butoxyethanol		0.0031	17		
											butoxyethanol		0.00027			200
$C_6H_5Cl_2^+$	0.018	0.018	0.018	0.019	0.019	0.019	0.01	0.011	0.01	0.01	dichlorobenzene		0.0019	130	130	10
$C_7H_9O^+$	0.18	0.17	0.17	0.15	0.14	0.14	0.1	0.11	0.11	0.1	cresols		0.0011	140		
$C_4H_9O^+$	0.76	0.76	0.76	0.75	0.74	0.78	1.3	1.5	1.5	1.2	ethyl methyl ketone		0.00088		1700	
											tetrahydrofuran	*	0.0022		680	
$C_8H_9^+$	0.14	0.14	0.14	0.15	0.14	0.15	0.16	0.17	0.17	0.15	styrene		0.00085	210	240	200
$C_4H_3O_3^+$	0.014	0.015	0.014	0.019	0.019	0.019	0.015	0.016	0.016	0.014	maleic anhydride	*	0.11#	0.17		
$C_4H_7O_2^+$	0.69	0.68	0.69	0.59	0.58	0.6	0.59	0.62	0.62	0.56	vinyl acetate	*	0.012	57	57	10 (int)
$C_3H_4N^+$	0.022	0.021	0.021	0.022	0.022	0.022	0.034	0.035	0.035	0.033	acrylonitrile	*	0.038	2.3	0.92	
$C_6H_{13}O^+$	0.23	0.22	0.23	0.16	0.16	0.16	0.21	0.21	0.21	0.19	2-hexanone	*	0.032		7.3	
											methyl isobutyl ketone	*	0.00032		730	
$C_9H_{13}^+$	0.13	0.12	0.12	0.14	0.14	0.13	0.16	0.18	0.18	0.14	ethylmethylbenzene	*	NA	NA	NA	NA
											cumene	*	0.0023		80	
											trimethylbenzene	*	0.015		12	
$C_5H_9O_2^+$	0.54	0.53	0.54	0.31	0.31	0.31	0.31	0.32	0.32	0.28	acetylpropionyl		NA	NA	NA	NA
											glutaraldehyde	*	27#	0.02		0.03 (int)
											methyl methacrylate	*	0.0032		170	

448

Source apportionment reveals that acrolein, acetaldehyde and acrylic acid at these study sites are principally attributable to continuous indoor sources with important contributions from cooking and smaller contributions from outdoor-to-indoor transport. During the H1 summer and H1 winter campaigns, acetaldehyde exposures were principally attributed to continuous indoor sources (~60-70%) with contributions from cooking (~20-30%) and outdoor-to-indoor transport (~5-10%). In contrast, during the H2 winter campaign, continuous indoor sources accounted for half of occupant exposures, with significant contributions from both cooking (~20%) and unidentified indoor source events (~30%). Acrylic acid exposures were principally attributed to continuous indoor sources (~60-80%) with contributions from cooking (~5-20%) and outdoor-to-indoor transport (~15-25%) across the three campaigns. Acrolein exposures were principally attributed to continuous indoor sources (~70-90%) with contributions from cooking (~5-10%) and outdoor-to-indoor transport (~5-20%) across the three campaigns.

We highlight other VOCs with concentrations within an order magnitude of health guidelines as meriting further consideration. Concentrations of benzene were well below the OEHHA health advisory limit but are within an order of magnitude of the USEPA IRIS and ATSDR guidelines. Residential benzene exposures at these study sites were principally attributed to continuous indoor emissions (~50-60%) and outdoor-to-indoor transport (~40-50%), highlighting the importance of both indoor sources and outdoor emissions (which are likely traffic-related). Similar results are observed for other BTEX (benzene, toluene, ethylbenzene, xylene) compounds that have been the subject of significant interest and have been attributed to both indoor sources and outdoor fossil-fuel related sources (11).

There were no health guidelines available for ~90% of the 250 VOC ions observed. Furthermore, both VOC concentrations and associated toxicities can vary by orders of magnitude, indicating that it may not be sufficient to assume that there are minimal impacts on human health when compounds are present at relatively low concentrations. The possibility of additive or synergistic interactions arising from exposure to complex VOC mixtures may similarly influence health risks from air pollutant exposures in residences.

We were unable to conclusively assign some molecular ions to specific VOCs; these may represent an isomeric mixture of compounds with the same molecular formula but (potentially) different toxicities. We note that concentrations of the $C_8H_{11}^+$, $C_4H_3O_3^+$, and the $C_5H_9O_2^+$ ions, if attributed solely to xylene, maleic anhydride, and glutaraldehyde, respectively, would be of potential health-risk concern. Static measurements acquired by offline TD-GC×GC-ToF-MS at during the H2 winter campaign suggest that xylene isomers accounted for 80% of observed mass of $C_8H_{11}^+$ with ethylbenzene accounting for the remainder. There was no evidence of any analyte with structural formulas consistent with $C_4H_3O_3^+$ or $C_5H_9O_2^+$ that might correspond to maleic anhydride or glutaraldehyde in the TD-GC×GC-ToF-MS measurements. However, given instrumental parameters, the presence or absence of maleic anhydride and glutaraldehyde was not assessable.

Methodological considerations for future exposure studies. Occupant exposures in their homes were determined using time-resolved data and compared against simulated time-averaged methods using the H1 summer, H1 winter and H2 winter datasets. Time-averaged samples

490 collected on sorbent tubes for later offline analysis commonly use sampling durations in the
491 range of hours to weeks. We constructed simulated distributions of time-averaged samples using
492 three hypothetical sampling durations (1-hour, 1-day, 1-week). Then, we normalized each value
493 by the time-resolved best estimate of exposure. A value of "1" indicates that the time-averaged
494 exposure estimate equals the time-resolved exposure estimate. Summary statistics of these
495 distributions are compared against the relative standard deviation (RSD) of observed VOC
496 concentrations for each compound during the three measurement campaigns (Figure 4). As a
497 measure of variability, the RSD will increase with contributions from emission patterns that are
498 both periodic (typically related to the temperature-based diurnal cycle) and episodic (typically
499 related to emission events). Because the mean-to-median ratio (18), a measure of episodic
500 variability, strongly correlates with the RSD ($R^2 = 0.86$), it is qualitatively assumed that episodic
501 variability is more important than periodic variability at this site. For VOCs with small RSDs
502 (RSD < 0.4) indicating low periodic fluctuations and low episodic emissions, all three sampling
503 durations tend to produce exposures that are consistent (within ± 50%) with best-estimate
504 exposures. However, as the RSD of the VOC concentration time series increases, so too would
505 the variability in occupant exposures derived from time-averaged samples. These effects can be
506 particularly important when a sampling period directly coincides with an infrequently occurring
507 episodic emission, which would produce exposures estimates potentially much higher than the
508 best estimate based on time-resolved information. In the illustrative case of pyrrole during the
509 H2 winter campaign, estimated exposures were up to 100 times higher for occupant H2M1 than
510 the best-estimate when an hourly time-averaged sample coincided with an episodic cooking
511 event that released pyrrole. The effects of this bias decreased with increasing sampling duration.
512 Pyrrole exposures estimated from daily time-averaged samples were up to 13 times higher than
513 the time-resolved best estimate of exposure and pyrrole exposures from weekly time-averaged
514 samples were up to 3.3 times higher than the time-resolved best estimate of exposure.

515 Hourly time-averaged samples produce unsatisfactory estimates of exposures (> ±50% of best-
516 estimate) for most VOCs with moderate-to-high RSDs (RSD > 0.4). The performance of the
517 time-averaged method slightly improved when sampling durations increased to daily but was
518 similarly unsatisfactory for compounds with moderate-to-high RSDs (RSD > 0.4). Only when
519 the time-averaged method increased to weekly sampling intervals did performance appear
520 satisfactory for most VOCs (~90% of VOCs during H1 summer and H1 winter, ~75% during H2
521 winter), yielding exposure estimates that were within 50% of the best-estimate. However, even
522 with this longer sampling duration, the time-averaged and best-estimate time-resolved methods
523 were less comparable for VOCs with high RSDs, mostly due to the large influence of episodic
524 events.
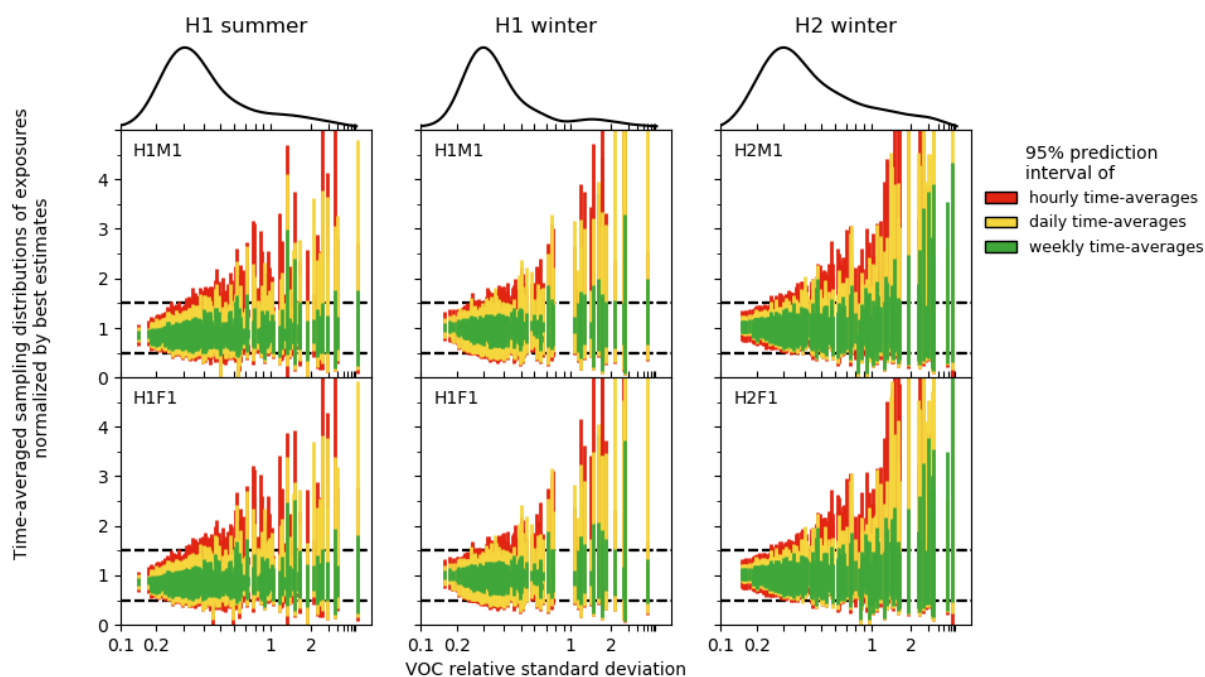
Fig. 4. Comparison of traditional and time-resolved exposure estimates against compound time-series variability. Occupant exposures during the H1 summer, H1 winter, and H2 winter campaigns were calculated from a) simulated time-averaged concentrations (1-h, 1-day, 1-week time-averages) coupled with occupant time budgets and b) time-resolved methods ('best-estimate'). Distributions of randomly sampled time-averaged exposure estimates ($n = 1000$) normalized by the time-resolved best-estimate are compared against a VOC's relative standard deviation. Vertical bars correspond to the 95% observation window for individual VOC distributions (with one outlier excluded in each campaign). Red, orange, and green colors indicate distributions of hourly, daily, and weekly time-averages, respectively. Columns correspond to the H1 summer, H1 winter, and H2 winter campaigns. Subpanels in each column correspond to exposures for individual occupants during a campaign. The kernel density estimate of the relative standard deviation is shown above each scatterplot. Horizontal dashed lines designate the ± 50% boundary of the best-estimate exposure. Note that the horizontal axis has non-linear scaling.

Population-level environmental risk assessments require the ability to estimate exposures with both adequate precision and ease of implementation. Often, samples are collected on sorbent tubes for offline analysis giving time-averaged VOC concentrations and then coupled with occupant time budgets to estimate pollutant exposures. A comparison of time-averaged methods with time-resolved methods has not been previously reported to substantiate this approach. In this study, time-averaged sampling methods appeared to yield adequate measures of occupant exposure, provided that the studied compound of interest has proportionately small contributions from episodic sources. As expected, longer sampling times produce more precise estimates of occupant exposures. Hourly and daily time-averaged samples would be ineffective at estimating exposures to VOCs with substantial contributions from episodic sources. Weekly time-averaged

551   samples can yield more precise (+/- 50%) estimates of exposures for VOCs with moderate
552   contributions from episodic sources and order of magnitude precision for compounds with
553   substantial contributions from episodic sources. Conversely, sampling duration matters little for
554   compounds with small contributions from episodic sources, indicating that many VOCs can be
555   measured rapidly for exposure estimates, provided that source mechanisms are well understood.

556   VOCs were sampled in two or three locations in the occupied portion of each studied residence
557   to provide some evidence about spatial variability. On the whole, concentrations were well-
558   coupled between open living spaces. It has been noted that the assumption of a well-mixed room
559   may not be sufficient when estimating exposures to strongly localized sources due to spatial
560   heterogeneities. (33, 34) For this reason, contributions from episodic sources to occupant
561   exposures within these residences may have been higher if an occupant was in close proximity to
562   an episodic source, regardless of whether time-averaged or time-resolved methods were used to
563   estimate exposures. Personal sampling overcomes this spatial limitation; however, no methods
564   are presently available for conducting personal sampling for VOC exposures with both high
565   chemical specificity and time-resolved concentrations.

566   This study incorporated health-risk data from three governmental organizations yielding advisory
567   guidelines for chronic exposures to 31 separate VOCs (22 VOC ions). We compared the
568   guideline values against VOC concentrations for summer (one residence) and winter seasons
569   (two residences). Residential VOC concentrations were above guideline values for two
570   compounds already well-known to the public health community (acrolein, acetaldehyde) and for
571   one compound for which there is less evident awareness (acrylic acid). We also note that
572   available advisory health guidelines address fewer than 10% of the 250 VOC ions observed.
573   Larger VOC ions likely correspond to many distinct chemical isomers, further reducing the
574   estimate of observed VOCs with associated health data. Because it is not feasible to acquire
575   detailed toxicology or exposure data for the thousands of chemicals to which populations may be
576   exposed, recent efforts have developed tools for high-throughput screening of chemical toxicities
577   (ToxCast) and exposures (ExpoCast).[56] High-throughput models like ExpoCast may benefit from
578   improved understanding that can be gained in high-resolution studies. This study was limited to
579   two residences and five occupants. While we expect that these residences are ordinary for their
580   age and location, it remains to be seen how well our findings generalize to other residences.
581   Further research is warranted to study the health effects of the substantial chemical diversity
582   found at levels much higher than outdoors in residential air.

4 SUPPORTING INFORMATION

Supporting Information: PTR-ToF-MS operating conditions, data analysis, absolute daily exposures, occupant time-activity budgets, seasonal concentration differences, H2 residence floor plan, representative time series of peak assignments, summary data tables, acute health guidelines.

5 ACKNOWLEDGEMENTS

6 REFERENCES

1. Wieslander, G.; Norbäck, D.; Björnsson, E.; Janson, C.; Boman, G. Asthma and the indoor environment: the significance of emission of formaldehyde and volatile organic compounds from newly painted indoor surfaces. *Int. Arch. Occup. Environ. Health* **1997**, *69*, 115–124.
2. Guo, H.; Lee, S. C.; Chan, L. Y.; Li, W. M. Risk assessment of exposure to volatile organic compounds in different indoor environments. *Environ. Res.* **2004**, *94*, 57–66.
3. Logue, J. M.; McKone, T. E.; Sherman, M. H.; Singer, B. C. Hazard assessment of chemical air contaminants measured in residences. *Indoor Air* **2011**, *21*, 92–109.
4. Logue, J. M.; Price, P. N.; Sherman, M. H.; Singer, B. C. A Method to Estimate the Chronic Health Impact of Air Pollutants in U.S. Residences. *Environ. Health Perspect.* **2012**, *120*, 216–222.
5. Allen, J. G.; MacNaughton, P.; Satish, U.; Santanam, S.; Vallarino, J.; Spengler, J. D. Associations of Cognitive Function Scores with Carbon Dioxide, Ventilation, and Volatile Organic Compound Exposures in Office Workers: A Controlled Exposure Study of Green and Conventional Office Environments. *Environ. Health Perspect.* **2016**, *124*, 805–812.
6. Klepeis, N. E.; Nelson, W. C.; Ott, W. R.; Robinson, J. P.; Tsang, A. M.; Switzer, P.; Behar, J. V.; Hern, S. C.; Engelmann, W. H. The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. *J. Expo. Anal. Environ. Epidemiol.* **2001**, *11*, 231–252.

621   7. Adgate, J. L.; Church, T. R.; Ryan, A. D.; Ramachandran, G.; Fredrickson, A. L.; Stock,
622   T. H.; Morandi, M. T.; Sexton, K. Outdoor, Indoor, and Personal Exposure to VOCs in
623   Children. *Environ. Health Perspect.* **2004**, *112*, 1386–1392.
624   8. Edwards, R. D.; Jurvelin, J.; Koistinen, K.; Saarela, K.; Jantunen, M. VOC source
625   identification from personal and residential indoor, outdoor and workplace
626   microenvironment samples in EXPOLIS-Helsinki, Finland. *Atmos. Environ.* **2001,** *35*,
627   4829–4841.
628   9. Wallace, L. A. Human Exposure to Volatile Organic Pollutants: Implications for Indoor
629   Air Studies. *Annu. Rev. Energy Environ.* **2001**, *26*, 269–301.
630   10. Salthammer, T.; Mentese, S.; Marutzky, R. Formaldehyde in the Indoor Environment.
631   *Chem. Rev.* **2010**, *110*, 2536–2572.
632   11. Bolden, A. L.; Kwiatkowski, C. F.; Colborn, T. New Look at BTEX: Are Ambient Levels
633   a Problem? *Environ. Sci. Technol*. **2015**, *49*, 5261–5276.
634   12. Salthammer, T. Very volatile organic compounds: an understudied class of indoor air
635   pollutants. *Indoor Air* **2016**, *26*, 25–38.
636   13. Salthammer, T.; Zhang, Y.; Mo, J.; Koch, H. M.; Weschler, C. J. Assessing Human
637   Exposure to Organic Pollutants in the Indoor Environment. *Angew. Chem. Int. Ed.* **2018**,
638   *57*, 12228–12263.
639   14. Wolkoff, P. How to measure and evaluate volatile organic compound emissions from
640   building products. A perspective. *Sci. Total Environ*. **1999**, *227*, 197–213.
641   15. Weschler, C. J.; Carslaw, N. Indoor Chemistry. *Environ. Sci. Technol.* **2018**, *52*, 2419–
642   2428.
643   16. Steinemann, A. Volatile emissions from common consumer products. *Air Qual. Atmos.*
644   *Health* **2015**, *8*, 273–281.
645   17. Farmer, D. K.; Vance, M. E.; Abbatt, J. P. D.; Abeleira, A.; Alves, M. R.; Arata, C.;
646   Boedicker, E.; Bourne, S.; Cardoso-Saldaña, F.; Corsi, R.; DeCarlo, P. F.; Goldstein, A.
647   H.; Grassian, V. H.; Hildebrandt Ruiz, L.; Jimenez, J. L.; Kahan, T. F.; Katz, E. F.;
648   Mattila, J. M.; Nazaroff, W. W.; Novoselac, A.; O'Brien, R. E.; Or, V. W.; Patel, S.;
649   Sankhyan, S.; Stevens, P. S.; Tian, Y.; Wade, M.; Wang, C.; Zhou, S.; Zhou, Y.
650   Overview of HOMEChem: House Observations of Microbial and Environmental
651   Chemistry. *Environ. Sci.: Processes Impacts* **2019**, *21*, 1280–1300.
652   18. Liu, Y.; Misztal, P. K.; Xiong, J.; Tian, Y.; Arata, C.; Weber, R. J.; Nazaroff, W. W.;
653   Goldstein, A. H. Characterizing sources and emissions of volatile organic compounds in
654   a northern California residence using space- and time-resolved measurements. *Indoor Air*
655   **2019**, *29*, 630–644.
656   19. Liu, S.; Li, R.; Wild, R. J.; Warneke, C.; de Gouw, J. A.; Brown, S. S.; Miller, S. L.;
657   Luongo, J. C.; Jimenez, J. L.; Ziemann, P. J. Contribution of human-related sources to
658   indoor volatile organic compounds in a university classroom. *Indoor Air* **2016**, *26*, 925–
659   938.
660   20. Tang, X.; Misztal, P. K.; Nazaroff, W. W.; Goldstein, A. H. Volatile Organic Compound
661   Emissions from Humans Indoors. *Environ. Sci. Technol.* **2016**, *50*, 12686–12694.

21. Rackes, A.; Waring, M. S. Do time-averaged, whole-building, effective volatile organic compound (VOC) emissions depend on the air exchange rate? A statistical analysis of trends for 46 VOCs in U.S. offices. *Indoor Air* **2016**, *26*, 642–659.

22. Wang, C.; Collins, D. B.; Arata, C.; Goldstein, A. H.; Mattila, J. M.; Farmer, D. K.; Ampollini, L.; DeCarlo, P. F.; Novoselac, A.; Vance, M. E.; Nazaroff, W. W.; Abbatt, J. P. D. Surface reservoirs dominate dynamic gas-surface partitioning of many indoor air constituents. *Sci. Adv*. **2020**, *6*, eaay8973.

23. Xiong, J.; Zhang, P.; Huang, S.; Zhang, Y.; Comprehensive influence of environmental factors on the emission rate of formaldehyde and VOCs in building materials: Correlation development and exposure assessment. *Environ. Res.* 2016, *151*, 734–741.

24. Park, J. S.; Ikeda, K. Variations of formaldehyde and VOC levels during 3 years in new and older homes. *Indoor Air* **2006**, *16*, 129–135.

25. Shin, S.-H.; Jo, W.-K. Longitudinal variations in indoor VOC concentrations after moving into new apartments and indoor source characterization. *Environ. Sci. Pollut. Res.* **2013**, *20*, 3696–3707.

26. Holøs, S. B.; Yang, A.; Lind, M.; Thunshelle, K.; Schild, P.; Mysen, M. VOC emission rates in newly built and renovated buildings, and the influence of ventilation – A review and meta-analysis. *Int. J. Vent.* **2019**, *18*, 153–166.

27. Son, B.; Breysse, P.; Yang, W. Volatile organic compounds concentrations in residential indoor and outdoor and its personal exposure in Korea. *Environ. Int.* **2003**, *29*, 79–85.

28. Su, F.-C.; Mukherjee, B.; Batterman, S. Determinants of personal, indoor and outdoor VOC concentrations: An analysis of the RIOPA data. *Environ. Res.* **2013**, *126*, 192–203.

29. Jia, C.; Batterman, S.; Godwin, C. VOCs in industrial, urban and suburban neighborhoods—Part 2: Factors affecting indoor and outdoor concentrations. *Atmos. Environ*. **2008**, *42*, 2101–2116.

30. Guo, H. Source apportionment of volatile organic compounds in Hong Kong homes. *Build. Environ.* **2011**, *46*, 2280–2286.

31. Bari, M. A.; Kindzierski, W. B.; Wheeler, A. J.; Héroux, M.-È.; Wallace, L. A. Source apportionment of indoor and outdoor volatile organic compounds at homes in Edmonton, Canada. *Build. Environ.* **2015**, *90*, 114–124.

32. Wallace, L. A.; Pellizzari, E. D.; Hartwell, T. D.; Sparacino, C. M.; Sheldon, L. S.; Zelon, H. Personal Exposures, Indoor-Outdoor Relationships, and Breath Levels of Toxic Air Pollutants Measured for 355 Persons in New Jersey. *Atmos. Environ.* **1985**, *19*, 1651–1661.

33. Earnest, C.M.; Corsi, R.L.; Inhalation Exposure to Cleaning Products: Application of a Two-Zone Model. *J. Occup. Environ. Hyg.* **2013**, *10*, 328–335.

34. Huang, L.; Ernstoff, A.; Fantke, P.; Csiszar, S.A.; Jolliet, O. A review of models for near-field exposure pathways of chemicals in consumer products. *Sci. Total Environ.* **2017**, 1182–1208.

35. Acevedo-Bolton, V.; Cheng, K.-C.; Jiang, R.-T.; Ott, W. R.; Klepeis, N. E.; Hildemann, L. M. Measurement of the proximity effect for indoor air pollutant sources in two homes. *J. Environ. Monit.* **2012**, *14*, 94–104.

36. Acevedo-Bolton, V.; Ott, W. R.; Cheng, K.-C.; Jiang, R.-T.; Klepeis, N. E.; Hildemann, L. M. Controlled experiments measuring personal exposure to PM2.5 in close proximity to cigarette smoking. *Indoor Air* **2014**, *24*, 199–212.

37. Licina, D.; Tian, Y.; Nazaroff, W. W. Inhalation intake fraction of particulate matter from localized indoor emissions. *Build. Environ*. **2017**, *123*, 14–22.

38. Liu, Y.; Misztal, P. K.; Xiong, J.; Tian, Y.; Arata, C.; Nazaroff, W. W.; Goldstein, A. H. Detailed investigation of ventilation rates and airflow patterns in a northern California residence. *Indoor Air* **2018**, *28*, 572–584.

39. Kristensen, K.; Lunderberg, D. M.; Liu, Y.; Misztal, P. K.; Tian, Y.; Arata, C.; Nazaroff, W. W.; Goldstein, A. H. Sources and dynamics of semivolatile organic compounds in a single-family residence in northern California. *Indoor Air* **2019**, *29*, 645–655.

40. Lunderberg, D. M.; Kristensen, K.; Liu, Y.; Misztal, P. K.; Tian, Y.; Arata, C.; Wernis, R.; Kreisberg, N.; Nazaroff, W. W.; Goldstein, A. H. Characterizing Airborne Phthalate Concentrations and Dynamics in a Normally Occupied Residence. *Environ. Sci. Technol.* **2019**, *53*, 7337–7346.

41. USEPA. *Integrated Risk Information System (IRIS)*. USEPA, 2010. https://cfpub.epa.gov/ncea/iris/search/index.cfm (accessed 2020-06)

42. CalEPA, Office of Environmental Health Hazard Assessment (OEHHA). *OEHHA Acute, 8-hour and Chronic Reference Exposure Level (REL) Summary*. OEHHA, 2019. https://oehha.ca.gov/air/general-info/oehha-acute-8-hour-and-chronic-reference-exposure-level-rel-summary (accessed 2020-06).

43. Agency for Toxic Substances and Disease Registry (ATSDR). *MINIMAL RISK LEVELS (MRLS)*. ATSDR, 2020. https://www.atsdr.cdc.gov/mrls/pdfs/ATSDR%20MRLs%20-%20May%202020%20-%20H.pdf (accessed 2020-06).

44. Agence nationale de sécurité sanitaire de l'alimentation, de l'environnement et du travail (ANSES). *Indoor Air Reference Levels*. Paris, France, March 2018. https://www.anses.fr/en/content/indoor-air-quality-guidelines-iaqgs (accessed 2021-04).

45. Fromme, H.; Debiak, M.; Sagunski, H.; Röhl, C.; Kraft, M.; Kolossa-Gehring, M. The German approach to regulate indoor air contaminants. *Int. J. Hyg. Environ. Health* **2019**, *222*, 347–354.

46. Kunkel, S.; Kontonasiou, E.; Arcipowska, A.; Mariottini, F.; Atanasiu, B. *Indoor air quality, thermal comfort and daylight*; Report for the Buildings Performance Institute Europe (BPIE), March 2015. https://www.bpie.eu/wp-content/uploads/2015/10/BPIE__IndoorAirQuality2015.pdf (accessed 2021-04)

47. Government of Canada. *Indoor Air Reference Levels*. Ottawa, Canada, February 2018. https://www.canada.ca/en/health-canada/services/air-quality/residential-indoor-air-quality-guidelines.html (accessed 2021-04).

48. WHO. *WHO Guidelines for Indoor Air Quality: Selected Pollutants*. Geneva, Switzerland, 2010. https://www.euro.who.int/__data/assets/pdf_file/0009/128169/e94535.pdf (accessed 2021-04).

49. Seaman, V. Y.; Bennett, D. H.; Cahill, T. M. Origin, Occurrence, and Source Emission Rate of Acrolein in Residential Indoor Air. *Environ. Sci. Technol.* **2007**, *41*, 6940–6946.

747 50. Seaman, V. Y.; Bennett, D. H.; Cahill, T. M. Indoor acrolein emission and decay rates
748   resulting from domestic cooking events. *Atmos. Environ*. **2009**, *43*, 6199–6204.
749 51. Katragadda, H. R.; Fullana, A.; Sidhu, S.; Carbonell-Barrachina, Á. A. Emissions of
750   volatile aldehydes from heated cooking oils. *Food Chem.* **2010**, *120*, 59–65.
751 52. Stevens, J. F.; Maier, C. S. Acrolein: Sources, metabolism, and biomolecular interactions
752   relevant to human health and disease. *Mol. Nutr. Food Res.* **2008**, *52*, 7–25.
753 53. Destaillats, H.; Spaulding, R. S.; Charles, M. J. Ambient Air Measurement of Acrolein
754   and Other Carbonyls at the Oakland-San Francisco Bay Bridge Toll Plaza. *Environ. Sci.*
755   *Technol.* **2002**, *36*, 2227–2235.
756 54. Chan, W. R.; Sidheswaran, M.; Sullivan, D. P.; Cohn, S.; Fisk, W. J. Cooking-related
757   PM2.5 and acrolein measured in grocery stores and comparison with other retail types.
758   *Indoor Air* **2015**, *26*, 489–500.
759 55. Alapieti, T.; Mikkola, R.; Pasanen, P.; Salonen, H. The influence of wooden interior
760   materials on indoor environment: a review. *Eur. J. Wood Wood Prod*. **2020**, *78*, 617–634.
761 56. National Research Council. *Exposure Science in the 21st Century: A Vision and a*
762   *Strategy*. The National Academies Press: Washington, DC, 2012.