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Dynamics of residential water-soluble organic gases: Insights into sources and sinks

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Abstract

Water-soluble organic gas (WSOG) concentrations are elevated in homes. However, WSOG sources, sinks, and concentration dynamics are poorly understood. We observed substantial variations in 23 residential indoor WSOG concentrations measured in real time in a North Carolina, U.S. home over several days with a high-resolution time-of-flight chemical ionization mass spectrometer equipped with iodide reagent ion chemistry (I-HR-ToF-CIMS). Concentrations of acetic, formic, and lactic acids ranged from 30 – 130, 15 – 53, and 2.5 – 360 $\mu\text{g m}^{-3}$, respectively. Concentrations of several WSOGs, including acetic and formic acids, decreased considerably (~ 30-50%) when the air conditioner (AC) cycled on, suggesting that the AC system is an important sink for indoor WSOGs. In contrast to non-polar organic gases, indoor WSOG loss rate coefficients were substantial for compounds with high O:C ratios (e.g., 1.6 – 2.2 h^{-1} for compounds with O:C > 0.75 when the AC system was off). Loss rate coefficients in the AC system were more uncertain, but were estimated to be 1.5 hr^{-1} . Elevated concentrations of lactic acid coincided with increased human occupancy and cooking. We report several WSOGs emitted from cooking and cleaning as well as transported in from outdoors. In addition to indoor air chemistry, these results have implications to exposure and human health.

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Supporting Information

Details about experimental conditions; Air-exchange rate measurements; I-HR-ToF-CIMS and ESI-HR-QTOF-MS operation details; List and perturbations details (Table S1); Estimated indoor loss rate coefficient (Table S2); Calculated sources for acetic and formic acids (Table S3); Schematic of sampling area (Figure S1); Typical indoor, outdoor, and AC supply temperature, RH and ozone concentration (Figure S2); I-HR-ToF-CIMS calibration for acetic, formic and lactic acids (Figure S3); Comparison of the sampled residence with 13 other homes (Figure S4); I-HR-ToF-CIMS mass spectra (Figure S5); Concentrations of acetic, formic and lactic acids during the field campaign (Figure S6); A/C cycle peak-to-trough ratio vs O:C ratio and Henry's law constant (Figure S7); Chromatogram of a mist chamber sample using IC (Figure S8); Time traces of chlorine-containing compounds during the cleaning event (Figure S9); Measured and modeled formic and acetic acid concentrations (Figure S10).

Notes

The authors declare no competing financial interest

Introduction

According to the National Human Activity Pattern Survey, on the population level in the United States (U.S.), people spend almost 70% of their time in their residences.¹ Recent integrated measurements of 13 homes demonstrated that water-soluble organic gas (WSOG) concentrations are higher inside homes than directly outside those homes (15 times higher, on average).² However, little is known about the sources, sinks, chemical processing, and concentration dynamics of indoor WSOGs.

While real-time analytical measurements are known to provide valuable insights into sources, sinks, and chemistry, only recently have real-time mass spectrometric methods been applied to the measurement of polar organic gases in buildings. This work to date has focused on public buildings. Liu et al. used proton-transfer-reaction mass spectrometry (PTR-MS) to detect compounds (molecular formulas) consistent with formaldehyde, methanol, acetaldehyde, ethanol, acetone, and propanol in a university classroom.³ These PTR-MS measurements provide exact mass resolution with some compound fragmentation, without structural information needed to distinguish between isomers of the same mass. Despite the inherent limitations, the real-time PTR-MS measurements provided valuable insights concerning the emissions of occupants. Concurrently, the same group measured organic acids using a high-resolution time-of-flight chemical ionization mass spectrometer using acetate reagent ion chemistry (acetate-HR-ToF-CIMS) in the same classroom setting. The HR-ToF-CIMS also provides exact mass but without fragmentation, and also without the ability to distinguish between isomers of the same mass. (The choice of ionization agent determines the compound classes measured.) They concluded that indoor lactic and formic acid concentrations were 5 to 10 times higher than outdoor concentrations, and the concentration dynamics demonstrated that building materials and human occupants were major sources.⁴ Tang et al. also used PTR-ToF-MS to measure selected organic gases in another university classroom and found humans to be the dominant source of the compounds they measured.⁵ PTR-MS has also been used to study real-time emissions in an occupied movie theatre.⁶ To our knowledge, no study has been published using real-time high resolution mass spectrometry to study the sources, sinks, and concentration dynamics of polar organic gases in homes.

In this work, we examine the concentration dynamics of WSOGs in residential indoor air by deploying an HR-ToF-CIMS equipped with iodide (I^-) reagent ion chemistry in one home during a humid southeastern U.S. summer. The representativeness of this home is first established by comparing integrated concentrations and building data with 13 other homes. During the sampling campaign, we perturbed the indoor environment through cooking, cleaning, and by increasing human occupancy and activity levels. Outdoor measurements were also made for comparison. This work provides insights into residential sources and sinks of 23 WSOGs and informs efforts to predict residential chemistry, concentrations, and human exposures.

Materials and Methods

Field sampling and site characterization

Sampling occurred at a two-story single-family home in Chapel Hill, North Carolina, U.S. from 8:00 am to 5:00 pm local time daily from July 18 – 23, 2017. The home (built in 1999) had a floor area of 180 m², air volume of 490 m³, and surface area-to-volume ratio of 1.6 m² m⁻³ (neglecting furniture). The home was in a planned residential community with trees and was far from industrial emissions sources. Flooring was hardwood with area rugs. One new rug was placed in the sampling area to protect the homeowner's floors; the rug was first allowed to off-gas in a laboratory building for two weeks. The house had forced air natural gas heating (not used during the study), air conditioning, an electric stove without outdoor ventilation, and a natural gas fireplace (not used) with a pilot light that vented outdoors. Two house cats were present during sampling. Insecticide roach baits were present under the kitchen sink and typical consumer products (e.g., scented cat litter, chlorine-based dishwashing detergent, and ammonia-based glass cleaner) were stored under the kitchen sink and used in the home periodically.

Table S1 displays activities during sampling. During the first day (7/18/17), referred to as a "background" day, two technicians were present, but care was taken to avoid activities that result in emissions (such as cooking and using personal care products). The second was a "no occupancy" day (7/19/17), with the exception of occasions of regular instrument servicing (30 seconds every 30 minutes, and approximately 10 minutes every 2 hours). A substantial portion (5 hours) of the next day (7/20/17) was deemed "high occupancy" and included a period where the occupants engaged in physical activity indoors. On 7/22/17 and 7/23/17 cleaning and cooking were performed three times at equal intervals during the day.

Real-time and integrated WSOG measurements were made 0.5 to 1 m away from the wall and 1.0 – 1.5 m above the floor in the eat-in-kitchen, in the main living area of the home (see Figure S1). Auxiliary measurements were taken approximately 3 m away in the adjacent living room which was not separated from the eat-in-kitchen by any walls. Room temperature and relative humidity (RH) were recorded each minute (Extech SD800 CO₂/humidity/temperature data logger; Extech, Nashua, New Hampshire). A HOBO UX100-023 (Onset Computer Corporation, Borne, MA) measured temperature and RH in an air supply vent in the living room at minute intervals. When the air conditioning (AC) system cycled on, the supply vent temperature dropped and the RH rose; when the AC system cycled off, the supply vent temperature rose and the RH dropped (Figure S2). Therefore, the supply temperature and RH measurements provided a surrogate indicator for the cycling of the AC system. Ozone concentrations were also measured at minute intervals (Model 202 Ozone Monitor; 2B Technologies, Boulder, Colorado, limit of detection = 3ppb). Outdoor temperature and RH were reported from nearby Chapel Hill Williams Airport, Chapel Hill, NC NOAA Climatological data station, and 8-hour max outdoor ozone was reported from Durham Armory, Durham, NC. Figure S2 depicts the indoor, outdoor, and AC supply temperature and RH and indoor ozone concentrations for a low-occupancy day.

Air exchange was measured with a dynamic carbon dioxide (CO₂) release 2-3 times daily (Extech SD800 CO₂/humidity/ temperature data logger).⁷ Details are provided in the supplementary information (SI).

Real-time sampling

I-HR-ToF-CIMS (Aerodyne Research, Inc., Billerica, Massachusetts) was operated in negative ion mode (V mode, mass resolution of $m/m \sim 4,000$) at two second intervals. Ultra-high purity N₂ (Airgas) was flushed (2.0 L/min) through a heated (40 °C) permeation tube containing methyl iodide (CH₃I, Sigma Aldrich). CH₃I was then ionized in a ²¹⁰Po source and introduced into the ion-molecule reaction chamber at a pressure of 80 mbar. The instrument was operated without an inlet, so that air was pulled directly into the instrument at 2.2 L min⁻¹. For 20 minutes at approximately 8:00 am and 2:00 pm each day, a 2 m length ¼ in (O.D.) polytetrafluoroethylene (PTFE) inlet (residence time < 1 s) was connected and run directly outside the nearest window to sample outside. For comparison and to understand inlet tubing losses, immediately afterwards, indoor sampling was also conducted for an additional 20 min with identical inlet tubing; no significant steady-state signal differences were detected indoors with or without the inlet tubing. Calibration (Figure S3) and quality control information are provided in SI. Compounds were detected using exact mass (considering ionization with I⁻ only) without fragmentation and time traces were corrected by I⁻ ion signal. Data were averaged at the median over 120 data points (4 minutes) for all compounds except for acetic, formic, and lactic acids.

Because our focus is on WSOGs and to simplify I-HR-ToF-CIMS data analysis, we focused on the signals of compounds that we also detected in the integrated samples (see below) by high-resolution quadrupole time-of-flight mass spectrometry equipped with an electrospray ion source (ESI-HR-QTOF-MS, Agilent 6520, Agilent Technologies, Santa Clara, California) operated in both positive and negative ion modes. We also searched for the signals of compounds that were recently measured by acetate-HR-ToF-CIMS in a university classroom.⁴

Integrated sampling

In addition to real-time sampling, integrated WSOG samples were collected at 25 L min⁻¹ into 25 mL of refluxing water using Cofer scrubbers, or mist chambers, as described previously.^{2,8} Three mist chambers sampled indoor air, while one sampled outdoor air. The sampling inlets were 1 m of ½ in Teflon tubing. Samples were collected for two hours three times per day, from 9:00 am – 11:00 am, 12:00 pm – 2:00 pm, and 3:00 pm – 5:00 pm local time. Concurrently collected samples from the three indoor sampling mist chambers were composited.

Samples were analyzed for WSOGs with high-mass resolution ($m/m \sim 12,000$) using ESI-HR-QTOF-MS. The soft ionization is designed to avoid fragmentation. Instrumentation information is provided in SI. Negative ion-mode ESI-HR-QTOF-MS indicates the presence of an organic acid group, while positive ion-mode ESI-HR-QTOF-MS indicates the presence of alcohols, carbonyls, peroxides, and amine compounds.

Results and Discussion

Representativeness of the sampled residence

A comparison of integrated total WSOG measurements and building data (temperature, RH, air exchange rate, home age, and floor area) for the current home and 13 previously sampled single family homes with integrated sampling only² suggests that the home we selected for real-time I-HR-ToF-CIMS (current home) is not unusual (Figure S4). The red-dashed lines in Figure S4 represent the unperturbed current home (7/18/17; Table S1); box plots describe the range of values for the 13 previously-sampled homes. Measured (green) and estimated (red) air exchange rates for the current home are compared with estimated air exchange rates (using the method from Chan et al.^{9,10}) for previously sampled homes.² Home area, calculated air exchange rate, indoor temperature, outdoor ozone, and total WSOG concentrations for the current home are within the interquartile range (25 – 75%) of previously sampled homes. Indoor RH, indoor-outdoor temperature difference, and indoor-outdoor WSOG ratios were within the range, but outside of the interquartile range. Note that previous homes were sampled in June in New Jersey (N=3) and between August and October in North Carolina (N=10), whereas this North Carolina home was sampled in July. Based on this comparison, we conclude that the home environment in which we conducted real-time measurements, and which is the focus of the discussion herein is comparable (with respect to the total WSOG, air exchange rate, and other properties) to this larger set of East coast US, summertime home environments.

Overview of Concentration Dynamics

Twenty-three compounds (molecular formulas), selected as described above, and detected inside the sampled residence by real-time I-HR-ToF-CIMS are listed in Table 1. I-HR-ToF-CIMS provides exact mass, however, in many cases more than one isomer could be present. As indicated in Table 1, concurrent detection of most of these compounds (molecular formulas) by ESI-HR-QTOF-MS (positive and/or negative ion mode) after integrated collection into water provided additional information about molecular structure. Structures provided in Table 1 reflect information given by both mass spectral methods and insights from the indoor air literature.

Acetic ($C_2H_4O_2$), formic (CH_2O_2), and lactic acid ($C_3H_6O_3$) signals dominated the I-HR-ToF-CIMS spectra (Figure S5). Indoor acetic, formic, and lactic acid concentrations varied from 30 – 130, 15 – 53, and 2.5 – 360 $\mu g\ m^{-3}$, respectively (Figure S6). These concentrations are substantially higher than concentrations measured concurrently outdoors (outdoors: 1 – 6 $\mu g\ m^{-3}$ for acetic acid; 0.8 – 2.2 $\mu g\ m^{-3}$ for formic acid; lactic acid not detected). Formic acid concentrations are higher than real-time concentrations measured previously in a university classroom (0.4 to 6.5 $\mu g\ m^{-3}$).⁴ Acetic and formic acid concentrations are within the range of offline time-integrated concentrations measured in other indoor locations (9 – 200 $\mu g\ m^{-3}$ and 3 – 60 $\mu g\ m^{-3}$, respectively; Liu et al.⁴ and references therein).

Real-time concentration dynamics provided several new insights. Interestingly, concentrations of acetic and formic acids as well as several other compounds decreased

rapidly every time the AC system turned on (as detailed below). In contrast, the concentration dynamics of lactic acid were only slightly driven by AC use, and more impacted by occupancy, human activity, and cooking, with the highest concentrations measured during cooking. Emission of several additional compounds was observed during cooking and cleaning. Below we use real-time concentration dynamics and indoor-outdoor concentration differences to provide insights into residential sources and sinks for these 23 oxidized, WSOGs. In some cases, we were able to provide estimates of emission and loss rates.

Dramatic effect of AC use on WSOG concentrations

Without purposeful perturbations and with windows closed, real-time acetic and formic acid concentrations dropped precipitously approximately every hour in a cyclical fashion (Figure 1). Concentrations dropped by 30 – 40% for acetic acid and 40 – 50% for formic acid from their peak values every time the AC supply temperature dropped, indicating that once the AC system began cooling, these acids were scrubbed out of the air. These changes could not be explained by the much smaller, more gradual and offset changes in room temperature and RH (Figure S2). To our knowledge, this is the first definitive evidence of WSOG losses in an AC system. We expect that these highly water-soluble compounds ($H = 4,000 \text{ M/atm}$ for acetic acid and $8,000 \text{ M/atm}$ for formic acid¹¹) are taken up by water condensed on the AC surfaces and/or in the AC condensate.

As shown in Figure 2, 11 signals in addition to those for acetic and formic acids, also cycled with AC use: $\text{C}_2\text{H}_4\text{O}_3$, $\text{C}_2\text{H}_6\text{O}_2$, $\text{C}_4\text{H}_8\text{O}_2$, $\text{C}_4\text{H}_8\text{O}_3$, $\text{C}_4\text{H}_{10}\text{O}_3$, $\text{C}_5\text{H}_8\text{O}_3$, $\text{C}_5\text{H}_{10}\text{O}_2$, $\text{C}_6\text{H}_{14}\text{O}_3$, $\text{C}_7\text{H}_6\text{O}_2$, $\text{C}_7\text{H}_{14}\text{O}_2$, and $\text{C}_8\text{H}_8\text{O}_3$. $\text{C}_2\text{H}_4\text{O}_3$ (likely glycolic acid), $\text{C}_4\text{H}_8\text{O}_2$ (likely butyric acid), $\text{C}_5\text{H}_8\text{O}_3$ (likely oxopentanoic acid or levulinic acid), and $\text{C}_7\text{H}_6\text{O}_2$ (likely benzoic acid), detected here, were previously measured in a university classroom.⁴ Glycolic acid is used in many personal care products¹² and is commonly measured in outdoor air.¹³ Butyric acid is present in linoleum and paint.¹⁴ Oxopentanoic and levulinic acids are both skin lipid decomposition byproducts.¹⁵ Benzoic acid is a secondary product from VOC emission by carpets.¹⁶ In addition, $\text{C}_2\text{H}_6\text{O}_2$ (likely ethylene glycol), $\text{C}_4\text{H}_8\text{O}_3$ (possibly methyl lactate), $\text{C}_4\text{H}_{10}\text{O}_3$ (likely diethylene glycol), and $\text{C}_6\text{H}_{14}\text{O}_3$ (likely dipropylene glycol) are common solvents.¹⁷⁻²⁰ $\text{C}_5\text{H}_{10}\text{O}_2$ may be 3-methylbutanoic acid, which has been measured in moldy buildings²¹ or valeric acid, found in animal facilities²² and may also be emitted from other animals such as house cats. $\text{C}_7\text{H}_{14}\text{O}_2$ could be heptanoic acid which has been previously measured indoors and is released from building materials.^{4,23} $\text{C}_8\text{H}_8\text{O}_3$ could be methylparaben, measured indoors and present in personal care products,²⁴ or methyl salicylate, released from plants.²⁵

The behaviors and possible structures of these compounds suggest that the AC system in cooling mode is a substantial sink. These compounds are all oxidized with at least two oxygen atoms with oxygen-to-carbon (O:C) ratios between 0.3 and 1.5. Henry's law constants for their suggested structures (Table 1) range from $1 \times 10^3 \text{ M atm}^{-1}$ (butyric and heptanoic acids) to $5 \times 10^5 \text{ M atm}^{-1}$ (diethylene glycol). The decrease in signal intensity when the AC turns on (peak/trough ratio) is more dramatic as O:C ratio and Henry's law constant increase (Figure S7), where the decrease is expressed as the ratio of the signal

intensity immediately before the AC turns on (e.g. 9:45 am on 7/18/17) to the signal intensity immediately before the AC turns off (e.g. 10:23 am)). These observations suggest that indoor WSOG losses during air conditioning are substantial, and that losses increase with increasing water solubility and that losses are to damp surfaces (e.g., ducts) and into liquid water in the AC condensate. Leaks in the duct system may also contribute by increasing outdoor air exchange.^{26,27} Estimated sources and loss rate coefficients for some of these compounds are provided below.

Most US homes have air conditioning, with >70% using central air systems such as in this home.²⁸ Use of air conditioning in hot-humid regions of the southeastern US results in substantial removal of water vapor from the occupied spaces. In this home, about 2.2 ± 0.2 L of water vapor was condensed in the air conditioning system during each cooling cycle, approximately hourly (calculated from temperature-dependent saturation vapor pressures). While most of the water drains to the condensate tray, some water remains adhered to coils and other surfaces within the cooled sections of the AC system. This residual water may release some of the absorbed WSOG between cycles as the AC system warms.

This work demonstrates that a damp AC environment aids in the removal (or recycling) of WSOGs. The AC system may also be a source of volatile organics to occupied spaces if aqueous chemistry in the wetted AC system (e.g., onto wet ducts and in condensate during condensation/evaporation cycles) is substantial.² Interestingly, WSOGs may plausibly provide a substantial source of nutrients for microbial communities found on AC coils.²⁹⁻³¹ In turn, microbial growth could alter and contribute to WSOGs in residential spaces.³²

Response to occupancy and human activity level

Lactic acid ($C_3H_6O_3$), which is a human effluent,³³ was highly sensitive to the proximity, number, and activity level of occupants. On 7/20/2017, for example, indoor lactic acid concentrations varied from $2.5 - 6 \mu g m^{-3}$ from 8:00 – 11:00 am, when 2 people were present and increased up to $23 \mu g m^{-3}$ from 11:00 – 4:00 pm, when 7 – 8 people were present (Figure 3). While not outside the range of variability, concentration increases were observed when these occupants ran, jumped, and danced through the house (shaded periods, Figure 3). Short duration lactic acid concentration spikes could also be detected when a technician approached the sampling area.

Cooking and cleaning as a source of oxidized organic gases

Lactic acid concentrations were highest during the cooking events. They increased from about $5 \mu g m^{-3}$ to 170, 360, and $320 \mu g m^{-3}$ during the three episodes in which bacon and onions were fried (Figure 4). Lactic acid is a major component of red meat.³⁴ Recently, Reyes-Villegas also detected $C_3H_6O_3$ from cooking events but identified this compound as hydroxypropionic acid.³⁵ However, concurrent detection by ion chromatography (IC) in integrated samples confirms the presence of lactic acid in this study (Figure S8). It must be noted, however, that IC quantitation of lactic acid was not possible because of inadequate separation from acetic acid. Thus, it is possible that both isomers were present.

In total, 17 WSOGs were detected whose concentrations increased substantially with the cooking of bacon and onions (Figure 4), suggesting that emissions of those compounds were

considerable during these events. $C_3H_6O_3$ (lactic acid), $C_7H_6O_2$, and $C_8H_{10}O$ peaked first, while there was a 4-minute lag in the peak time for some compounds ($C_2H_4O_3$, $C_2H_6O_3$, $C_4H_8O_3$, $C_4H_{10}O_3$, $C_4H_{11}NO$, $C_5H_8O_3$, $C_5H_{10}O_2$, $C_6H_8O_5$, $C_6H_{10}O_3$, $C_6H_{14}O_3$, and $C_7H_{10}O_{14}$) and an 8-minute lag for others (C_4H_8O , $C_5H_8O_2$, and $C_7H_{14}O_2$). The lag might occur because the onions were fried after the bacon. Alternatively, the lag could occur if these compounds were products of secondary chemistry. Since glycolic acid ($C_2H_4O_3$) is a byproduct of photosynthesis,³⁶ it could be released during the cooking of onions. $C_5H_8O_3$ is likely α -ketoisovaleric acid and $C_6H_8O_5$ may be α -ketoadipic acid which are byproducts of the metabolism of the amino acids, valine and lysine, respectively.^{37,38} $C_5H_{10}O_2$ and $C_6H_{10}O_3$ are likely to be the fatty acids 3-methylbutanoic acid and oxohexanoic acid, respectively, or other degradation products of fatty acids present in meat.^{39,40} $C_7H_{14}O_2$ is likely heptanoic acid, which is released from meat cooking.⁴¹ C_4H_8O is consistent with butyraldehyde, which is released from vegetable cooking.⁴² $C_4H_8O_3$ could be methyl lactate or hydroxybutyric acid, although the source is unknown. $C_5H_8O_2$ could be 4-oxopentanal which is a product of squalene oxidation which may also be released during cooking.^{15,43} It is possible that $C_7H_6O_2$ is benzoic acid, an antimicrobial/preservative used in food packaging.⁴⁴ The structures of $C_2H_6O_3$, $C_4H_{10}O_3$, C_4H_8O , $C_4H_{11}NO$, $C_6H_{14}O_3$, $C_7H_{10}O_4$, $C_8H_{10}O$ all released during these cooking events are unknown. Note that some of these molecular formulas (e.g., $C_5H_{10}O_2$ and $C_7H_{14}O_2$ from Figure 5a; $C_2H_4O_3$ and $C_4H_8O_3$ from Figure 5b) are also emitted or formed via other sources indoors or penetrate from outdoors.

Several chlorinated compounds and one nitrogen-containing organic compound (C_2H_3NO) were detected during cleaning, as shown in Figure S9. Many of these compounds have been measured in real time previously.⁴⁵ Since the focus of this work is WSOGs, not inorganic chlorine species, we do not discuss these further.

Outdoor-to-indoor transport as a source of oxidized organics

Figure 5a shows indoor and outdoor measurements for several compounds that are elevated indoors (indoor/outdoor ratios; I/O = 2.1 – 11.5), suggesting that they are dominated by indoor sources. Other compounds are elevated outdoors (I/O = 0.12 – 0.56), suggesting they are dominated by outdoor sources (Figure 5b). Those elevated indoors have been discussed above, with the exception of $C_3H_6O_2$, which is likely propionic acid. Propionic acid has been measured indoors previously and is a common preservative.^{4,46} The molecular formulas for the four compounds with elevated outdoor concentrations are: $C_2H_4O_3$, $C_4H_8O_3$, $C_5H_8O_3$, $C_6H_{10}O_3$. $C_2H_4O_3$ (likely glycolic acid) is a commonly measured organic acid in outdoor air¹³ and formed during atmospheric photochemistry. Outdoors, $C_5H_8O_3$ is more likely to be oxopentanoic acid, than levulinic acid, since it has been measured outdoors in the particle phase.⁴⁷ $C_6H_{10}O_3$, previously measured in the atmosphere,⁴⁸ was also detected by Liu et al. and quantified as oxohexanoic acid.⁴ The outdoor source of $C_4H_8O_3$ (found in the positive mode by ESI-HR-QTOF-MS) is unknown. Structures, I/O ratios, and additional compound information are provided in Table 1.

Among the four detected compounds with higher outdoor than indoor concentrations (Figure 5b; Table 1), the compounds with lower carbon numbers and higher O:C ratios tended to

experience greater concentration differences between outdoors and indoors (C2 and C4, I/O = 0.16 and 0.12 respectively) than the compounds with higher carbon numbers and lower O:C ratios (C5 and C6, I/O = 0.39 and 0.56, respectively). Non-polar volatile organic gases (e.g., benzene, xylene, toluene) are usually assumed to penetrate the building envelope with 100% efficiency (penetration factor, $p = 1.0$) and have indoor loss rate coefficients (k_{other}) of zero, although this is not always the case.^{25,49,50} Larger concentration differences with outdoor-to-indoor transport for compounds with higher O:C ratios are consistent with the hypothesis that more oxidized, polar and WSOGs are more readily removed to surfaces than are non-polar hydrocarbons. Losses of oxidized organic gases could be greater because of increased losses to indoor surfaces (affecting k_{other}) and/or increased losses with transport through the building envelope (affecting p).

Indoor loss rates (k_{other}) for compounds elevated outdoors (I/O < 1)

Indoor loss rate coefficients (k_{other}) for compounds with I/O < 1 were estimated to be 0.2 – 2.2 hr⁻¹ (Table S2) with higher values for more oxygenated compounds. Assuming that the building air volume is well mixed, the rate of change in the indoor concentration is given by Equation 1:

$$\frac{dC_{in}}{dt} = \left(C_{out}p\lambda + \frac{S}{V} \right) - (\lambda + k_{AC} + k_{other})C_{in} \quad (\text{Eq 1:})$$

where V is the volume of the house, C_{out} is the outdoor concentration, C_{in} is the indoor concentration, p is the penetration efficiency, λ is the air exchange rate, S is the indoor source strength (i.e., emission rate), k_{AC} is the AC removal rate coefficient, and k_{other} is the loss rate coefficient associated with all other indoor sinks. Values of k_{other} for compounds that were elevated outdoors compared to indoors when the AC system was off (Figure 5b) were estimated by using measured λ , C_{out} , and C_{in} , and assuming steady state, as shown in Equation 2:

$$k_{other} = \frac{C_{out}p\lambda + \frac{S}{V}}{C_{in}} - \lambda \quad (\text{Eq 2:})$$

S/V was assumed to be much less than $C_{out}p\lambda$ for these compounds for which I/O < 1. Base case values were determined when $p = 0.8$, and the sensitivity of k_{other} to the choice of p was examined by estimating k_{other} for $p = 0.5$ and 1 (Table S2). Compounds with higher O:C ratios (O:C = 1.5 and 0.75) had higher base case values of k_{other} (1.6 and 2.2 h⁻¹) than the compounds with lower O:C ratios (O:C = 0.6 and 0.5; $k_{other} = 0.4$ and 0.2 h⁻¹). p is usually assumed to be 1 for non-polar volatile organic compounds but this is not necessarily the case for oxidized gases. For the more oxidized compounds (higher O:C), loss rate coefficients were substantial even assuming $p = 0.5$. Note that it was not possible to separately determine p and k_{other} in this field campaign. Despite this, it is clear that residential indoor losses of oxidized organic gases can be substantial.

Indoor AC loss rates (k_{AC}) and source strengths (S) for acetic and formic acids

As documented below, k_{AC} was estimated to be 1.5 hr^{-1} for both acetic and formic acids. By first estimating indoor source strengths (S) when the AC system was off, we were then able to estimate AC removal rate coefficients (k_{AC}) for acetic and formic acids when the AC system was on. Assuming a value of k_{other} of 2.0 h^{-1} for acetic acid (O:C = 1) and formic acid (O:C = 2) (based on the base case k_{other} estimates for high O:C compounds described above), estimates of S were made for each sampling day at the top of the first acetic and formic acid peaks at which time we assumed the concentrations had reached steady state (e.g. 9:28 AM on 7/19/18, see Figure 1). To determine S at steady state, Equation 1 becomes Equation 3:

$$S = ((\lambda + k_{AC} + k_{other})C_{in} - C_{out}p\lambda)V \quad (\text{Eq 3:})$$

Using these assumptions, we estimated base case indoor source strengths for acetic and formic acids of $106 \pm 32 \text{ mg h}^{-1}$ and $49.5 \pm 10 \text{ mg h}^{-1}$, respectively. Here, source strengths of these acids are about one order of magnitude higher than source strengths of carbonyl compounds reported elsewhere.^{4,51-53} For acetic and formic acids, these base case source strengths were determined from measured values when the AC system was off ($k_{AC} = 0$). The sources of these acids are unknown. They may come from building materials, or building materials may serve as a large reservoir for these compounds; they may be products of indoor chemistry or microbiology.^{54,55} Using these rates, we report base case estimates of k_{AC} using measured values plus $p = 0.8$ and $k_{other} = 2 \text{ hr}^{-1}$. We then examine the sensitivity of k_{AC} to uncertainty in S . To accomplish this, we use the solution of Equation 1, shown below as Equation 4:

$$C_t = \frac{S}{V(\lambda + k_{other} + k_{AC})} + \frac{p\lambda}{(\lambda + k_{other} + k_{AC})} \times C_{out} + \left(C_0 - \frac{S}{V(\lambda + k_{other} + k_{AC})} - \frac{p\lambda}{(\lambda + k_{other} + k_{AC})} \times C_{out} \right) e^{-(\lambda + k_{other} + k_{AC}) \times t} \quad (\text{Eq 4:})$$

Using the base case estimates of S above, k_{AC} was estimated to be 1.5 hr^{-1} for both acetic and formic acids (by fitting concentration values for periods when the AC system was on; Figure S10). To explore the sensitivity of k_{AC} to S , k_{AC} was calculated for the mean of $S \pm 1$ and 2 standard deviations (Table S3). For $S \pm 1$ standard deviation (74 mg h^{-1} and 138 mg h^{-1} for acetic acid and 39.5 mg h^{-1} and 59.5 mg h^{-1} for formic acid), k_{AC} was 0.5 h^{-1} and 2.7 h^{-1} and 0.8 h^{-1} and 2 h^{-1} for acetic and formic acids, respectively. k_{AC} was much more sensitive to an increase in S than a decrease.

It is important to note that an assumption made in the estimates of S and k_{AC} above is that emissions of acetic and formic acids did not change with AC cycling; this may not be true. If acetic and formic acids exist in a readily available reservoir, such as in wet/dry materials, and there is no internal resistance to emissions, as gas-phase concentrations decrease, the source strengths will increase.⁵⁶ In accordance with Equation 3, as S increases k_{AC} estimates

increase as well; for acetic acid, an increase of S from 106 mg h^{-1} to 170 mg h^{-1} (+ 2 standard deviations) would produce an estimated k_{AC} of 4.0 h^{-1} (Table S3). Because dramatic acetic and formic acid losses correspond precisely with the onset of AC cooling, it appears that liquid water present in the air conditioning system is a major sink for these water-soluble organic acids; using our assumptions, indoor losses of acetic and formic acids ($k_{other} + k_{AC}$) are substantially larger than exfiltration (indoor-to-outdoor air exchange (λ)).

Implications

This paper provides new insights into the sources, sinks, and concentration dynamics of selected WSOGs measured in residences. Since people spend considerable time at home, a location where WSOGs are elevated, the indoor residential environment is a key location for WSOG exposure. This work clearly shows that the lifetimes and fate of WSOGs in indoor air differs from those of non-polar VOCs. Their indoor loss rates (k_{other}) are substantial and may be enhanced at high humidity levels. Loss rate coefficients estimated herein may be useful inputs to indoor air models that will help to further explore indoor chemistry and determine indoor exposures.

We identified, for the first time, the importance of the AC system as a sink for WSOGs in homes, presumably through removal into the AC condensate and wet ductwork; the AC system could alter the indoor composition of WSOGs in other ways as well. It is quite possible that WSOGs deposited to damp surfaces in the AC system provide important nutrients for microbial growth (e.g., on AC coils),^{30,31} and WSOGs emitted by microorganisms (e.g., acetic acid)⁵⁷ could subsequently alter the indoor air composition in occupied spaces; microbial growth in itself has potential implications to air quality and health. It is quite possible that the indoor air composition of WSOGs is altered by reactions driven by water evaporation (condensation/evaporation cycling) on wetted AC surfaces. For example, non-radical reactions between aldehydes and amines have been shown to occur within seconds during water droplet evaporation and form low-volatility brown oligomers.⁵⁸ To some extent, condensation/evaporation cycling may lead to the recycling, rather than the removal of scrubbed WSOGs. The AC system will be a source of volatile organics to occupied spaces if it contributes substantially to microbial growth or if aqueous chemistry on wetted AC ducts (e.g., during condensation/evaporation cycles) and in AC condensate leads to volatile products; it will otherwise be a sink or reservoir.

Roughly 18-50% of homes in the United States are considered to be damp.⁵⁹ In addition to chemistry in AC systems, multiphase (aqueous) chemistry may occur on wetted surfaces in damp homes and could be an important sink, and possible source, of WSOGs in damp homes, as proposed by Duncan et al.² In addition to chemistry in the AC system, aqueous chemistry in damp homes could occur on windows, walls, carpeting, human skin, and in the respiratory tract of residents.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Acetic, formic, and lactic acids concentrations in the room air and temperature and RH at the air supply vent on 7/19/17. When the temperature decreased and RH increased abruptly, acetic and formic acids decreased rapidly, suggesting that these organic acids were taken up into the AC system.

Figure 2. Additional compounds that fluctuate with the AC cooling cycle (7/18/17). I-HR-ToF-CIMS signals shown as rolling averages.

Figure 3.
Lactic acid concentration during the “high occupancy” day (7/20/17).

Figure 4.

Compounds emitted during cooking events (7/23/17). Lactic acid emission rates were 10.9, 16.3, and 10.3 mg h^{-1} per cooking event, when 4 strips of bacon and $\frac{1}{4}$ medium yellow onion were cooked.

Figure 5.

a) Compounds with higher concentrations indoors than outdoors (7/23/17). b) Compounds with higher concentrations outdoors than indoors (7/20/17).

Table 1.

Molecular formulas of compounds detected by I-HR-ToF-CIMS

Molecular formula	Mass + iodide (I-MW = 126.9)	ESI ionization mode (+/-)	O:C	Context	Peak/trough	Indoor/outdoor	Probable compounds	Structures	Henry's Law Constant (M/atm) ¹¹	Sources
CH ₂ O ₂	172.925	n/d	2	AC cycle, indoor elevated	1.7	n/a	Formic acid		9 x 10 ³	Previously measured indoors ^{4,53,54,60}
C ₂ H ₄ O ₂	186.952	-	1	AC cycle, indoor elevated	1.5	n/a	Acetic acid		4 x 10 ³	Previously measured indoors ^{53,54,60}
C ₂ H ₄ O ₃	202.951	n/d	1.5	AC cycle, outdoor elevated, cooking	1.7	0.16	Glycolic acid		2.8 x 10 ⁴	Previously measured indoors ⁴ , outdoors ¹³ , personal care products, ¹² food (vegetables) ³⁶
C ₂ H ₆ O ₂	188.968	+	1	AC cycle, indoor elevated	1.8	9.8	Ethylene glycol		7.3 x 10 ⁴	Building materials ¹⁷
C ₂ H ₆ O ₃	204.967	n/d	1.5	cooking	n/a	n/a	-	-	-	-
C ₃ H ₆ O ₂	200.979	-	0.67	Indoor elevated	-	11.5	Propionic acid		6 x 10 ³	Previously measured indoors ⁴
C ₃ H ₆ O ₃	216.978	-	1	human activity	n/a	n/a	Lactic acid		12 x 10 ⁴	Previously measured indoors ⁴
C ₄ H ₈ O	199.006	+	0.25	cooking	n/a	n/a	Butyraldehyde		8	Food (vegetable cooking) ⁴²
C ₄ H ₈ O ₂	215.005	-	0.5	AC cycle, indoor elevated	1.3	4.2	Butyric acid		1 x 10 ³	Previously measured indoors ⁴
C ₄ H ₈ O ₃	231.004	+	0.75	AC cycle, outdoor elevated, cooking	1.5	0.12	Methyl lactate		1.2 x 10 ⁵	Unknown

Molecular formula	Mass + iodide (I- MW = 126.9)	ESI ionization mode (+/-)	O:C	Context	Peak/ trough	Indoor/ outdoor	Probable compounds	Structures	Henry's Law Constant (M/atm) ¹¹	Sources
							Hydroxybutyric acid		1.2 x 10 ⁵ ^a	Unknown
C ₄ H ₁₀ O ₃	233.020	+	0.75	AC cycle, cooking	1.6	-	Diethylene glycol		5 x 10 ⁵	Solvent ¹⁹
C ₄ H ₁₁ NO	216.036	+	0.25	cooking	n/a	n/a	-	-	-	-
C ₅ H ₈ O ₂	227.016	+	0.4	cooking	n/a	n/a	4-Oxopentanal		3 x 10 ⁴ ^a	Food byproduct ^{15,43}
C ₅ H ₈ O ₃	243.015	n/d	0.6	AC cycle, outdoor elevated, cooking	1.4	0.39	Levulinic acid		4 x 10 ³ ^a	Previously measured indoors ⁴ , skin lipid byproduct ¹⁵
							α-Ketoisovaleric acid		2 x 10 ³ ^a	Food (metabolic byproduct) ³⁸
							Oxopentanoic acid		4 x 10 ³	Previously measured indoors ⁴ , skin lipid byproduct ¹⁵
C ₅ H ₁₀ O ₂	229.032	-	0.4	AC cycle, indoor elevated cooking	1.3	8.5	Valeric acid		2 x 10 ³	Animals ^{2,2}
							3-Methylbutanoic acid		1.6 x 10 ³	Microbial VOC, ⁶¹ food (fatty acid) ⁴⁰
C ₆ H ₈ O ₅	287.025	-	0.83	Cooking	n/a	n/a	α-Ketoadipic acid		2 x 10 ⁸ ^a	Food (metabolic byproduct) ³⁷
C ₆ H ₁₀ O ₃	257.042	n/d	0.5	Outdoor elevated, cooking	-	0.56	Oxohexanoic acid		1 x 10 ³ ^a	Previously measured indoors ⁴ , outdoors, ⁴⁸ food ³⁹

Molecular formula	Mass + iodide (I- MW = 126.9)	ESI ionization mode (+/-)	O:C	Context	Peak/ trough	Indoor/ outdoor	Probable compounds	Structures	Henry's Law Constant (M/atm) ¹¹	Sources
C ₆ H ₁₄ O ₃	261.074	+	0.5	AC cycle, cooking	1.6	-	Dipropylene glycol		5 x 10 ⁵ ^a	Solvent ²⁰
C ₇ H ₆ O ₂	249.021	n/d	0.29	AC cycle, cooking	1.8	-	Benzoic acid		2 x 10 ⁴	Previously measured indoors ⁴ , food (preservative) ⁴⁴
C ₇ H ₁₀ O ₄	285.052	+	0.57	cooking	n/a	n/a	-	-	-	-
C ₇ H ₁₄ O ₂	257.085	+,-	0.29	AC cycle, indoor elevated, cooking	1.4	2.1	Heptanoic acid		1 x 10 ³	Previously measured indoors ⁴ building materials, ²³ food (meat cooking) ⁴¹
C ₈ H ₈ O ₃	279.047	-	0.38	AC cycle	1.4	-	Methylparaben		4.6 x 10 ⁵	Previously measured indoors, personal care products ²⁴
							Methyl salicylate		1.5 x 10 ³	Previously measured indoors ²⁵
C ₈ H ₁₀ O	249.064	+	0.13	cooking	n/a	n/a	-	-	-	-

Molecular formulas ordered by increasing carbon numbers, followed by: mass + iodide detected in L-HR-ToF-CIMS; presence in ESI-QTOF-MS mist chamber samples in the positive (+) or negative (-) mode or not detected (n/d); oxygen-to-carbon ratios; observations concerning concentration dynamics; peak-to-trough ratios of compounds that cycle with AC use; indoor-to-outdoor ratios for compounds that were elevated indoors relative to outdoors or vice versa; probable compound identification; structure; and Henry's Law constant. Finally, previous measurements of the corresponding compound in indoor air or outdoor air or insights pertaining to likely indoor air emissions (e.g., biological compounds present in food, solvents present in indoor building materials).

^aHenry's Law constants were not available, reported value is that of a close isomer or structurally similar compound.