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# Dynamics of residential indoor gas- and particle-phase water-soluble organic carbon: measurements during the CASA experiment†

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Previous time-integrated (2 h to 4 h) measurements show that total gas-phase water-soluble organic carbon (WSOC<sub>g</sub>) is 10 to 20 times higher inside homes compared to outside. However, concentration dynamics of WSOC<sub>g</sub> and total particle phase WSOC (WSOC<sub>p</sub>)—are not well understood. During the Chemical Assessment of Surfaces and Air (CASA) experiment, we measured concentration dynamics of WSOC<sub>g</sub> and WSOC<sub>p</sub> inside a residential test facility in the house background and during scripted activities. A total organic carbon (TOC) analyzer pulled alternately from a particle-into-liquid sampler (PILS) or a mist chamber (MC). WSOC<sub>g</sub> concentrations ( $215 \pm 29 \mu\text{g-C m}^{-3}$ ) were generally 36× higher than WSOC<sub>p</sub> ( $6 \pm 3 \mu\text{g-C m}^{-3}$ ) and 20× higher than outdoor levels. A building-specific emission factor ( $E_f$ ) of  $31 \text{ mg-C h}^{-1}$  maintained the relatively high house WSOC<sub>g</sub> background, which was dominated by ethanol ( $46 \mu\text{g-C m}^{-3}$  to  $82 \mu\text{g-C m}^{-3}$ ). When we opened the windows, WSOC<sub>g</sub> decayed slower ( $2.8 \text{ h}^{-1}$ ) than the air change rate ( $21.2 \text{ h}^{-1}$ ) and  $E_f$  increased ( $243 \text{ mg-C h}^{-1}$ ). The response (increased  $E_f$ ) suggests WSOC<sub>g</sub> concentrations are regulated by large near surface reservoirs rather than diffusion through surface materials. Cooking and ozone addition had a small impact on WSOC, whereas surface cleaning, volatile organic compound (VOC) additions, or wood smoke injections had significant impacts on WSOC concentrations. WSOC<sub>g</sub> concentration decay rates from these activities ( $0.4 \text{ h}^{-1}$  to  $4.0 \text{ h}^{-1}$ ) were greater than the normal operating  $0.24 \text{ h}^{-1}$  air change rate, which is consistent with an important role for surface removal.

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## Environmental significance

People spend a considerable amount of time indoors, and thus the indoor environment is a potentially important exposure location. As part of the Chemical Assessment of Surfaces and Air (CASA) experiment, influences on the concentration dynamics of gas and particle water-soluble organic carbon (WSOC) in indoor air were investigated in a residential test facility. A system for semi-continuous, real-time monitoring of gas and particle WSOC was used to provide quantitative insights into the concentration dynamics of organic matter in indoor air and the role of surfaces as a source, sink and reservoir.

## Introduction

People spend the majority of their time indoors,<sup>1</sup> where they are exposed to elevated air concentrations of many organic

compounds. In fact, total gas-phase water soluble organic carbon (WSOC<sub>g</sub>) concentrations are 10 to 20 times higher inside homes compared to outside, as demonstrated by a study of 13 eastern U.S. homes with 2 h to 4 h integrated measurements.<sup>2</sup>

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Drawing from studies of individual water-soluble compounds, we expect indoor (total) WSOC<sub>g</sub> concentrations would be elevated due to limited outdoor ventilation<sup>3</sup> and that WSOC<sub>g</sub> concentration dynamics would be influenced by a plethora of indoor sources such as material off-gassing,<sup>4–8</sup> oxidation chemistry,<sup>9,10</sup> human occupancy,<sup>8,11</sup> cooking,<sup>12</sup> cleaning,<sup>13</sup> fire-place usage,<sup>14</sup> and other human activities.<sup>6,8</sup> We also expect WSOC<sub>g</sub> to partition to indoor particles, surface films, and other reservoirs, prolonging and altering indoor exposures.<sup>15–19</sup> Additionally, we expect the surface partitioning and chemistry of WSOC<sub>g</sub> (*i.e.*, oxygenated VOCs or OVOCs) to depend on relative humidity, surface properties, and hygroscopicity of surface soiling.<sup>20</sup> For this reason, it is not clear whether emission rates of WSOC<sub>g</sub> from indoor surfaces will be unaffected (as they are for VOCs),<sup>21–23</sup> or will be enhanced (as they are for semi-volatile organic compounds)<sup>24,25</sup> when air concentrations are reduced, *i.e.* due to increased outdoor ventilation. Reactive uptake of water soluble organics by atmospheric waters (*i.e.*, in aerosols, fogs and clouds) is an important source of secondary organic aerosol (SOA) outdoors,<sup>26–28</sup> and reactive uptake may also play a role in the chemistry of damp indoor surfaces. However, only a few of these inferences have been tested in indoor environments, so the sources, sinks, reservoirs, and dynamics of WSOC<sub>g</sub> and particle-phase WSOC (WSOC<sub>p</sub>) in indoor air are not well understood. Furthermore, an understanding the composition of WSOC is important to developing a comprehensive understanding of the chemistry, and yet there is little data to assess the species mass closure of WSOC in indoor air.<sup>2,29</sup>

Insights into the composition and dynamics of WSOC<sub>g</sub> have been provided by recent time-resolved measurements of *individual* compounds in real indoor environments. Proton transfer reaction-mass spectrometry (PTR-MS)<sup>8,30–38</sup> and high-resolution time-of-flight chemical ionization mass spectrometry (HR-ToF-CIMS)<sup>6,29,31–33,39</sup> have been used to identify formulas consistent with a variety of water soluble organic compounds indoors. For example, Tang *et al.* performed PTR-MS measurements in a university classroom and reported masses consistent with water-soluble aldehydes (*e.g.*, acetaldehyde and 4-oxo-pentanal), ketones (*e.g.*, acetone and hydroxyacetone), alcohols (*e.g.*, methanol and ethanol), organic acids (*e.g.*, formic acid and acetic acid) and precursors to WSOC<sub>g</sub> (*i.e.*, terpenes).<sup>8</sup> Furthermore, Tang *et al.* described significant source rates from human occupancy (57%), supply air (35%) and material surfaces (8%).<sup>8</sup> Nonoccupant sources such as material off-gassing were important contributors to the top 20 most abundant compounds that Tang *et al.* measured which were mainly oxygenated gases such as organic acids (*e.g.*, acetic acid), ketones (*i.e.*, acetone), alcohols (*e.g.*, methanol), aldehydes (*e.g.*, acetaldehyde) and C8 aromatics;<sup>8</sup> surface emissions likely included emissions from surface film reservoirs and not just the underlying materials.<sup>16,19,40</sup> Liu *et al.* used HR-ToF-CIMS and reported formulas consistent with nearly 100 organic acids including monoacids, diacids, hydroxy acids, carbonyl acids and aromatic acids, with an average measured carboxylic acid mixing ratio of 6.8 ppbv in a university classroom.<sup>6</sup> Note: we define mixing ratio as the ratio of the number density of

a gaseous compound to the dry air number density (approximately  $2.43 \times 10^{19}$  molecules per cm<sup>3</sup> at standard ambient temperature and pressure) expressed here as parts-per-billion by volume (ppbv). Duncan *et al.* deployed a HR-ToF-CIMS in a single home in North Carolina (NC) and reported formulas consistent with 23 water soluble organic compounds: organic acids, glycols, parabens and methyl esters.<sup>29</sup> Duncan *et al.* quantified a small number of organic acids and determined the most abundant species were acetic ( $30 \mu\text{g m}^{-3}$  to  $125 \mu\text{g m}^{-3}$ ), formic ( $15 \mu\text{g m}^{-3}$  to  $53 \mu\text{g m}^{-3}$ ) and lactic acids ( $2.5 \mu\text{g m}^{-3}$  to  $13.5 \mu\text{g m}^{-3}$ ).<sup>29</sup> Using integrated mist chamber (MC) sampling and total organic carbon (TOC) analysis in 13 homes in the eastern U.S., Duncan *et al.* determined that those same acids comprised 30% to 54% of WSOC<sub>g</sub> ( $87 \mu\text{g-C m}^{-3}$  to  $215 \mu\text{g-C m}^{-3}$ ) in those homes.<sup>2</sup> To our knowledge, that was the first time that total airborne WSOC species mass closure was attempted in homes. However, WSOC species mass closure has not been reported for real-time indoor sampling and a more comprehensive, real-time mass balance is warranted.

Real-time gas-surface dynamics of some common water soluble organic gases has been investigated in field studies in real indoor environments where they were shown to decay at rates faster than the concurrent air change rate (*i.e.*, defined herein as air change rate with outdoor air; ACR; h<sup>−1</sup>) due to substantial surface removal.<sup>29,33</sup> For example, surfaces in an art museum (wood, glass, wallboard, concrete, paint, *etc.*) were found to be significant sinks for emitted acetic and formic acids. Those surfaces became net sources when outdoor ventilation increased.<sup>33</sup> CIMS measurements captured rapid decays and rebounds of small water-soluble organic acids and alcohols measured at the University of Texas at Austin test house (UTest House) at the House Observations of Microbial and Environmental Chemistry (HOMEChem) experiment; this was attributed to substantial gas-surface partitioning dynamics.<sup>19</sup> Duncan *et al.*, observed substantial loss rates coefficients ( $1.6 \text{ h}^{-1}$  to  $2.2 \text{ h}^{-1}$ ) for compounds with oxygen to carbon ratios greater than 0.75 using HR-ToF-CIMS real-time monitoring even though the home outdoor ventilation rate was only  $0.4 \text{ h}^{-1}$  (ACR).<sup>29</sup> Decay rates were elevated for 13 compounds (C1 to C7 organic acids and possible glycols and parabens) with air conditioning (AC) usage likely due to enhanced surface removal in cold, damp AC ducts and loss to AC condensate.<sup>29</sup> Since then, decay and rebounding of water soluble organic compounds with AC cycling has been observed in other indoor environments<sup>19,41</sup> and in modeled results.<sup>42</sup> Additionally, partitioning of water soluble organic gases to wet aerosols and subsequent reaction is important to the chemistry of outdoor SOA formation and similarly, reactive uptake in surface-associated water could be important indoors, where surface soiling is common and surface to volume (S/V) ratios are large, especially in damp homes.<sup>43</sup> Thus, time-resolved WSOC<sub>g</sub> measurements may prove valuable to the assessment of partitioning and chemistry in indoor environments.

WSOC<sub>p</sub> concentrations, behavior and composition in residential air are even less well understood than WSOC<sub>g</sub>.<sup>44</sup> WSOC<sub>p</sub> can be of outdoor origin (*i.e.*, through infiltration and outdoor ventilation)<sup>45–47</sup> or indoor origin (*i.e.*, primary sources and

secondary formation through oxidation chemistry).<sup>17,48–55</sup> Outdoors, WSOC<sub>p</sub> can account for the majority of organic carbon (OC) in aerosols in non-pristine locations ranging from 40% to over 90% by mass on a carbon basis.<sup>44</sup> The composition of organic carbon in indoor aerosols is poorly characterized,<sup>56</sup> but some fraction is predicted to be water-soluble.<sup>44,57,58</sup> Duarte and Duarte tabulated a list of the few studies on WSOC<sub>p</sub> in different indoor scenarios including measurements of  $0.3 \pm 0.02 \mu\text{g-C m}^{-3}$  in a church and  $0.7 \mu\text{g-C m}^{-3}$  to  $1.4 \mu\text{g-C m}^{-3}$  in retirement homes.<sup>44</sup>

For these reasons, we investigated the dynamics of airborne total water-soluble organic carbon (WSOC<sub>g</sub> and WSOC<sub>p</sub>) at the unoccupied and unfurnished National Institute of Standards and Technology (NIST) Net-Zero Energy Residential Test Facility (NZERTF) during unperturbed periods and a variety of scripted activities as part of the Chemical Assessment of Surfaces and Air (CASA) experiment. This study provided a unique opportunity to measure total airborne WSOC concentrations and dynamics and assess the role of building materials and their associated reservoirs in a well-characterized building that lacked the typical complexity of occupied residences (*i.e.*, high human occupancy, regular activities, and furnishings). These measurements provide useful insights into WSOC concentration mass closure, distribution (gas-, particle-, and surface-phases), perturbation by activities and modulation by indoor surfaces.

## Materials & methods

As part of the CASA experiment at the NZERTF, an on-line total carbon analyzer alternated every 6 min between a mist chamber (MC) and particle-into-liquid sampler (PILS) for semi-continuous, real-time monitoring (4 s resolution) of (total) WSOC<sub>g</sub> and WSOC<sub>p</sub>, respectively. Measurements were conducted from March 7<sup>th</sup>, 2022 to April 11<sup>th</sup>, 2022, during business days (Monday to Friday) and hours (8 am to 6 pm) inside the unfurnished, unoccupied NZERTF located on the NIST Campus in Gaithersburg, MD. Measurements were also obtained immediately outside the NZERTF on April 11<sup>th</sup>.

### Net-zero energy residential test facility (NZERTF)

The NZERTF is 3-bedroom, 3-bathroom home with a basement (380 m<sup>3</sup>), main house (1<sup>st</sup> and 2<sup>nd</sup> floors; 624 m<sup>3</sup>)<sup>59</sup> and attic (99 m<sup>3</sup>), and S/V ratio of 2.7 (m<sup>-1</sup>) associated with the superficial surface areas (1681 m<sup>2</sup>) of painted walls, painted ceilings, and wooden floors in the main house. The building was tightly constructed with low-VOC emitting building materials, particularly those with no formaldehyde additives (NAF) and with low acetic acid emissions.<sup>59,60</sup> The NZERTF was constructed of NAF paints/coatings, adhesives/sealants, insulation binders, and plywood, and with materials tested using VOC emissions testing standards set by the California Department of Public Health and/or the California Air Resources Board (CARB).<sup>61</sup> Furthermore, gypsum board was mechanically fastened without use of adhesives and only adhesives/sealants with limited quantities of acetic acid were used when needed.<sup>61</sup> The building

ventilation system was operated at an outdoor ACR of  $0.24 \text{ h}^{-1}$  under normal conditions to meet American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) Standard 62.2. A variable heat recovery ventilator (HRV) exchanged indoor air with outdoor air. A heating and air conditioning (HAC) system constantly circulated air among rooms of the main house and basement with an internal circulation rate of about  $1.3 \text{ h}^{-1}$ . Filters rated at a minimum efficiency reporting values (MERV) of 7 and 8 were used in the HRV and HAC systems, respectively. Air circulated between the attic and the house *via* passive vents. The house temperature and RH were generally 24 °C and 30% under normal unperturbed conditions.

### Experimental design of CASA

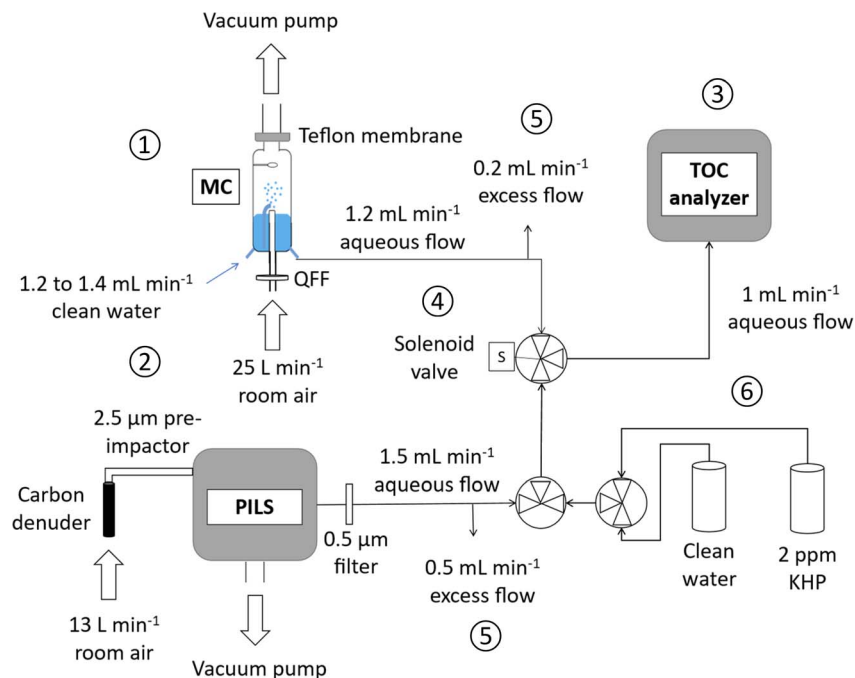
The CASA experiment was designed to assess how air concentrations and surfaces responded to perturbations in conditions. There were 8 types of perturbation experiments conducted: cooking, cleaning, or injections, *i.e.*, pesticide products, a mixture of volatile organic compounds (VOCs) called “CASA cocktail,” wood smoke, ammonia (NH<sub>3</sub>), carbon dioxide (CO<sub>2</sub>), or ozone (O<sub>3</sub>). Detailed descriptions of perturbations performed inside the NZERTF are summarized in ESI Section S1.† Specific days were dedicated to each experiment type where activities or injections were made repeatedly 2 to 4 times under normal outdoor ventilation (windows and doors closed). Some experiments were repeated under both low and high RH conditions on different days. Wood smoke injections occurred late in the campaign to avoid changing the house background before other experiments. Prior to, and in between, perturbation experiments, the house was operated in a standard mode to allow the building conditions to stabilize and allow researchers to measure the house background, which reflects emissions from the building itself.

### Air sampling for WSOC<sub>g</sub> and WSOC<sub>p</sub>

Indoor air was sampled for WSOC inside the dining room on the 1<sup>st</sup> floor of the NZERTF (Section S2, Fig. S1†) using a MC, PILS, and TOC analyzer (Fig. 1) located on the enclosed porch connected to the test house (Fig. S1 and S2†). Sample lines were extended into the dining room of the house through drilled holes in the blocked door shared between the porch and dining room in the locations noted on Fig. S1.† The sampling inlets (Fig. S3†) were positioned 2 m above the floor and extended 2 m into the dining room. A 7.6 m long 0.9525 cm inner diameter (ID; 3/8 inch ID) polytetrafluoroethylene (PTFE) tube was used to collect  $25 \text{ L min}^{-1}$  of indoor air into the MC. A 12 m long 0.9525 cm outer diameter (OD; 3/8 inch OD) refrigeration grade copper tube was used to collect  $13 \text{ L min}^{-1}$  of indoor air into the PILS from the same location. Indoor air was drawn continuously by the MC and PILS throughout each experiment. Occasionally equivalent sample lines were extended outdoors to enable collection of residential outdoor WSOC concentrations.

### Mist chamber (MC) – WSOC<sub>g</sub>

WSOC<sub>g</sub> was continuously scrubbed into a  $1.2 \text{ mL min}^{-1}$  flow of water by pulling  $25 \text{ L min}^{-1}$  of filtered indoor air through



**Fig. 1** MC/PILS-TOC system for sampling of total airborne WSOC. The MC (1) and PILS (2) continuously collect WSOC<sub>g</sub> and WSOC<sub>p</sub>, respectively, from room air into aqueous flows. These were analyzed in an on-line TOC analyzer (3) alternatively via a 6 min timed solenoid 3-way valve switch (4). Sample flow was sent to excess (5) when either instrument was not on-line with the TOC analyzer. Clean water or 2 ppm<sub>m</sub> potassium hydrogen phthalate (KHP) standard was directed to the TOC via manual 3-way valves (6) for water flushes and calibrant checks as needed (QFF: quartz fiber filter).

a 190 mL modified mist chamber, also known as Cofer scrubber,<sup>57,58</sup> equipped with a 10 mL water reservoir (Fig. 1). Water exiting the MC was analyzed semi-continuously for TOC, alternating at 6 min intervals with TOC analysis of the PILS sample flow. For some experiments, only the MC was sampled, and near-real-time results are reported here. MCs use a continuous, fine aqueous mist providing large air–water surface area to efficiently scrub water soluble gases from the sampled air into a refluxing water reservoir that can be analyzed.<sup>62,63</sup> Field deployed MCs have been mostly operated as integrated samplers both outdoors<sup>26,64</sup> and indoors,<sup>2,29</sup> but at least one study used a system of two MCs in parallel for real-time sampling of WSOC outdoors.<sup>65</sup> For the present study, a single MC was modified and configured to operate as a real-time sampler to capture WSOC<sub>g</sub> dynamics when coupled to an on-line TOC analyzer. To convert the MC into a real-time sampler, a new exit nozzle was added opposite from the MC inlet nozzle to accommodate a continuous  $1.2 \text{ mL min}^{-1}$  outlet flow (peristaltic pump-controlled) that was supplied to the TOC analyzer. The nozzle nearest the inner capillary tube where water is drawn into the mist was used as the inlet nozzle (Fig. S4†). The MC was initially loaded with 10 mL of deionized water daily and the meniscus level of bulk water inside the mist chamber was maintained by controlling the water flow rate at the MC inlet nozzle using a peristaltic pump set between  $1.2 \text{ mL min}^{-1}$  to  $1.4 \text{ mL min}^{-1}$  to replace water removed in exit flow and loss to evaporation.

The MC sampled particle-free indoor air by placing a quartz fiber filter (QFF; 47 mm) upstream; this filter provided a low-

pressure drop that does not interfere with creating a mist as described by Duncan *et al.* 2019.<sup>29</sup> Particle-free air entering the glass mist chamber encountered a refluxing water mist from the 10 mL reservoir of bulk water. A hydrophobic Teflon membrane (47 mm) at the air flow exit prevented loss of water droplets; which refluxed back into the water reservoir.<sup>63</sup> The MC was operated with water reservoir and mist droplet residence times of 8.3 min and 0.43 s, respectively; the droplet residence time refers to the time a sprayed droplet in the mist is suspended and in contact with sampled air.

Several quality control procedures were implemented (Section S3†). Briefly, dynamic blanks were collected by running the MC at the same water flow rate while setting the air flow rate to zero (*i.e.*, without generating mist). The WSOC<sub>g</sub> limit of detection (LOD), estimated as three times the standard deviation ( $\sigma$ ) of the dynamic blank, was  $0.5 \mu\text{g-C m}^{-3}$ . The collection efficiency of WSOC<sub>g</sub> in MC samplers is largely controlled by Henry's law partitioning constants ( $K_H$ ).<sup>2,63,66</sup> The mean ( $n = 10$ ) collection efficiency of the MC operated in continuous sampling mode was 57% for the WSOC<sub>g</sub> mixture found in indoor air inside an empty university seminar room/teaching kitchen at UNC, determined by operating two real-time MCs in series. It was 63%, 75%, 74%, and 41% for glyoxal ( $K_H$ :  $4\,000\,000 \text{ M atm}^{-1}$ ), formic acid ( $K_H$ :  $8000 \text{ M atm}^{-1}$ ), acetic acid ( $K_H$ :  $4000 \text{ M atm}^{-1}$ ), and acetone ( $K_H$ :  $31 \text{ M atm}^{-1}$ ), respectively. The 57% collection efficiency, determined in the university teaching kitchen, was used as an effective collection efficiency to correct measurements from the NZERTF under the assumption that the relative composition of WSOC<sub>g</sub> was similar in both locations.



Experimental set-up (Fig. S5A†), sample data (Fig. S5B†), collection efficiency calculation (eqn (S1)†) and tabulated collection efficiency results (Table S1†) are shown in Section S3.† Based on the TOC accuracy ( $\pm 15\%$ ), air flow uncertainty ( $\pm 5\%$ ) and relative standard deviation of dynamic blank concentrations ( $\pm 1\%$ ), the uncertainty for  $\text{WSOC}_g$  measurements was estimated, by propagation of error, to be  $\pm 16\%$ .

### Particle-into-liquid sampler (PILS) – $\text{WSOC}_p$

$\text{WSOC}_p$  was continuously measured using a PILS and TOC analyzer at 6 min intervals, alternating with TOC analysis of MC sample flow. The PILS uses supersaturated water vapor to condense water on aerosol particles, increasing particle diameters and impaction collection efficiencies. The aerosol is impacted onto a liquid water flow that can be analyzed.<sup>67,68</sup> PILS instruments have previously been coupled to on-line TOC analyzers to measure  $\text{WSOC}_p$  in outdoor environments, and the method is well-detailed in previous literature.<sup>69–71</sup> The PILS sampled indoor air through a parallel-plate carbon strip denuder (Sunset Laboratory Inc.) to remove organic gases (breakthrough: 11%; Section S3†) and a 2.5  $\mu\text{m}$  aerodynamic diameter cut point round jet impactor (Brechtel Manufacturing Inc.) that removed larger particles, so that the instrument collected  $\text{WSOC}_p$  in  $\text{PM}_{2.5}$  into a 1.5  $\text{mL min}^{-1}$  aqueous flow. The aqueous sample flow was filtered of insoluble particles using a 0.5  $\mu\text{m}$  in-line liquid PEEK (polyetheretherketone) filter before introduction to the TOC analyzer.

Measures to describe the quality control of  $\text{WSOC}_p$  are summarized here and provided in more detail in Section S3.† For the dynamic blank, a filter was placed at the PILS sample air inlet to remove particles from the sampled air. The LOD was 2.0  $\mu\text{g-C m}^{-3}$  calculated as  $3\sigma$  of the dynamic blank. These LOD values are higher than reported for outdoor  $\text{WSOC}_p$  measurements,<sup>69</sup> likely because more variable (and higher) indoor  $\text{WSOC}_g$  concentrations resulted in more variable (and higher) dynamic blank values.  $\text{WSOC}_p$  measurements were corrected for  $\text{WSOC}_g$  breakthrough. The PILS collection efficiency is reported to be 97% in the particle size range of 0.03  $\mu\text{m}$  to 10  $\mu\text{m}$ .<sup>67</sup> The on-line PILS-TOC method was previously shown to agree within 10% of traditional integrated filter methods;<sup>72,73</sup> and have an estimated precision of 10%.<sup>69</sup>

### Total organic carbon analysis

The TOC was calibrated one week prior to the start of the study using commercial potassium hydrogen phthalate (KHP) calibration standards (range: 0.25  $\text{ppm}_m$  to 5  $\text{ppm}_m$ ), a sucrose verification standard (1  $\text{mg-C L}^{-1}$ ) and verified calibration blanks (low TOC water); calibration checks were performed throughout the campaign. Note: we define  $\text{ppm}_m$  as the grams of compound per million grams of solution. The TOC was operated to perform real-time analysis with  $\pm 15\%$  accuracy, 2% precision, 4 s analysis time, 3.25 min response and a dynamic analytical range of 0.20  $\text{ppb}_m$  to 10  $\text{ppm}_m$ . The TOC analyzer sampled the liquid flows at a flow rate of 1.1  $\text{mL min}^{-1}$  through an approximately 1 m long, 0.0254 cm ID, 0.1588 cm OD (0.01 inch ID, 1/16 inch OD) PTFE tubing; excess flow from the MC or

PILS was sent to waste or collected in vials and stored frozen. Due to the TOC instrument response time (3.25 min) and the residence time in tubing (about 45 s), our system had an approximately 4 min system response time to changes in  $\text{WSOC}$  in indoor air.

### Daily operation

Each sampling day began with either a 20 min calibrant check and/or 20 min clean water flush of the TOC analyzer before collection of dynamic blanks and sampling of indoor air. A 20 min calibrant check was performed 1 to 2 times a week using a 2.0  $\text{ppm}_m$  KHP solution followed by a 20 min de-ionized water flush. The measured calibrant concentration was  $1.915 \text{ ppm}_m \pm 0.076 \text{ ppm}_m$  over the duration of the study. MC and PILS dynamic blanks ( $n = 3$ ) were then measured alternately in 6 min intervals for a total of 36 min for blank-correction of  $\text{WSOC}$  in indoor air. Next,  $\text{WSOC}_g$  and  $\text{WSOC}_p$  in indoor air were continuously collected, switching every 6 min between the MC and PILS, respectively, for the duration of the day. The last 2 min of data before each valve switch was used. Measurements of indoor air typically began at least 36 min prior to experimental perturbations in the house to obtain average ( $n = 3$ ) unperturbed  $\text{WSOC}_g$  and  $\text{WSOC}_p$  concentrations (house background). On days with early perturbation start times, dynamic blank collection was skipped (2 to 3 times a week) to ensure enough time to collect indoor background measurements before perturbations began. A single day was selected for extended collection of the KHP standard, clean water, and dynamic blanks (Fig. S6†). In addition, airborne  $\text{WSOC}$  was measured indoors and then outdoors for 2 h each on a single day (April 11<sup>th</sup>) toward the end of the campaign (Section S4, Fig. S7†).

### Calculations

The building-specific  $\text{WSOC}_g$  emission rate ( $E_f$ ) without the introduction of purposeful sources was calculated using eqn (1):

$$E_f = \text{ACR} \times V \times (C_{\text{in}} - C_{\text{out}}) \quad (1)$$

where  $V$  is the volume of the main house,  $C_{\text{in}}$  is the mean  $\text{WSOC}_g$  house background concentration, and  $C_{\text{out}}$  is the outdoor  $\text{WSOC}_g$  concentration measured on April 11 (mean:  $5 \pm 1 \text{ } \mu\text{g-C m}^{-3}$ ; see Fig. S7†).

### Additional measurements

The following additional measurements were performed in the NZERTF and are described in detail in Section S5.† Gas-phase mixing ratios of C2 to C4 water-soluble aldehydes, ketones, and alcohols were measured using a Vocus proton-transfer-reaction (PTR-MS) mass spectrometer.<sup>74</sup> A fast-scanning gas chromatograph<sup>75</sup> was periodically interfaced to the inlet of the PTR-MS which provided chromatographic separation for each sampled ion and enabled correction for interferences. The gas-phase mixing ratios of C1 to C5 water-soluble carboxylic acids (*i.e.*, formic, acetic, propanoic, butanoic, and pentanoic acids) were measured using a Time-of-Flight Chemical Ionization

Mass Spectrometer (ToF-CIMS) equipped with iodide ( $I^-$ ) reagent ions.<sup>76,77</sup> Mixing ratio uncertainties for formic, acetic, propanoic, and pentanoic acids, ethanol and acetaldehyde are estimated to be within 20%; they are likely factor of two for acetone, butanone, and hydroxyacetone. Formaldehyde and formic acid mixing ratios were measured on the 1<sup>st</sup> floor and outside the NZERTF using a quantum cascade tunable infrared direct absorption spectrometer (QC-TILDAS; LOD of 0.1 ppb<sub>v</sub>). O<sub>3</sub> mixing ratios were measured using an ozone analyzer (LOD: 0.5 ppb<sub>v</sub>) on the 1<sup>st</sup> floor and outside the NZERTF.

## Results

### WSOC in house background

The vast majority of WSOC in the house background was in the gas phase (Section S6, Table S2†). On average, the house background WSOC<sub>g</sub> concentration was 36 times higher than WSOC<sub>p</sub>. In other words, only 3% of total airborne WSOC was in the particle phase ( $F_p$ ). The mean WSOC<sub>g</sub> and WSOC<sub>p</sub> in the house background were  $215 \mu\text{g-C m}^{-3} \pm 29 \mu\text{g-C m}^{-3}$  and  $6 \mu\text{g-C m}^{-3} \pm 3 \mu\text{g-C m}^{-3}$ , respectively. Using an average organic molecular weight to carbon weight for gaseous water soluble organic matter (WSOM<sub>g</sub>) of 2.1, estimated as described below, and an organic molecular weight to carbon mass for particle-phase water-soluble organic matter (WSOM<sub>p</sub>) of 2, previously reported for outdoor aerosol,<sup>44,78</sup> the house background concentrations of WSOM<sub>g</sub> and WSOM<sub>p</sub> were  $452 \mu\text{g m}^{-3}$  and  $12 \mu\text{g m}^{-3}$ , respectively. The 2.1 value is the average molecular weight-to-carbon mass ratio for the compounds identified in this study and for elemental formulas of species detected *via* positive mode high-resolution quadrupole time-of-flight mass spectrometry with an electrospray ion source (ESI-QTOF-MS) in indoor mist chamber sampling by Duncan *et al.*<sup>2</sup> (Table 2 in Duncan *et al.*).<sup>2</sup>

WSOC<sub>g</sub> in the house background was substantial (Table S2†), suggesting the importance of contributions from house reservoirs such as building materials to indoor air WSOC concentrations. The indoor-outdoor ratio (I/O) of WSOC<sub>g</sub> measured on April 11<sup>th</sup> was approximately 19 (outdoor WSOC<sub>g</sub> concentration:  $5 \mu\text{g-C m}^{-3} \pm 1 \mu\text{g-C m}^{-3}$ ; Fig. S7†); indoor WSOC<sub>p</sub> was consistently equal to or greater than the outdoor concentration (WSOC<sub>p</sub> I/O  $\geq 1$  using the LOD as an upper-bound estimate for outdoor WSOC<sub>p</sub> concentrations below LOD). The reported I/O ratio could be underestimated because it was measured on a day when the house was more open than usual (*i.e.*, frequently opened or propped open front door) resulting in lower indoor air concentrations of airborne WSOC; indoor WSOC<sub>p</sub> concentrations were near or below LOD (Fig. S7†). The fact that a dramatic reduction in the WSOC<sub>g</sub> concentration was also observed with window opening, discussed later, also supports the conclusion that there is a substantial indoor source of WSOC<sub>g</sub>.

The building-specific emission rate of WSOC<sub>g</sub> was roughly  $31 \text{ mg-C h}^{-1}$ . Normalized to the area associated with painted walls, painted ceilings, and wooden floors in the main house, the surface area-specific  $E_f$  was approximately  $18 \mu\text{g-C h}^{-1} \text{ m}^{-2}$ . Average whole-house emission factors for various VOCs which

included water-soluble organic acids, alcohols, aldehydes, ketones and glycols were previously measured over a 15 month sampling period 1 year after the NZERTF was constructed (2013).<sup>59</sup> When summed, the average emission factors from January to July 2014 equated to an average WSOC<sub>g</sub> emission rate of  $148 \text{ mg-C h}^{-1}$  (using only measured compounds with  $K_H > 10 \text{ M atm}^{-1}$ );<sup>59</sup> note this study did not directly measure total WSOC and so the sum of measured water-soluble species provides a lower bound for total WSOC<sub>g</sub> emissions. Our  $E_f$  suggests at least a 79% reduction in (total) WSOC<sub>g</sub> emissions in the 8 years that followed; more substantial reduction likely occurred in the first few years after construction.<sup>79</sup>

The sum of measured water-soluble species accounted for 51% to 72% of the WSOC<sub>g</sub> house background mass (Fig. 2; Table S3†). The remaining approximately 28% to 49% is expected to include organic compounds with  $K_H$  values from  $10^1 \text{ M atm}^{-1}$  to greater than  $10^3 \text{ M atm}^{-1}$ , which we verified we collected with efficiencies of 41% to greater than 75%. The most abundant species from each compound class were ethanol ( $46 \mu\text{g-C m}^{-3}$  to  $82 \mu\text{g-C m}^{-3}$ ), acetic acid ( $12 \mu\text{g-C m}^{-3}$  to  $24 \mu\text{g-C m}^{-3}$ ), acetone ( $11 \mu\text{g-C m}^{-3}$  to  $16 \mu\text{g-C m}^{-3}$ ), and acetaldehyde ( $7 \mu\text{g-C m}^{-3}$  to  $9 \mu\text{g-C m}^{-3}$ ), which have been measured in a variety of indoor air studies and have known building- and human-derived sources of acetic acid,<sup>2,6,29,32,33,80,81</sup> acetone,<sup>2,30,32,33,80–84</sup> acetaldehyde.<sup>23,30,33,81–87</sup> Notably, they could be emitted from building materials such as wood-based products,<sup>86–89</sup> paints,<sup>33,90,91</sup> and finishes (*e.g.*, adhesives).<sup>59,92,93</sup> Oxidation chemistry is also a potential source.<sup>34,94–96</sup>

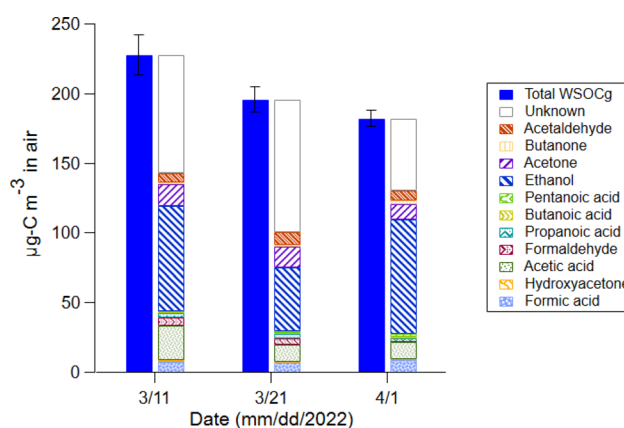


Fig. 2 WSOC<sub>g</sub> (blue bar) measured with the MC with TOC analyzer and reconstructed WSOC<sub>g</sub> (multicolored stack) which was taken to be the sum of carbon in measured individual water-soluble organic gases ( $K_H > 13 \text{ M atm}^{-1}$ ) and the remaining mass of carbon (difference between WSOC<sub>g</sub> and sum of species; white) from unperturbed periods (*i.e.*, the house background) on March 11<sup>th</sup>, March 21<sup>st</sup>, and April 1<sup>st</sup> (see Tables S2 and S3†). Compounds are stacked from most (bottom) to least (top) water soluble. The concentration of total WSOC<sub>g</sub> was corrected for the effective WSOC<sub>g</sub> collection efficiency (57%). Error bars represent  $\pm 1\sigma$ . "House background periods" refer to time periods immediately before conditions were perturbed by scripted activities (typically 1 h to 2 h before the perturbation), 12 h to 16 h after the last perturbation, and sometimes shortly (1 h to 2 h) after perturbations that did not induce an observable change in WSOC<sub>g</sub>.

## WSOC during perturbations

Fig. 3, 4 and Table 1 show the effect of several perturbations on  $WSOC_g$  and  $WSOC_p$  in the house (NZERTF). Some perturbations increased (e.g., cooking with vinegar, wood smoke additions,

CASA cocktail addition, ozone injection, and closing windows) or decreased (e.g., surface cleaning and window opening)  $WSOC$ , but others did not result in a measurable change in airborne  $WSOC$  (e.g., pesticide product additions, inorganic

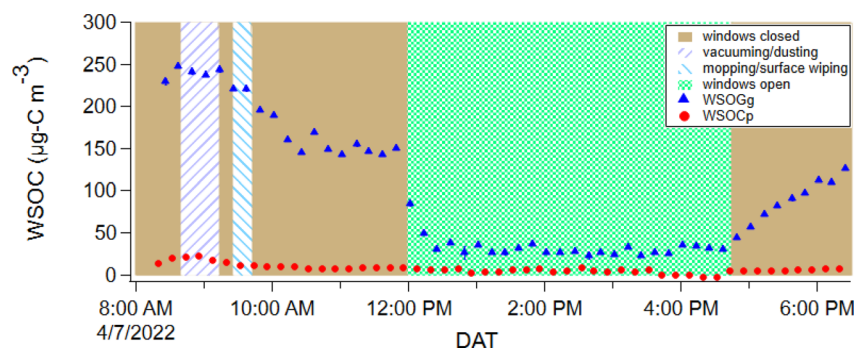


Fig. 3 Indoor  $WSOC_g$  (blue triangles) and  $WSOC_p$  concentrations (red dots) during surface cleaning of the wood smoke contaminated house (cleaning times indicated by purple and blue-bands), window opening (green band) and subsequent window closing (brown band). Error bars represent measurement uncertainties ( $\pm 1 \sigma$ ) and are mostly smaller than the data point markers (DAT = date and time).

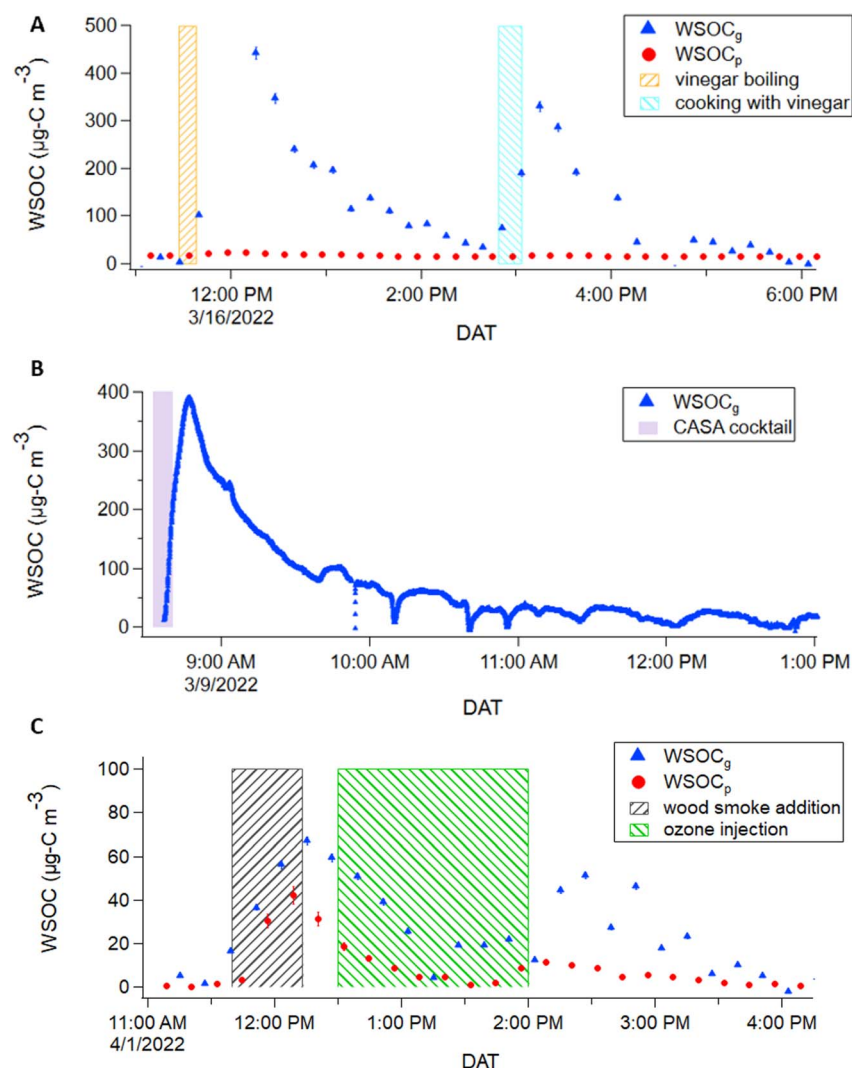


Fig. 4 Indoor  $WSOC_g$  (blue triangles) and  $WSOC_p$  concentrations (red dots) in indoor air during selected perturbations.

**Table 1** Change in WSOC<sub>g</sub> and WSOC<sub>p</sub> peak heights ( $\Delta$ WSOC) during perturbations compared to average unperturbed house background concentration<sup>a</sup>

| Perturbation            | Duration (min) | Amount added                                                                       | $\Delta$ WSOC based on peak ( $\mu\text{g-C m}^{-3}$ ) |                   | House background ( $\mu\text{g-C m}^{-3}$ ) |                   |
|-------------------------|----------------|------------------------------------------------------------------------------------|--------------------------------------------------------|-------------------|---------------------------------------------|-------------------|
|                         |                |                                                                                    | WSOC <sub>g</sub>                                      | WSOC <sub>p</sub> | WSOC <sub>g</sub>                           | WSOC <sub>p</sub> |
| Surface cleaning        | 45             | —                                                                                  | (–) 75                                                 | 9                 | 215 $\pm$ 29                                | 6 $\pm$ 3         |
| Air cleaning            | 60             | —                                                                                  | No change                                              | No change         |                                             |                   |
| Window opening          | 315            | —                                                                                  | (–) 119                                                | (–) 4             |                                             |                   |
| Window closing          | —              | —                                                                                  | 98                                                     | 3                 |                                             |                   |
| Cooking without vinegar | 40             | Varied by meal <sup>b</sup>                                                        | No change                                              | No change         |                                             |                   |
| Cooking with vinegar    | 10–15          | 30 mL                                                                              | 329–444                                                | No change         |                                             |                   |
| CASA cocktail           | 8              | 0.5 mL of each chemical                                                            | 100–390                                                | 20                |                                             |                   |
| Wood smoke addition     | 2              | 0.5 g woodchips burned                                                             | 25–220 <sup>c</sup>                                    | 16–100            |                                             |                   |
| Pesticide addition      | 0.5            | 425–502 g sprayed                                                                  | No change                                              | No change         |                                             |                   |
| Ozone injection         | 90             | 70 ppb peak levels                                                                 | 25–80                                                  | 7–12              |                                             |                   |
| Acid/base addition      | 30             | 500 g min <sup>–1</sup> CO <sub>2</sub><br>40 mg min <sup>–1</sup> NH <sub>3</sub> | No change                                              | No change         |                                             |                   |

<sup>a</sup> The “(–)” denotes a decrease in WSOC, positive values denote an observed maximum peak above the house background, and “no change” denotes perturbations that did not induce a measurable change in WSOC in our system. <sup>b</sup> See ESI Section S1. <sup>c</sup> The 220  $\mu\text{g-C m}^{-3}$  peak was from a smoke injection on the morning of March 29<sup>th</sup> that was much higher than any other observed peak for this perturbation type despite similar mass of woodchips burned. The next highest peak concentration was 93  $\mu\text{g-C m}^{-3}$ .

acid/base additions, portable air cleaner operation and selected cooking activities that did not include vinegar).

Surface cleaning inside the wood smoke contaminated NZERTF on April 7<sup>th</sup> caused a reduction in WSOC<sub>g</sub> concentrations (Fig. 3). First, a small peak of WSOC<sub>p</sub> (8  $\mu\text{g-C m}^{-3}$ ) was observed as researchers were in the house preparing to clean, presumably because of resuspension of particles from researchers' movement.<sup>97</sup> Then, following vacuuming, dusting, mopping and surface wiping, WSOC<sub>g</sub> concentrations decayed at a rate of 0.42 h<sup>–1</sup>, decreasing by 39% after surfaces were cleaned, which may be due to removal of WSOC reservoirs on wood smoke-contaminated surfaces. Li *et al.* observed concentration reductions of individual water-soluble organic gases, specifically formic acid and formaldehyde, during the same time period inside the NZERTF and previously drew the same conclusion.<sup>77</sup> Air cleaners used on a separate day after smoke injections (March 24) did not result in an observable change in WSOC (see Table 1, Section S7 and Fig. S8†).

The “Window Opening and Closing” perturbation (Fig. 3) provided evidence consistent with emissions and air concentrations being influenced by surface reservoirs. WSOC<sub>g</sub> concentrations were diluted upon window opening and reduced by 81% from 147  $\mu\text{g-C m}^{-3}$  to 28  $\mu\text{g-C m}^{-3}$  before rebounding after windows were closed, increasing from 28  $\mu\text{g-C m}^{-3}$  to 125  $\mu\text{g-C m}^{-3}$ . The dramatic decrease with window opening and subsequent rebound provided additional evidence that WSOC in building materials/reservoirs are responsible for the high house background. WSOC<sub>g</sub> decayed at a rate of 2.8 h<sup>–1</sup> post window opening due to dilution with outdoor air and an increased air change rate (outdoor ACR = 21.2 h<sup>–1</sup>; see Section S8, Fig. S9 and S10†). The decrease in air concentrations also likely increased emissions from surfaces reservoirs, causing WSOC<sub>g</sub> concentrations to decay slower than they would if the emission rates were constant. The estimated  $E_f$  of WSOC<sub>g</sub>

during the steady-state period of window opening was 301 mg-C h<sup>–1</sup>, which is much greater than the steady-state  $E_f$  associated with the typical house background (31 mg-C h<sup>–1</sup>) and before windows were opened (21 mg-C h<sup>–1</sup>). Approximately 90 minutes after closing windows, the WSOC<sub>g</sub> concentration had nearly returned to pre-perturbation levels. The characteristic rate for WSOC<sub>g</sub> rebound from window closing was 0.8 h<sup>–1</sup>, which is faster than the ventilation rate (outdoor ACR). Gas exchange with surface reservoirs is likely responsible for this rapid rise in the indoor air concentration of WSOC<sub>g</sub>.<sup>16,19,40</sup> Effects on WSOC<sub>p</sub> concentrations were too small to measure but concentrations appear to slightly decrease upon window opening and increase after window closing. It is important to note that the measurement of such a high outdoor ventilation rate in the fully open house (*i.e.*, during the window opening perturbation; Section S1†) is expected to be somewhat uncertain due to increased variations in interzonal mixing, but even an error of 50% would still produce a substantially increased  $E_f$  during the period of window opening.

The change in WSOC from cooking activities depended on the food items cooked. Cooking bacon, peppers, and tater tots (pan fry or air fry) did not result in a measurable response in either gas or particle phase WSOC, likely due to low water-solubility of cooking emissions (*e.g.*, cooking oils and long-chain fatty acids). However, cooking with vinegar did produce a large WSOC<sub>g</sub> response due to acetic acid emissions. The first peak (approximately 450  $\mu\text{g-C m}^{-3}$ ) in Fig. 4a shows a large WSOC<sub>g</sub> peak from boiling 2 tablespoons of balsamic vinegar to produce a balsamic glaze. The second peak (approximately 350  $\mu\text{g-C m}^{-3}$ ) shows the signal from cooking a similar glaze with 2 tablespoons of balsamic vinegar, but with vegetables included in the dish. The smaller peak is likely due to the other food ingredients absorbing some of the acetic acid leading to less vinegar evaporating from the glaze. Although an increase in



indoor  $\text{PM}_{2.5}$  was observed during the second cooking event (with vegetables; up to  $10 \mu\text{g m}^{-3}$  to  $15 \mu\text{g m}^{-3}$ ),  $\text{WSOC}_p$  did not increase.

The addition of the CASA cocktail (Fig. 4b) and wood smoke (Fig. 4c) significantly increased indoor WSOC concentrations over background levels, but pesticide addition did not result in a measurable change in WSOC (Table 1). The pesticide product contained water insoluble or sparingly soluble chemicals that were not expected to be captured in our system (see ESI Section S1†). Injection of the CASA cocktail, which contained many compounds that are relatively water soluble, resulted in a  $100 \mu\text{g-C m}^{-3}$  to  $390 \mu\text{g-C m}^{-3}$  increase in  $\text{WSOC}_g$  (Table 1; Fig. 4b). Wood smoke injections increased  $\text{WSOC}_g$  and  $\text{WSOC}_p$  by  $25 \mu\text{g-C m}^{-3}$  to  $220 \mu\text{g-C m}^{-3}$  and  $16 \mu\text{g-C m}^{-3}$  to  $100 \mu\text{g-C m}^{-3}$ , respectively (Table 1; Fig. 4c).  $\text{WSOC}_p$  concentrations were highest for wood smoke, with gas to particle concentration ratios of approximately 1 to 2. The WSOC system was run for only 1 of the 2 high RH (approximately 74% RH) smoke injections, precluding investigation of an RH effect on airborne WSOC from wood smoke injections. Li *et al.* reported the bulk organic chemical composition of the CASA campaign wood smoke aerosols was 95% organic, 3% nitrate, 1% sulfate, and 1% ammonium, and that gaseous wood smoke emissions included formic acid, acetic acid, and formaldehyde.<sup>77</sup> Based on Li *et al.* organic aerosol data<sup>77</sup> and an OM:OC conversion factor of 2.0 derived from fireplace wood combustion,<sup>78,98</sup> about 32% to 67% of wood smoke organic aerosol mass (OM) is water soluble.

The addition of inorganic species (*i.e.*, ozone,  $\text{NH}_3$ , or  $\text{CO}_2$ ; Section S9†) had moderate to no impact on WSOC levels measured by our system. Although the MC chamber is well-suited for collecting oxidation products,<sup>63</sup> ozone additions did not consistently produce a measurable increase in  $\text{WSOC}_p$  or  $\text{WSOC}_g$ . A change in WSOC in our system was observed for 3 out of the 9 ozone additions that took place during times of WSOC sampling, perhaps due to the high loading of  $\text{WSOC}_g$  in the house air to begin with (house background). In some cases spikes in WSOC were observed when ozone was added shortly after wood smoke injections (Table 1, Fig. 4c); the mixing ratio of  $\text{O}_3$  in the main house was typically about 10 ppb<sub>v</sub> when not intentionally perturbed. Additions of basic  $\text{NH}_3$  and acidic  $\text{CO}_2$  did not induce a measurable change in WSOC, but measurements of gas-phase total inorganic carbon (TIC) in the system became more sensitive to indoor  $\text{CO}_2$  after  $\text{NH}_3$  injection, presumably due to pH elevation of MC water as discussed in Section S9 (see Fig. S11†).

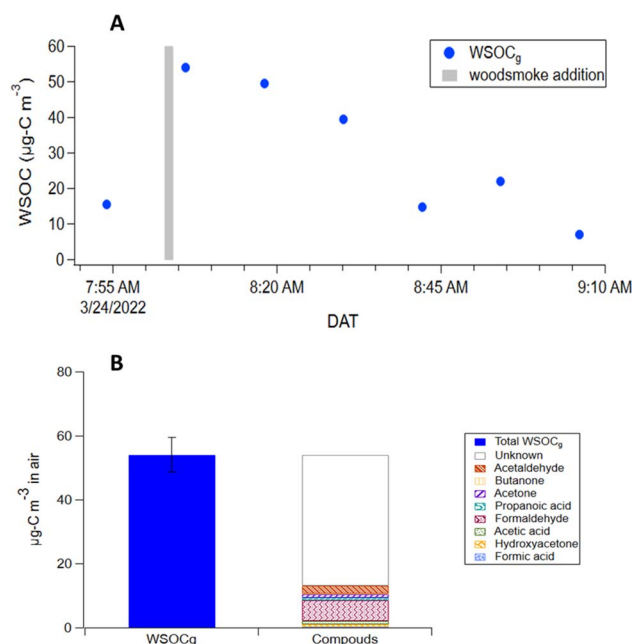
$\text{WSOC}_g$  peaks decayed at rates ranging from  $0.4 \text{ h}^{-1}$  to  $4.0 \text{ h}^{-1}$  across the perturbations (Table 2). These rates are 1.7 to 16.7 times faster than the ventilation rate, suggesting the presence of surface reservoirs that amplified the loss rates of  $\text{WSOC}_g$  in air. When surface reservoirs and gas-phase concentrations approach steady-state, outdoor ventilation and exfiltration become the dominant removal mechanisms. Decay rates were influenced by internal mixing ( $1.3 \text{ h}^{-1}$ ), surface removal rates, and ventilation ( $0.25 \text{ h}^{-1}$ ), slowing with time. For example, decay of the CASA cocktail injection was rapid to begin with (*initial* decay rate:  $2.6 \text{ h}^{-1} \pm 0.02 \text{ h}^{-1}$ ), perhaps associated

**Table 2** Decay rate for each perturbation that resulted in a  $\text{WSOC}_g$  peak<sup>a</sup>

| Perturbation                | Peak decay rates ( $\text{h}^{-1}$ ) | House parameters ( $\text{h}^{-1}$ ) |             |
|-----------------------------|--------------------------------------|--------------------------------------|-------------|
|                             | $\text{WSOC}_g$                      | Internal mixing                      | Outdoor ACR |
| Wood smoke                  | 4.0–0.4                              | 1.3                                  | 0.24        |
| Window opening              | 2.8                                  |                                      |             |
| CASA cocktail               | 2.6–1.0                              |                                      |             |
| Cooking with vinegar        | 2.0–1.0                              |                                      |             |
| Ozone                       | 1.6                                  |                                      |             |
| Window closing <sup>b</sup> | 0.80–0.20                            |                                      |             |
| Surface cleaning            | 0.42                                 |                                      |             |

<sup>a</sup> The house background WSOC signal was subtracted to isolate the contribution from perturbations. (A) Cooking with vinegar, (B) CASA cocktail (VOC mixture) injection; only  $\text{WSOC}_g$  was measured to focus on gas-phase and (C) wood smoke followed by ozone addition. Error bars represent measurement uncertainties ( $\pm 1 \sigma$ ) and are mostly smaller than the data point markers. <sup>b</sup> Rebound rate during  $\text{WSOC}_g$  house background recovery.

with some mixing with the rest of the house, but also uptake by surfaces (see Fig. S12†). The initial peak decay rate held for about 15 minutes before the decay rate reduced (*later* decay rate:  $1.7 \pm 0.02 \text{ h}^{-1}$ ), indicating that surface reservoirs were beginning to shift away from being a net sink, but had not yet become a net source (see Fig. S12†). Long-term decay (*i.e.*, longer than 2 h to 3 h) of WSOC when concentrations were just elevated over



**Fig. 5** (A)  $\text{WSOC}_g$  concentrations in indoor air during wood smoke injection. (B) Mass closure of peak  $\text{WSOC}_g$  concentration observed during wood smoke injection. Specifically, panel (B) includes  $\text{WSOC}_g$  (blue bar) measured with the MC with TOC analyzer and reconstructed  $\text{WSOC}_g$  (multicolored stack) which was taken to be the sum of carbon in measured individual water-soluble organic gases ( $K_H > 13 \text{ M atm}^{-1}$ ) and the remaining mass of carbon (difference between  $\text{WSOC}_g$  and sum of species; white).

normal conditions and associated variability were not captured in our system. After internal mixing is complete and there is neither net surface uptake nor removal, decay rates reduce to the ventilation rate, consistent with tracer gas ( $\text{SF}_6$ ) decay.

Wood smoke injections introduced water soluble organic gases in indoor air that were not detected in the house background. Based on the mass closure on peak  $\text{WSOC}_g$  concentrations ( $54.1 \mu\text{g-C m}^{-3}$ ) during wood smoke injections, 75% (by mass) of  $\text{WSOC}_g$  in the wood smoke was uncharacterized and 25% was composed of gases also detected in the house background (Fig. 5). The most abundant of the characterized fractions was formaldehyde ( $6.5 \mu\text{g-C m}^{-3}$ ) and acetaldehyde ( $2.6 \mu\text{g-C m}^{-3}$ ), which comprised 17% of peak  $\text{WSOC}_g$  during the perturbation.

## Discussion

The concentrations and dynamics of  $\text{WSOC}_g$  and  $\text{WSOC}_p$  were semi-continuously monitored in real-time. Airborne  $\text{WSOC}$  in the test house background mostly resided in the gas phase and not particle phase (see Table S2†), which was predicted by Weschler and Nazaroff to be true for individual compounds that partition strongly to surfaces.<sup>16</sup> The small fraction in the particle phase ( $F_p = 0.03$ ) also suggests that indoor particles in the test house would have a small impact on  $\text{WSOC}_g$  dynamics,<sup>16</sup> likely because airborne particles are removed *via* outdoor ventilation and contribute negligibly to total surface area and volume compared to that of the building structure.<sup>16,99</sup>  $\text{WSOC}_p$  ranged from  $3 \mu\text{g-C m}^{-3}$  to  $10 \mu\text{g-C m}^{-3}$  in the house background. This is comparable in magnitude to the average  $7 \mu\text{g-C m}^{-3}$  of organic carbon (OC) in  $\text{PM}_{2.5}$  that Polidori *et al.* measured in 173 occupied homes across CA, TX, and NJ as part of the Relationship of Indoor, Outdoor and Personal Air (RIOPA) study;<sup>55</sup> although the Polidori *et al.* measurements would have included water insoluble organic compounds such as oily fatty acids from cooking emissions that would not have been captured in our system.

The house background of  $\text{WSOC}_g$  ( $215 \mu\text{g-C m}^{-3}$  on average) compares to  $\text{WSOC}_g$  concentrations reported for some occupied homes.<sup>2</sup> Duncan *et al.* performed extensive measurements of  $\text{WSOC}_g$  concentrations in 13 homes in the eastern U.S., reporting a range of  $87 \mu\text{g-C m}^{-3}$  to  $215 \mu\text{g-C m}^{-3}$  and I/O ratios of 10 to 20.<sup>2</sup> The Duncan *et al.* study homes were regularly occupied, cooked in, cleaned, more loosely constructed and likely built of more conventional materials than the NZERTF.<sup>2</sup> The CASA  $\text{WSOC}_g$  concentrations (this study) were on the upper end of the Duncan *et al.* range, which may be due, at least in part, to the NZERTF being more air tight ( $0.24 \text{ h}^{-1}$ ) than homes investigated by Duncan *et al.* ( $0.3$  to  $0.8 \text{ h}^{-1}$ ). Although buildings constructed of low-VOC emitting materials tend to maintain lower VOC concentrations than typical buildings,<sup>85,100–102</sup> outdoor air change rates are known to have the strongest influence on indoor VOC levels.<sup>85,103,104</sup> The CASA  $\text{WSOC}_g$  house background was also similar to the sum of measured reactive organic carbon species during the HOMEChem study when that home was unoccupied (median indoor =  $223 \mu\text{g-C m}^{-3}$ ; median outdoor =  $54 \mu\text{g-C m}^{-3}$ ).<sup>105</sup> However, it must be noted that the

HOMEChem measurements included some compounds with low water solubility and did not include all water soluble species.

The high  $\text{WSOC}_g$  concentration from house background emissions is also consistent with observations of individual water soluble organic gases that contributed to “high baselines” of VOCs in other houses.<sup>81,89</sup> For example, Arata *et al.* and Liu *et al.* determined individual water soluble organic gases (*i.e.*, acetic acid, formic acid and methanol) dominated house background emissions inside the unoccupied UTest House<sup>81</sup> and an occupied California home.<sup>89</sup> Methanol was not directly measured during our study because of the insensitivity of iodide-HR-ToF-CIMS to mono-alcohols<sup>76</sup> and the poor transmission of low mass-to-charge ions through the ion quadrupole guide of the Vocus PTR-MS.<sup>74</sup>

Building-associated emissions (*e.g.*, structural materials, finishing materials, and paint) and/or surface reservoirs, maintained a high house background concentration of  $\text{WSOC}_g$  which was dominated by ethanol (23% to 45% of  $\text{WSOC}_g$ ). Ethanol mixing ratios in indoor air are typically associated with human-activities (*e.g.*, spikes in ethanol during cooking, cleaning, and consuming alcohol) and not continuous material emissions,<sup>81,89</sup> so the consistently high background of ethanol inside the unoccupied NZERTF is unusual. In a previous indoor air quality study on the NZERTF, ethanol was identified as the dominant VOC and had an average emission factor of  $64 \text{ mg-C h}^{-1}$  that remained constant over a 15 month sampling period (June 2013 through July 2014). During the previous study, Poppendieck *et al.* observed large spikes in ethanol mixing ratios during maintenance of the ground source heat pump (GSHP).<sup>102</sup> The potential for contaminated building materials to be a long-term source of ethanol warrants further investigation.

Typically, small organic acids have been the most abundant  $\text{WSOC}_g$  in measured indoor air.<sup>2,29,94</sup> For example, Duncan *et al.* determined formic, acetic and lactic acids made up 30% to 54% of  $\text{WSOC}_g$  across studied (occupied) homes and the only alcohols identified were butanol and 2-butoxyethanol.<sup>2</sup> In the current study, measured organic acids accounted for 12% to 16% of  $\text{WSOC}_g$ . The  $7 \mu\text{g-C m}^{-3}$  to  $9 \mu\text{g-C m}^{-3}$  of formic acid and  $12 \mu\text{g-C m}^{-3}$  to  $24 \mu\text{g-C m}^{-3}$  of acetic acid reported here for the NZERTF fall into reported ranges for the acids in indoor air,<sup>2,5,6,29,94,106</sup> but the acetic acid concentrations were about 3 to 4 times smaller than the average concentrations reported by Duncan *et al.* ( $34 \mu\text{g-C m}^{-3}$  to  $87 \mu\text{g-C m}^{-3}$ ).<sup>2</sup> This, in part, may be related to materials selection in NZERTF construction. Both formaldehyde and acetic acid were reported to have lower concentrations in the NZERTF than other new/existing homes.<sup>59,107</sup> In addition, occupancy, regular human activities, and consumer product usage likely played a role in higher acetic acid concentrations reported in the Duncan *et al.* study.<sup>2</sup>

A total of 28% to 49% of  $\text{WSOC}_g$  in the NZERTF house background and 75% of  $\text{WSOC}_g$  during contrasting chemical wood smoke infiltration was unidentified at the molecular level. The unidentified house background mass may include: lactic acid, propylene glycol, ethyl acetate, butanol, 2-butoxyethanol, hexanone, 4-oxopentanal, various amines, amides, and organophosphates, which have been identified (based on elemental

formula) in previous mist-chamber studies in residences,<sup>29</sup> phenol and benzaldehyde,<sup>59</sup> which were measured previously in the NZERTF,<sup>59</sup> and propanol and methanol, quantified in other indoor studies.<sup>30,80</sup> The unidentified mass during wood smoke infiltration may include glycolic acid, phenols, furanones, furfurals, oxobutanoic acid, and hydroxybenzaldehyde.<sup>14,108–111</sup>

Water is expected to be an important component of shallow and deep surface reservoirs and has been demonstrated to facilitate surface uptake of water-soluble organic gases.<sup>20</sup> It is worth noting that the aqueous concentration of WSOC<sub>g</sub> scrubbed into the MC bulk water under unperturbed conditions was 4.4 mg-C L<sup>-1</sup>, on average (correcting for collection efficiency). The WSOC (aq) concentrations in MC water could provide an order-of-magnitude estimate of WSOC concentrations in NZERTF aqueous surface films from the partitioning of WSOC<sub>g</sub> in the test house, particularly in deep reservoirs that are hard to access and measure; however, aqueous concentrations of ionizable species (*i.e.*, acids/bases) may depend on pH of surface-associated water.

## Implications

Decay rates that were larger than the ventilation rate, followed by concentration rebound when windows and doors were closed after periods of elevated outdoor ventilation, demonstrate the substantial role that surface reservoirs play in WSOC<sub>g</sub> concentration dynamics (*i.e.*, the building surfaces themselves, irrespective of house activities). Previous studies point to differences in the behavior of VOCs compared to semi-volatile organic compounds (SVOCs) in response to window opening and closing; comparison with these past studies aids our understanding of the behavior of WSOC<sub>g</sub>. Although adequate ventilation reduces airborne concentrations, it does not reduce or generally influence building material emission rates of nonpolar VOCs because slow bulk diffusion within deep reservoirs in the material limits the emission rate.<sup>21–23</sup> SVOC emission rates are typically enhanced when the concentration gradient between the material and air increases (*i.e.*, by increasing ventilation), suggesting emission is not limited by diffusion in the material (*i.e.*, SVOCs are readily available from near surface reservoirs).<sup>24,25</sup> This is because SVOCs are more uniformly distributed in their host materials and evaporate more slowly at the surface than VOCs.<sup>24,25</sup> We observed that WSOC<sub>g</sub> emissions are enhanced at elevated ventilation, similar to the emission behavior of SVOCs and individual polar VOCs (*e.g.*, formaldehyde).<sup>22,85,104</sup> This behavior suggests that WSOC (or oxygenated VOCs) are readily available from near surface reservoirs and emissions are not limited by diffusion in the materials. The indoor WSOC<sub>g</sub> concentration reduced by 81% from 147 µg-C m<sup>-3</sup> to 28 µg-C m<sup>-3</sup> during the period of elevated outdoor ventilation associated with open windows which was 5.6 times higher than outdoors (*I/O* = 5.6). If emission rates were instead constant and independent of the ventilation rate, the *I/O* ratio would have approached 1.0 and the WSOC<sub>g</sub> concentration would have been reduced by 95% to 7 µg-C m<sup>-3</sup>.

## Limitations

Although this study was performed inside a test house, data was discussed in the context of related indoor measurements from literature that were often performed in real, occupied homes. The homes across various indoor air studies are not identical buildings and will have considerable variations in conditions (*e.g.*, ventilation rate, dimensions, contents, materials, outdoor air composition, and human activities). Major differences between the NZERTF and typical homes include a lack of substantial occupancy, furniture, exposure history (*e.g.*, years of cooking emissions), the use of low-VOC emitting building materials in construction, and building envelope air leakage rates at the lower end of the range for typical homes. Therefore, comparisons to the measurements taken inside the NZERTF test house are used to provide insights into how the building (*i.e.*, walls, flooring, and ceilings) in the absence of typical features of occupied residences may contribute to and control airborne WSOC, and how perturbations induce spikes of WSOC above the house background. The high house background prevented measurements of relatively small changes in WSOC<sub>g</sub>. Also, it should be noted that a QFF was used to remove particles upstream of the MC sampler. Organic gases can adsorb to QFFs, reducing measured WSOC<sub>g</sub> concentrations until gases come into equilibrium between the QFF and the gas phase. Thus, reported WSOC<sub>g</sub> concentrations should be considered lower bound values.

## Disclaimer

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## Data availability

All data are available on request.

## Author contributions

MW: writing – original draft, review and editing; conceptualization, methodology, investigation, formal analysis, data curation, visualization. GCM: writing – review and editing, conceptualization, methodology, investigation, supervision. KB: writing – review and editing, methodology, supervision. JL: writing – review and editing, investigation, formal analysis, data curation. JCD: writing – review and editing, investigation, formal analysis. HNH: writing – review and editing, investigation, formal analysis, data curation. KM: writing – review and editing, investigation, formal analysis. LM: writing – review and editing, investigation, formal analysis. MEV: writing – review and editing, conceptualization, methodology, supervision,

funding acquisition, project administration. DKF: writing – review and editing, conceptualization, methodology, supervision, funding acquisition, project administration. JA: writing – review and editing, conceptualization, methodology, supervision, funding acquisition. DP: writing – review and editing, conceptualization, methodology, investigation, resources, project administration. BJT: writing – review and editing, conceptualization, methodology, validation, supervision, funding acquisition.

## Conflicts of interest

There are no conflicts of interest to declare.

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