Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting information

Residential water-soluble organic gases: Chemical characterization of a substantial contributor to indoor exposures

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Participant questionnaire

This questionnaire was provided to participants who volunteered for the indoor sampling campaign. Questions were asked and answered verbally. Table S1 provides respective answers for each home.

How do you heat your home? Natural gas furnace, Oil furnace, Wood/ pellet stove, Electric heating, Other:

Do you have a gas or electric stove? Gas, Electric

Do you have an exhaust fan above your stove? Yes, No
If yes, do you use it when you use the stove? Yes, No, Sometimes. When? _____
If yes, does it vent outside or inside above the stove? Outside, Inside

What food have you cooked or heated up in the past twenty-four hours and how did you cook it? _____

Do you use candles, incense or air fresheners in the home? Yes, candles, Yes, incense, Yes, candles, No
If yes, how frequently do you use them and where? _____

Have you done any remodeling to the home or are you aware of any remodeling since it was built? Yes, No
If yes, what has been done and when? _____

Have any of the interior rooms in the home been painted in the last year? Yes, No
If yes, when, where, and what type of paint was used? _____

Have you installed any new carpeting in the past year? Yes, No
If yes, where and when? _____

Have you installed any new wood flooring in the past year? Yes, No
If yes, where and when? _____

Have you brought in any new furniture in the past year (such as couches, ottomans, tables, chairs, etc)? Yes, No
If yes, what pieces of furniture and where? _____

Do you have any hobbies that release "smelly" compounds such as painting, wood working, nail painting, kids' crafts, etc.? Yes, No
If yes, which hobbies and when was the last time they were done? _____

Are there any office appliances such as printers, copiers, or scanners in the home? Yes, No
If so, what are they and where are they located? _____

Are there any pets in the home? Yes, No

If yes, what type and how many of each? _____

Are there any plants in the home? Yes, No
If yes, what type, where, and how many? _____

Do you have any dry-cleaned clothes in the home? Yes, No
If yes, when was the last time you brought dry cleaning into the home? _____

Have you or a professional used any pesticides, termiticides, or insecticides in the past year in the home? Yes, myself, Yes, professional, No

If yes, what was used, where, and when? _____

Do you have an attached garage? Yes, No

If yes, do you park your car in it or do you have other gasoline burning engines in it such as lawn mowers, weed wackers, or leaf blowers? Yes, car (gasoline/ diesel (circle one)), Yes, other two stroke engines: _____, No

If yes, do you store gasoline in containers in the garage? Yes, No

Do you use any air purifiers such as HEPA filters, ozone generators, or ionizers? Yes, HEPA filter, Yes, ozone generator, Yes, ionizer, Yes, other type of air purifier. Please specify: _____, No

When was the last time any cleaning agents were used in the home such as Pinesol, bleach, Windex, etc.? _____

What exactly were the cleaning agents? Feel free to go and check if you can't remember. _____

When was the last time the main area of the house was vacuumed? _____

Does your vacuum have a HEPA filter? Yes, No, Don't know

Are you aware of any mold or mildew in the house (including bathrooms and basements)? Yes, No

If yes, where? _____

Are you currently using central air conditioning or air conditioning window units? Yes, central air conditioning,

Yes, air conditioning window units, No

Do you currently have any windows open? Yes, No

If yes, where? _____

If yes, are you using window fans? Yes, No

Has anyone smoked anything in the home in the last year? (for example: cigarettes, hooka, marijuana, e-cigarettes) Yes, No

If yes, how often and when was the last time? _____

For calculation purposes, what is the gross annual income for all family members in the household? Less than or equal to $23,850, More than $23,850, Don't know, Wish not to an

Table S1. Participant questionnaire responses. All homes were non-smoking. No participants brought dry cleaning in their homes within a week prior to sampling.

Home #	Stove type	If stove exhaust fan present, is it used? Vented?	Food cooked previous 24-hrs	Candles, incense, or air freshener use in last week?	Remodeling or new furniture installed in the past year?	"Smelly" hobbies?	Pets?	Plants?	Office appliances?	Pesticides, termiticides, insecticides used inside/ directly outside?
1	gas	sometimes, outside	eggs, red meat, pasta	no	yes	no	dogs and bird	leafy plant, kitchen herb garden	printer	yes
2	electric	sometimes, inside	eggs	soy candles	yes	painting furniture	no	no	no	no
3	electric	sometimes, outside	Mexican food	no	yes	nail painting, glue	cats, fish	cut flowers	laser printer	yes
4	electric	yes, inside	n/a	no	yes	no	dogs	leafy plants	laser printer	no
5	electric	no	pasta, bread, coffee	incense, candles	yes	nail painting	dog	yes	no	no
6	gas	yes, outside	chicken, pasta, vegetables, oatmeal, coffee	no	no	no	fish	cacti, leafy plants, flowering plants, succulents	laser printer	yes
7	gas	yes, inside	n/a	no	yes	no	no	kitchen herb garden	printer and scanner	no
8	gas	yes, inside	red meat, coffee	air fresheners	yes	no	dog	cactus, leafy plants	inkjet printer, scanner, copier unit	no
9	electric	yes, inside	eggs, chicken, vegetables	no	yes	wood-working	dogs	no	printer, copier, scanner unit	yes
10	gas and electric	yes, outside	bread	air fresheners	yes	no	dog, cats	flowering plants	front sitting room/ office	no
11	electric	no	n/a	no	no	no	dog	no	printer, office	no
12	gas	yes, outside	bread, pasta, vegetables, chocolate dessert, coffee	no	yes	no	cats	cacti	upstairs	yes
13	electric	sometimes, inside	Chinese food, Indian food	no	yes	no	no	flowering plants	printer, scanner unit	yes

Home #	Attached garage?	Car, two-stroke engines, or gasoline storage inside?	Air purifiers?	Cleaning agents used in last 24hrs?	Vacuum in last 24hrs? HEPA filter?	Mold or mildew in house?	AC?	Windows open?
1	yes	yes	no	Pine-sol	yes, yes	basement	central	no
2	no	n/a	AC filter	natural all-purpose cleaning agent	no	no	window unit	yes
3	yes	yes	no	no	no	bedroom, kitchen	central	no
4	no	n/a	no	Windex	no	no	central	no
5	no	n/a	no	-	no	no	central	yes
6	yes	yes	no	Windex	no	bathroom, basement	no	no
7	yes	yes	no	-	no	no	central	no
8	yes	yes	HEPA filter	natural antibacterial cleaner	yes, yes	basement	no	no
9	no	n/a	no	-	yes, yes	no	no	no
10	yes	yes	no	table wipes	yes, no	no	no	no
11	no	n/a	no	-	no	no	central	no
12	no	n/a	no	Windex, bleach	no	no	no	no
13	no	n/a	HEPA filter	bleach	yes, no	bedroom	central	no

Table S1. (continued)

Calculation of air exchange rates

Estimated air exchange rates were calculated using Equation S1 from Chan et al. 2005[1]:

$$AER\ [h^{-1}] = 48\ \left(\frac{2.5\ m}{H}\right)^{0.3}\ \frac{NL}{H \times F} \quad \text{(S1)}$$

where H = building height (in meters), NL = normalized leakage (function of year built and floor area), F = scaling factor = 16. Since all homes were above the poverty line, NL was calculated as shown in Equation S2:[1]

$$NL = e^{11.1-\left(1.07\times10^{-2}\times\ year\ built\right)-(2.20\times10^{-3}\times\ floor\ area)} \quad \text{(S2)}$$

Note that changes in air exchange rate with variations in indoor-outdoor temperature differences and wind speed are not evident in Equation S1.

ESI-QTOF-MS example spectrum

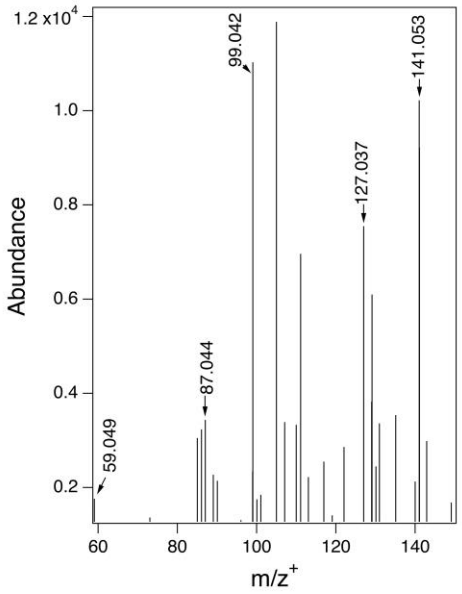

Figure S1. Example spectrum from m/z$^+$ 59 to 150 for Home 3 minus the spectrum from a deionized water blank.

Instrument precision and accuracy information

For TOC, the analytical accuracy of the standard TOC concentrations was 2%, field blanks averaged 7 ± 2.5 µM-carbon (not subtracted from samples), and the analytical precision (calculated as the pooled coefficient of variation of duplicate analyses of the *same samples*) was 10%. The analytical accuracies of the standards for acetic and formic acids were 27 and 12.5% respectively; the analytical precision for acetic and formic acids (calculated as the same way as the TOC analytical precisions) were 5 and 1%, respectively; and the method precisions for acetic and formic acid (calculated as the pooled coefficient of variation of the same bulk sample analyzed on *different days*) was 26 and 10%, respectively.

Mist chamber characterization

In theory, sampling for 10-minutes with Cofer mist chambers will collect compounds with Henry's law constants $>10^3$ M atm^{-1} with 100% efficiency.[2] In practice, Spaulding et al. (2002) found that glyoxal, methylglyoxal, hydroxyactone, and glycoaldehyde, which all have Henry's law constants over 10^3 M atm^{-1}, had collection efficiencies of >80%.[2] Recently, Hennigan et al. (2018) determined collection efficiencies of approximately 100% when sampling for 15-minutes for several WSOGs with Henry's law constants over 10^3 M atm^{-1} (including acetic and formic acids).[3] Since mist chamber water refluxes continuously during collection, longer collection times will result in higher concentrations of sampled compounds in the mist chamber water, but with lower collection efficiency, also supported by Hennigan et al. (2018).[3] Theoretically, if collection times are long enough, the concentrations of all compounds present in the mist chamber water will reach Henry's law equilibrium with their concentrations in the sampled air. At equilibrium, the proportion of a compound collected is determined by its Henry's law constant; an increasing fraction will be collected with increasing Henry's law constant (increasing water solubility). Once

equilibrium is achieved, additional net collection is zero. In this work, we aim to collect the ambient mix of WSOGs at high enough concentrations for analysis. Thus, sample collection times were selected to balance the desire for high collection efficiencies with the desire for high concentrations in the mist chamber water.

To examine the effect of sample collection time on concentrations of WSOG in mist chamber water samples, we conducted the following experiment in an additional home. First, four mist chambers sampled for a total of 1-hour, concurrently (25 mL of DI water; air flow rate of 25 L min^{-1}). The first mist chamber collected eight 7.5-min samples; the second collected four 15-min samples, the third collected two 30-min samples; and the fourth collected one 1-hour sample, which were composited respectively. Immediately after, the four mist chambers sampled for a total of 8 hours, concurrently. The first mist chamber collected 8 – 1-hour samples, the second 4 – 2-hour samples, the third 2 – 4-hour samples and the fourth 1 – 8-hour sample. Again, each mist chamber's samples were composited for analysis. See Figure S1 for schematic. This complete set of measurements was conducted three times over three days in the same home.

To determine mist chamber collection efficiencies, we collected 2-hour samples of residential indoor air 10 times with two sets of paired mist chambers in series (four mist chambers total). The order of the mist chambers was reversed after each test. Concentrations of WSOG, acetic acid, and formic acid in front and back mist chambers are provided in Figure S2. Collection efficiencies were calculated using Equation S3, as derived in the SI of Spaulding et al. 2002.[2] This equation takes into consideration breakthrough through the first mist chamber in the series as well as through the backup mist chamber. 2-hour sampling resulted in collection efficiencies of 43 ± 10% for total WSOG, 56 ± 4% for acetic acid, and 76 ± 5% for formic acid. Shorter sampling periods would have provided higher collection efficiencies and thus better precision for WSOG

and organic acid concentrations, but would have reduced the number of additional compounds that we could detect because the samples would be less concentrated. Given the goals of this work, we compromised with a two-hour collection time.

$$CE = 1 - \frac{C_2}{C_1} \tag{S3}$$

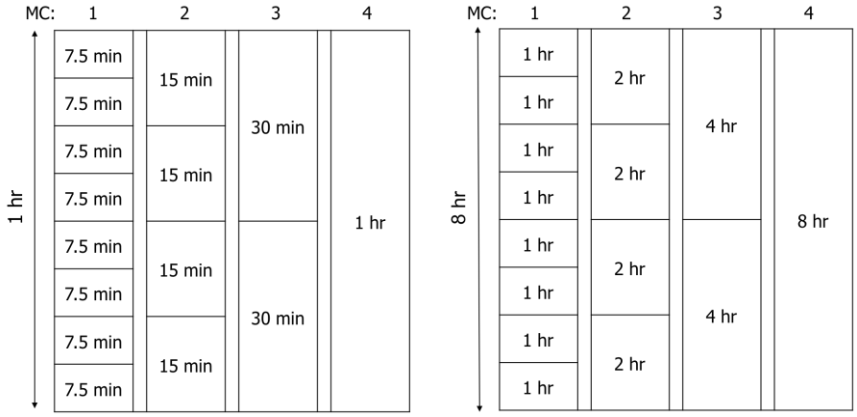

Figure S2. Sampling protocol to examine mist chamber collection and sampling time. The first set of four mist chambers (left) sampled the same air for 1 hour. The same four mist chambers then sampled the same air for 8 hours (right). MC = mist chamber

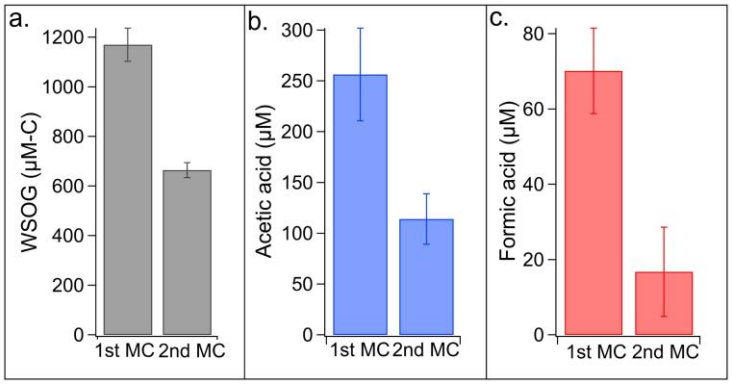

Figure S3. MC = mist chamber a) WSOG concentrations in first and second mist chamber in series. b) Acetic acid concentrations in first and second mist chamber in series. c) Formic acid concentration in first and second mist chamber in series.

Statistically significant WSOG regression

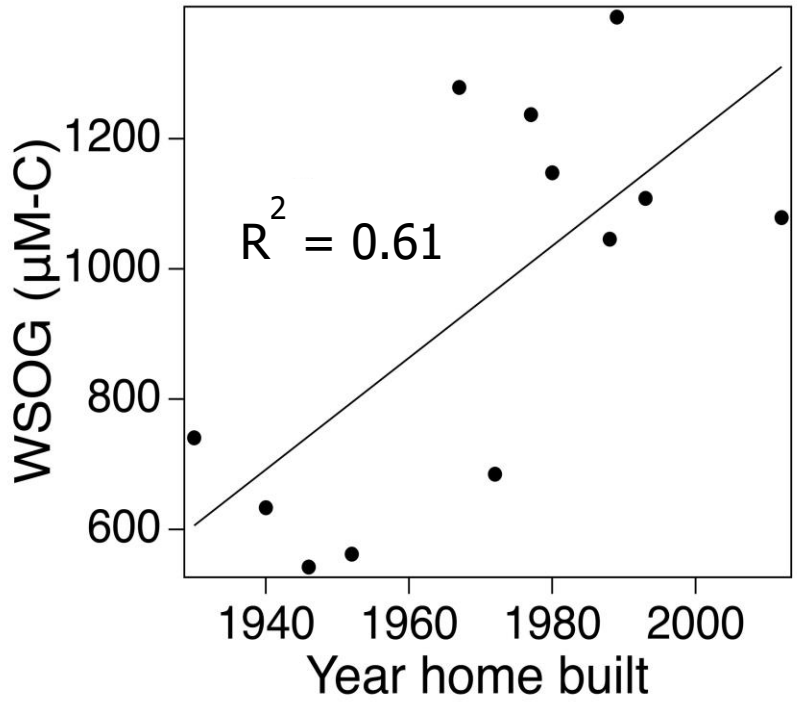

Figure S4: Regression of year the sampled homes were built against their respective WSOG concentratins in the mist chamber samples.

Example IC chromatogram

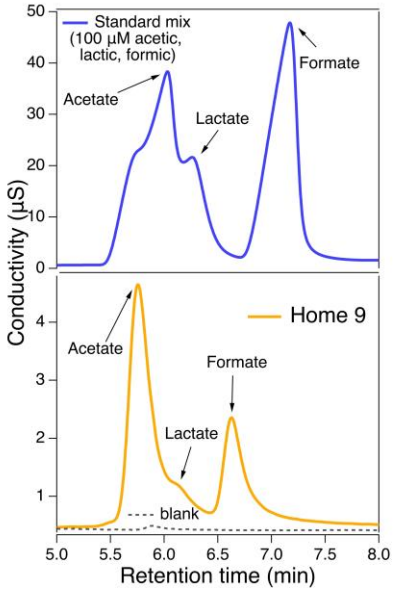

Figure S5. IC chromatogram of home 9 between 5- and 8-minutes

Acetic and formic acid gas phase concentrations

Home	Indoor acetic acid (gas phase) (μg m^{-3})	Indoor formic acid (gas phase) (μg m^{-3})
1	108	27
2	115	22
3	122	15
4	155	27
5	83	11
6	112	19
7	173	32
8	73	15
9	120	19
10	178	31
11	96	16
12	66	15
13	130	23

Table S2. Gas phase concentrations of acetic and formic acids using their respective collection efficiencies (μg-compound m^{-3} air).

Dose parameters

Average daily doses via the inhalation and dermal routes are calculated using Equations S4 and S5.

$$ADD_i = \frac{C \times InhR \times EF \times ED}{BW \times AT} \quad \text{(S4)}$$

$$ADD_d = \frac{DA \times SA \times EF \times ED}{BW \times AT} \quad \text{(S5)}$$

where, C is the WSOG concentration in the air, InhR is the inhalation rate, DA is the adsorbed dose, SA is the body surface area (assumed to be the entire body as these gases likely permeate clothing[4]), EF is the exposure factor, ED is the exposure duration, BW is the body weight, and AT is the averaging time. Adsorbed dose is calculated in Equation S6.

$$DA = K_p \times C \times t \quad \text{(S6)}$$

where K_p is the permeability coefficient, and t is time of exposure. Values used for Equations S4-6 are provided in Table S3.

WSOG concentration (µg m^{-3})		170
Exposure frequency (days $year^{-1}$)		365
time of dermal contact (hours day^{-1})		24
permeability coefficient (m hr^{-1})	DEP	3.4
	4-OPA	0.56
	butanol	0.053
Adult	Inhalation rate (m^3 day^{-1})	15.0
	Exposure duration (years)	70
	Body weight (kg)	80
	Skin surface area (m^2)	1.8
	Averaging time (days)	25550
Child (10 yrs)	Inhalation rate (m^3 day^{-1})	10.0
	Exposure duration (years)	10
	Body weight (kg)	30
	Averaging time (days)	3650
	Skin surface area (m^2)	1.1
Infant (0.5 years)	Inhalation rate (m^3 day^{-1})	3.6
	Exposure duration (years)	0.5
	Body weight (kg)	3.5
	Averaging time (days)	182.5
	Skin surface area (m^2)	0.25

Table S3. Parameters for dose calculations

References:

(1) Chan, W. R.; Nazaroff, W. W.; Price, P. N.; Sohn, M. D.; Gadgil, A. J. Analyzing a Database of Residential Air Leakage in the United States. *Atmos. Environ.* **2005**, *39* (19), 3445–3455.

(2) Spaulding, R. S.; Talbot, R. W.; Charles, M. J. Optimization of a Mist Chamber (Cofer Scrubber) for Sampling Water-Soluble Organics in Air. *Environ. Sci. Techn.* **2002**, *36* (8), 1798–1808.

(3) Hennigan, C. J.; El-Sayed, M. M. H.; Hodzic, A. Detailed Characterization of a Mist Chamber for the Collection of Water-Soluble Organic Gases. *Atmos. Environ.* **2018**, *188*, 12–17.

(4) Weschler, C. J.; Nazaroff, W. W. Dermal Uptake of Organic Vapors Commonly Found in Indoor Air. *Environ. Sci. Technol.* **2014**, *48* (2), 1230–1237.