Received: 11 April 2017 | Accepted: 30 June 2017
DOI: 10.1111/ina.12405

ORIGINAL ARTICLE

WILEY

Real-world volatile organic compound emission rates from seated adults and children for use in indoor air studies

C. Stönner | A. Edtbauer | J. Williams

Max Planck-Institute for Chemistry, Mainz, Germany

Correspondence
Christof Stönner, Max Planck-Institute for Chemistry, Mainz, Germany.
Email: c.stoenner@mpic.de

Abstract

Human beings emit many volatile organic compounds (VOCs) of both endogenous (internally produced) and exogenous (external source) origin. Here we present real-world emission rates of volatile organic compounds from cinema audiences (50-230 people) as a function of time in multiple screenings of three films. The cinema location and film selection allowed high-frequency measurement of human-emitted VOCs within a room flushed at a known rate so that emissions rates could be calculated for both adults and children. Gas-phase emission rates are analyzed as a function of time of day, variability during the film, and age of viewer. The average emission rates of CO_2, acetone, and isoprene were lower (by a factor of ~1.2-1.4) for children under twelve compared to adults while for acetaldehyde emission rates were equivalent. Molecules influenced by exogenous sources such as decamethylcyclopentasiloxanes and methanol tended to decrease over the course of day and then rise for late evening screenings. These results represent average emission rates of people under real-world conditions and can be used in indoor air quality assessments and building design. Averaging over a large number of people generates emission rates that are less susceptible to individual behaviors.

KEYWORDS
crowd breath, emission rate, indoor air quality, movie theatre, proton transfer reaction time-of-flight mass spectrometry, volatile organic compounds

1 | INTRODUCTION

Human beings are exposed to numerous volatile organic compounds (VOCs) in both outside and indoor air environments. More than half of the world's population now live in cities with significant airborne pollution[1] and exposure to outside air can have serious consequences for human health.[2] However, indoor sources of chemicals are also important, particularly since people spend much of their life (93% for the average American) in enclosed spaces such as buildings and vehicles.[3] Furthermore, as architects strive to improve the energy efficiency of buildings (eg, passive houses), the internal recirculation of air becomes key for heat conservation, and hence, indoor air quality becomes an important issue.[4] Known sources of indoor pollutants include building materials,[5,6] carpeting,[7] furnishings,[8] and products used or stored indoors such as paints[9,10] and cleaning products.[11] Commonly reported indoor air pollutants include gases such as carbon monoxide, sulfur dioxide, nitrogen dioxide, and ozone, and microbial debris, selected VOCs, and particulate matter.[12,13] It has been noted that even when the emitted contaminants are present below threshold limit values,[4] they may contribute to a significant time-weighted exposure.[14] Humans too are a potent, yet often overlooked, source of chemicals to the indoor air environment. Several hundred VOCs have been reported emanating from human breath, saliva, skin, blood, milk, urine, and feces.[15] The major endogenous compounds emitted in human breath are acetone

(1.2-1880 ppb), isoprene (12-580 ppb), ethanol (13-1000 ppb), and methanol (160-2000 ppb).[16] However, many other exogenous species may be uptaken (by inhalation and dermal uptake,[17] or on textile fabrics[18]) in outdoor polluted environments such as roadsides and subsequently reemitted indoors, thereby effectively being imported into more confined domestic spaces. In this study, average VOC emission rates have been determined from a large number of people (8300) under real-world conditions so as to include both endogenous and exogenous species. The aim is to provide a representative dataset of typical city dwelling human emission rates that can be used by architects, indoor air quality specialists, and medical researchers. Groups of people (50-238 at a time) were measured in a cinema which served as a convenient enclosed space that was ventilated at a known rate while the audience remained seated. By characterizing the human emission rates of VOCs and CO_2 in the real world, we may put other indoor sources into context and gauge the potential for indoor chemical reactions.

Here, we present emission rates for numerous VOCs from seated human beings measured with a proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS). This device allows quantification of numerous VOCs in real time.[19] The measurements presented here took place in a cinema in Mainz (Germany) over a period of four weeks during the winter holidays 2015-2016. The study was designed to continuously measure from one screening room of the cinema. Physiological parameters or the exact age of the 8300 audience members were not recorded, although via ticketing information the proportion of the audience under 12 was known. Presented are the average VOC emission per person (above and below 12 years of age) from a crowd of people and how the main VOC emissions vary over time. The measurement of VOC emissions from a crowd neatly circumvents the tedious problem of sampling a statistically significant number of individuals to encompass the main real-world source categories.[20] Such crowd measurement have been performed previously in enclosed, ventilated environments so that hundreds of people are monitored simultaneously, for example, class rooms,[21-24] office rooms,[25] other public buildings like a football stadium[26] and cinemas.[27] In contrast, much current breath research is focussed on the identification of biomarkers or chemical fingerprints from individuals to diagnose an illness.[28-30] However, the breath composition of an individual can vary significantly with dietary, sanitary and smoking habits, exposure to air pollutants,[31] position, and even the emotional state.[27] In future, the results provided here may be compared with individuals to assess their representativeness and with disease biomarker candidates to gauge potential interferences.

Practical Implications

- The contribution of human emissions of volatile organic compounds (VOCs) to indoor air is an important yet often overlooked source of chemicals. The presented emission rates of VOCs averaged over a total of 8000 people can be used for characterizing indoor air influenced by human presence, source strength comparisons, building ventilation design, and sick building syndrome assessments.

2 | MATERIALS AND METHODS

2.1 | Cinema/movie theatre

The measurements were made from screening room 2 in the Cinestar Cinema Complex in Mainz between December 15, 2015 and January 15, 2016. Within this time period, three films were screened: "Star Wars: The Force Awakens" and two German films "I′m off then" (German title "Ich bin dann mal weg") and "Help, I′ve shrunk my teacher" (German title "Hilfe, ich habe meine Lehrerin geschrumpft"). According to the "International Movie Database,"[32] the "Star Wars" film falls under the genre "Action," "Adventure," and "Fantasy" whereas the other two films were "Comedy" films. The third film was additionally categorized under "Family," indicating that it was targeted at younger audiences. Star Wars was classified as suitable for viewing by people of 12 and above, while the other two films had no age restriction (USK 0). Nonetheless, the subject matter of "I′m off then" was more adult in nature (recounting a pilgrimage) whereas "Help, I′ve shrunk my teacher" was more directed at children. Screening room 2 has a capacity of 238 people and ticket sales, which are discounted for children (under 12 years old), permitted the proportion of children under 12 to adults to be known for each screening. The number of screenings, viewers, and percentage of children (under 12 years old) in the audience are given in the Table S1. In total, 8300 viewers were assessed over 85 separate film screenings.

The three films assessed in this study were screened at different times of day, from 11:30 in the morning to 22:30 at night. The summary of the screening hours of each film can be found in the Table S2. It is important to note that the children's film "Help, I've shrunk my teacher" was screened mainly in the morning with only two screenings in the afternoon, whereas the other two films are distributed more evenly over the day. This distribution may bias the calculated VOC emission rates for this film and the consequences are explored later in the Emission Rates section.

The screening room was continuously flushed with outside air at a constant rate of 6500 $m^3 h^{-1}$. All air was drawn in from the outside without any internal recirculation. Air entered the cinema through vents in the floor and was drawn out though opening in the ceiling. The volume of the screening room was 1300 m^3 so that the overall air exchange rate was circa five times per hour. The entire exhaust airstream from the screening room was taken through a 75 × 75 cm stainless steel ventilation shaft to a separate technical room where the measurement instruments (PTR-TOF-MS and CO_2 Analyzer) were placed. In the middle of the ventilation shaft, a 1/4″ outer diameter (0.625 cm OD) Teflon sample line was inserted and 20 L min^{-1} air drawn continuously to the instruments.

2.2 | PTR-TOF-MS

The VOCs in the screening room exhaust air were continuously monitored with a PTR-TOF-MS (proton transfer reaction time-of-flight mass spectrometer, PTR-TOF-MS-8000, Ionicon Analytik GmbH, Innsbruck, Austria). The ionization of the analyte molecules is made via hydroxonium ions (H_3O^+) which, due to the relatively low energies involved, results in little fragmentation of the analyte. The protonation occurs only for molecules possessing a higher proton affinity than water (691 kJ mol^{-1}); thus, conveniently the system is blind to nitrogen, oxygen, and argon, the main components of air.[33,34]

A detailed description of the setup, the adjusted parameters of the PTR-TOF-MS, and the calibration procedure is provided in the supplement.

2.3 | CO_2 measurement

CO_2 was measured at 1 Hz using a commercially available Li-COR Li-7000 system. The linearity of the response was confirmed to 3400 ppmv using a second standard gas (10% CO_2, Air Liquide, Paris, France).

2.4 | Data analysis

All modeling and statistical analyses were performed using the software R.[35] The data from each film title was divided into sections of the equal length corresponding to 30 minutes before the beginning of the film until 15 minutes after the end. Screening room background mixing ratios were sampled during the night between 3:00 and 6:00 local time when the cinema was closed to the public. In order to extract the masses that changed in the presence of the audience, a paired Wilcoxon rank test for each mass was performed using the mean of the 15 minutes before the beginning of the film and the mean value during the film. A threshold *P*-value of .01 was chosen to extract the molecular mass signals which significantly increase in the presence of the audience.

2.5 | Box model

Instantaneous emission rates were calculated by applying a mass-balance approach. In this model, it was assumed that there is no pathway for mass loss except air exchange and that the emission rate *p* is small compared to the air exchange rate. As well-mixed conditions could not be assumed to apply in this model, a correction variable was introduced to account for the incompletely mixed air.[36] As stated previously, the volume of the screening room was 1300 m^3 and the air supply was 6500 $m^3\ h^{-1}$ with identical flows in and out of the showroom.

$$dm/dt = c_{in} \cdot q \cdot r \cdot + p - c_{out} \cdot q \cdot r \quad (1)$$

In Equation 1, *m* is the mass of the molecules at time *t* in the screening room air. The outside air is supplied with a ventilation rate *r* and a mixing ratio c_{in}. The mixing ratio c_{in} of each VOC in the inflowing air was interpolated from the two surrounding background nighttime measurements in the absence of people. The ventilation rate *r* is multiplied with the mixing parameter *q*, to account for the imperfect air mixing. The lower the mixing factor *q*, the worse the mixing of air in the room, providing a smaller effective room ventilation rate (product of $q \cdot r$). This accounts for the fact that the air less effectively mixed from the lower part of the cinema. This phenomenon leads to a slower exchange resulting in a flatter curve and in a later establishment of the steady state. The emission rate of a given gas from the audience is given by *p*. The effective ventilation rate was estimated by optimizing the mixing factor *q* and the emission rate of CO_2 p_{CO2} with a normal least squares fit. The estimated mixing factor was used thereafter for all other calculations.

Rearrangement of Equation 1 results in an expression for the emission rate, Equation 2. For the calculation of the emission rate, the data were smoothed and differentiated using a Savitzky-Golay filter with a span of 21 points and a polynomial order of 3.

$$p = dm/dt - c_{in} \cdot q \cdot r + c_{out} \cdot q \cdot r \quad (2)$$

In Equation 2, the emission rate *p* expresses the total emitted mass per unit time [$\mu g\ h^{-1}$] for a specific number of viewers. Equation 3 was applied in order to determine the average emission rate per person (ER) while at rest. Henceforth, the emission rate (ER) will be referred to as the average emission rate per person.

$$ER = p/N \quad (3)$$

The mean of the total emitted mass *p* over the course of the entire film was divided by the number of viewers N and reported for each film. This results in an emission rate of grams (of a particular molecule) per hour per person. All calculated values for the emission rate are presented as the average emission rate per person [$\mu g\ h^{-1}\ p^{-1}$]. The cinema provided also the number of children (younger than 12 years) watching the film based on the ticket sales. The mean emission rates per person estimated from the "I'm off then" film (ER_{adults}) were used to calculate the emission rate of children. To do this, it was assumed that the emission rate for children during the child film "Help, I've shrunk my teacher" is the difference between the total emission rate *p* minus the sum of the emission rate of the adults ($\Sigma(ER_{adults})$).

$$p_{children} = p - \sum (ER_{adults}) \quad (4)$$

The division of the total amount of emitted VOC per minute by the amount of children (Equation 3) resulted in the emission rate per child. The "I'm off then" film was only attended by adults because of the subject matter (a pilgrimage), even though the film is free for all age groups (unrestricted), see Table S1. Thus, the emission rates calculated from these screenings were labeled as pure "adult." In the case of the "Star Wars" film, the audience consisted of people from different age classes, beginning at the age of 12. The film "Star Wars" is more directed at younger viewers than the film "I'm off then," and therefore, the emission rates obtained from the Star Wars screenings were labeled as "mixed." Given the emission rate of "adults" calculated from the "I'm off then" screenings, the emission rates labeled as "children" were obtained by applying Equation 4.

3 | RESULTS AND DISCUSSION

3.1 | Calculated effective ventilation rate and results of the box model

The mean mixing factor derived from the CO_2 data from all screenings was found to be 0.3 ± 0.1 with a residual sum of squares ranging from 0.97 to 0.99. Previously reported literature values for this parameter range from 0.1 for imperfectly mixed rooms to 1 indicating fully mixed.[36] There is no dependence of the mixing factor on the number of viewers (correlation coefficient r^2=−0.07).

Further calculations were made using the mean of the mixing factor giving q=0.3. The second parameter estimated by the model is the emission rate of CO_2 per person. The calculated emission rate p_{CO2} was estimated to be $2.9{\cdot}10^7$ μg h^{-1} p^{-1} with a standard deviation of $0.1{\cdot}10^7$ μg h^{-1} p^{-1}.

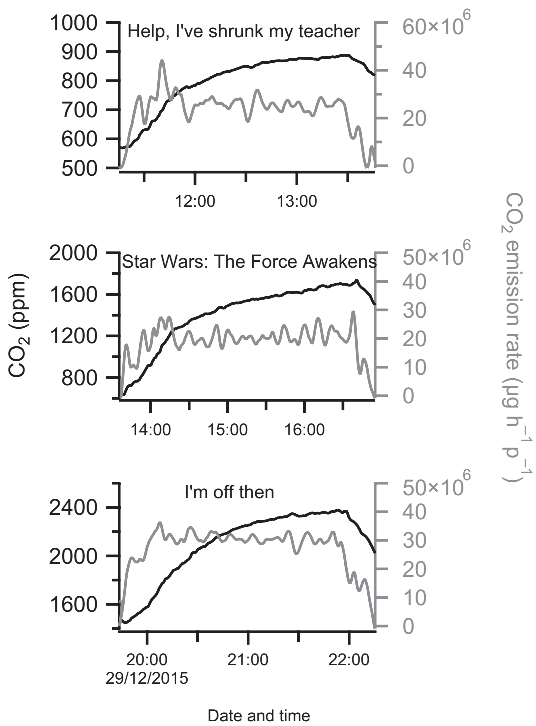

FIGURE 1 Behavior of the emission rate per person (gray) and the mixing ratio (black) of CO_2. The top panel shows the film "Help, I've shrunk my teacher," the middle panel "Star Wars: The Force Awakens," and the bottom panel "I'm off then"

3.2 | Emission rates

In Figure 1, the CO_2 mixing ratio (black) and the emission rate per hour per person (gray) are shown. Most of the measured VOC from human beings show a similar general behavior during all screenings with a slow steady increase as the audience enters the previously empty screening room and a steep decrease at the end of each film, when the audience departs. Typical mixing ratios of CO_2 lie between 400 and 2500 ppm, for acetone between 3.00 and 20.00 ppb, and for isoprene between 1.00 and 9.00 ppb. These molecules are known to be endogenously produced and emitted in human breath.[15,37] The emission rate at the beginning of each film cannot be evaluated quantitatively since the audience enters the screening room little by little and the door is open to the foyer area. During the film, the elevated emission rate remains on average reasonably stable albeit with clearly defined peaks at certain moments (associated with events in the film), and then decreases rapidly at the end of the film. The mean emission rates for the measured VOCs were calculated from the beginning of the film until 5 minutes before the end.

The mixing ratio of the VOCs entering the screening room (c_{in}) was estimated using the interpolated value between the two nighttime background measurements. Assuming lower mixing ratios of VOCs during the day time (true for CO_2) than during nighttime background measurements, the emission rate would be higher than reported. For CO_2, a maximum error of 30% percent was calculated for 54 viewers and a mixing ratio of CO_2 of 627 ppm at night. This condition depicts the maximum error and mixing ratios higher than 600 ppm at night were measured only for five films. The average mixing ratio during night was 483 ± 44 ppm CO_2 resulting in an error of 15% with 54 people attending the cinema. The higher the amount of viewers attending the cinema, the smaller the error becomes (on average of 98 people attended the screenings). In general, we assume that the error introduced in the emission rates by different diurnal VOC concentrations is small compared to the standard deviation presented in Table 1.

The emission rates of selected gaseous species from children and adults, provided by Equations 3 and 4, are shown in Table 1. The presented masses were either calibrated with the use of a gas standard

TABLE 1 Emission rates of various VOC and CO_2

Molecule	Protonated mass (m/z)	Adults (μg h^{-1} p^{-1})	Standard deviation (μg h^{-1} p^{-1})	Children (μg h^{-1} p^{-1})	Standard deviation (μg h^{-1} p^{-1})	Calibration method
Carbon dioxide	–	3.0 E7	0.5 E7	1.8 E7	0.6 E7	Calibration gas
Formaldehyde	31.0178	207	104	426	375	Calibration factor
Methanol	33.0335	650	736	1136	984	Calibration gas
Acetaldehyde	45.0335	221	76	252	160	Calibration gas
Ethanol	47.0491	216	154	116	171	Calibration factor
Acetone	59.0491	419	96	333	202	Calibration gas
Isoprene	69.0699	166	39	95	59	Calibration gas
Sum of all monoterpenes	137.1325 + 81.0699	201	170	189	181	Calibration gas
Siloxane (D_5)	355.0698	112	104	256	186	Calibration factor

or calibrated using the calibration factor of acetone (30.9 ncps/ppb). An overview of all detected VOC signals can be found in the Table S3.

In order to distinguish between exogenous and endogenous emissions, the standard deviation of the emission rates was examined over several screenings of the same film. We hypothesize that exogenous sources will be significantly more variable over the time of day. This is supported by the relatively small standard deviations that were observed for CO_2, acetaldehyde, acetone, and isoprene which are known to be predominately endogenous. The protonated mass of decamethylcyclopentasiloxane (D_5) would be *m/z* 371.0956, but the most abundant peak appears at *m/z* 355.0698 due to the elimination of a methyl group. Based on their relatively high standard deviation, we consider ethanol, the siloxane, methanol, and monoterpenes to be predominately exogenous.

The emission rate per person for CO_2 was estimated to be 30 ± 5 g h^{-1} p^{-1} for adults and 18 ± 6 g h^{-1} p^{-1} for children. Persily et al.[38] derived the CO_2 emission rates from well-established concepts concerning the human metabolism and physical activity. Assuming an average age between 21 and <30 and a physical activity of 1.4 met (between 1.3 for "sitting, reading, writing, typing" and 1.5 for "sitting at sporting event as spectator." The unit "met" quantifies the level of physical activity), we calculate an emission rate of 40 g h^{-1} p^{-1} for males and 32 g h^{-1} p^{-1} for females. The emission rate decreases continuously for younger or older people (both male and female). For children (younger than 12), the reported value of 18 ± 6 g h^{-1} p^{-1} underestimates the emission rate calculated by Persily et al. for an age class between 6 and <11 lying between 22 and 25 g h^{-1} p^{-1} for males and between 19 and 23 g h^{-1} p^{-1} for females.

Tang et al.[23] recently published emission rates from several VOCs measured in a classroom. Table 2 compares the emission rates calculated by Tang et al. with the values presented in this study. Especially, the emission rates per person of isoprene, monoterpenes, and the (iso) butyl fragment are in good agreement. For ethanol, the adult emission rate from the cinema is higher (216 μg h^{-1} p^{-1} for adults) which comes from the consumption of alcoholic beverages in the evening also resulting in a higher standard deviation. Comparing the ethanol emission between pre-evening and evening screenings, the estimated emission rate is calculated to be 132 μg h^{-1} p^{-1} for the pre-evening screenings (before 18:00) and 329 μg h^{-1} p^{-1} for the evening screenings (18:00 and later, compared to 94.9 μg h^{-1} p^{-1} from Tang et al.). Tang et al. summarized all sulfur-containing compounds resulting in an emission rate of 6.5 μg h^{-1} p^{-1} which is close to the emission rate of dimethyl sulfide or ethyl mercaptan derived in this study. The emission of methanol is discussed later in more detail but was found to be variable over the day exhibiting high values in the morning.

The skin oxidized VOCs like 6-methyl5heptene2one (6MHO) or 4oxopentanal (4OPA) were less abundant or were not detected in the cinema. Possible explanations might be the lower ozone mixing ratios in winter or the effective removal of ozone within the intake of the ventilation system and hence a lower amount of oxidation products. A previous study measuring the air within an open air football stadium using the same instruments in summer reported a signal of 6-MHO.[26] Another explanation could be that these products were already evaporated from the skin during the waiting time in the foyer of the cinema which would have low ambient ozone due to effective indoor deposition. This could be also true for acetone which is reported to be a product of skin lipid ozonolysis, too.[39] Compared to the emission rate presented in this paper of 419 μg h^{-1} p^{-1}, Tang et al. reported a value twice as high. In 1975, Wang et al.[24] published a study concerning emission rates of bioeffluents from humans. In general, their calculated emission rates lie above those presented in our study with the exception of CO_2. However, bearing in mind that the study from Wang et al. was conducted 40 years ago, that most of the values are in the same order of magnitude is reassuring.

Figure 2 shows the emission rate in μg per hour per person for different VOCs in a boxplot. The black solid line in the box indicates the median and the boxes encompass the 25th and 75th percentiles of the data. The whiskers are 1.5 times the interquartile range. The different

TABLE 2 Summarization of emissions rate of several VOC from this study and Tang et al[23]

Molecule	Protonated mass (m/z)	Tang et al. (μg h^{-1} p^{-1})	Adults (μg h^{-1} p^{-1})	Children (μg h^{-1} p^{-1})
Acetone	59.0491	1060	419	333
Acetic Acid	61.0284	329	205	357
Methanol	33.0335	156	650	1136
Acetaldehyde	45.0335	114	221	252
Monoterpene	137.1325 + 81.0699	187	201	189
Isoprene	69.0699	162	166	95
Ethanol	47.0491	94.9	216	116
C6H10H+	83.0855	88.8	22	32
(iso)butyl fragment	57.0699	39.7	41	52
Propionic acid/ hydroxyacetone	75.0440	40.4	19	27
6-MHO	127.1168	99.3	3	5
(iso)propyl fragment	43.0542	23.8	107	321
S-containing	63.0263	6.5	7	6

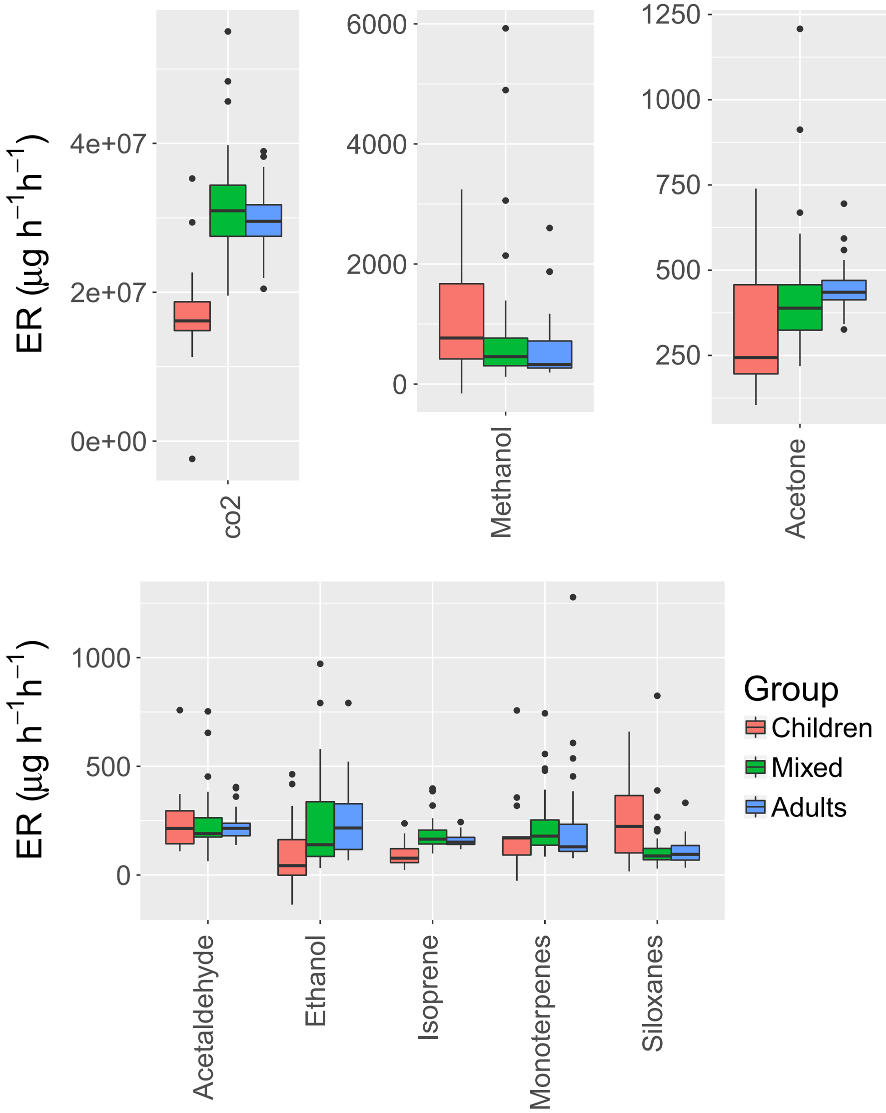

FIGURE 2 Boxplots for different VOCs and different age groups. In the upper part, carbon dioxide, methanol and acetone are shown (from left to right). The lower part includes acetaldehyde, ethanol, isoprene, pinene, monoterpenes, and decamethylcyclopentasiloxane

colors indicate the age classification of the film. The molecules shown in Figure 2 were those with the highest emission rates measured, whereby CO_2 was by far the greatest emission source (ca. 30 g per hour per person) followed by methanol and acetone (approximately four orders of magnitude less) along with the other VOCs.

Some of the VOCs show significantly different emission rates depending on the age classes. CO_2, acetone, and isoprene show similar behavior with the lowest emission rates for children and highest for adults. For CO_2 and isoprene, the emission rates for the mixed audience ("Star Wars," rating 12) and the adults only ("I'm off then," rating 0) are almost equal, but they differ significantly from the emission rates of children (calculated as shown in Equation 4).

Figure 2 shows a slightly higher emission rate for CO_2 for the mixed group than for adults. An explanation could be that the "Star Wars" film from which the emission rates of the mixed group were derived was screened mostly at 14:00 (20 screenings) and 22:30 (12 screenings). In the case of the screening at 22:30, only people of an age of 18 or older are allowed to enter and the target audience of the "Star Wars" film is probably younger than that of the "I'm off then" film (recounting a pilgrimage). This group specifically people between 21 and <31 emit the highest amount of CO_2. The calculated emission rate for CO_2 at 22:30 screening the "Star Wars" film is 36 ± 4 g h^{-1} p^{-1} compared to 28 ± 5 g h^{-1} p^{-1} at 14:00 (see Figure 3). There are no data available on the average age or gender distribution for the people attending the cinema.

The age dependency of the isoprene emission rate is in agreement with the previously reported age dependency of isoprene in human breath described in Smith et al.[40] Therein, it was recognized that children emit significantly less isoprene than adults. As for CO_2, the emission rate for isoprene is slightly higher for the mixed group than for the adults also showing an enhanced emission rate at 22:30 (233 ± 58 µg h^{-1} p^{-1} at 22:33 and 148 ± 23 µg h^{-1} p^{-1} at 14:00). Lechner et al.[41] reported a significant lower isoprene emission rate for 19- to 29-year-old subjects than for older adults. However, it should be noted that only 11 subjects were measured in 19- to 29-year-old age category in the Lechner et al. study. A much earlier study by Mendis et al.[42] also reported no age dependency of isoprene concentration in expired air, sampling from 43 healthy volunteers between 22

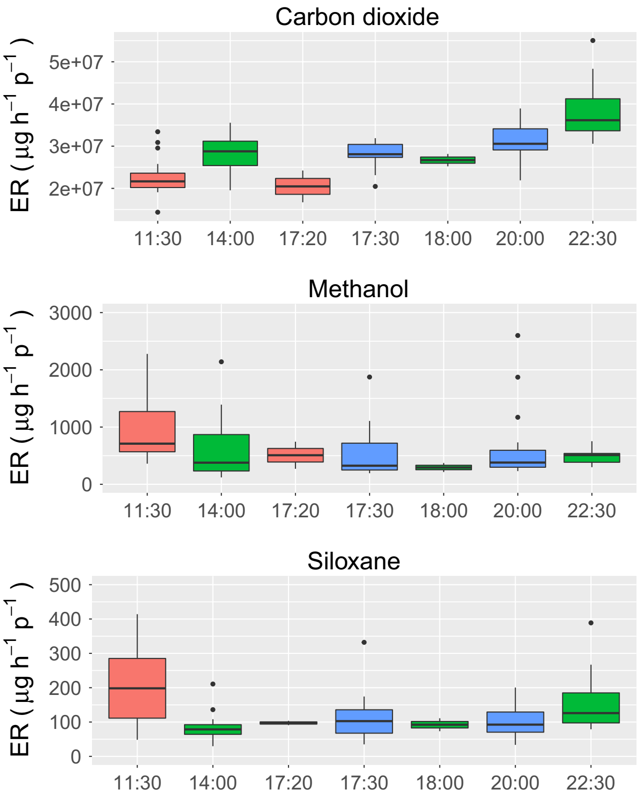

FIGURE 3 Emission rates of CO_2 (top) and methanol (middle) and decamethylcyclopentasiloxane (bottom) during the course of the day. The colors indicate the film screened in the showroom. The film "Help I've shrunk my teacher" is shown in red, "Star Wars" in green, and "I'm off then" in blue

and 75 years. It should be noted that this study differentiates only between children up to 12 years and older persons, based on ticket sale information. Thus, the exact average age of the viewers attending the measured films could not be determined. Interestingly, the function and source mechanism of isoprene is still a matter of debate. Isoprene is clearly endogenously produced and it is suggested that its production is linked to the cholesterologenesis.[43]

The emission rate for acetone shows significantly different emission rates between the children and adult age classes with a *P*-value of .05. A similar difference in breath acetone, whereby children emit less than adults, has been also reported by Enderby et al.[44] In our study, the "mixed" age class emission rate lies in between children and adults. However, Enderby et al. found no correlation between breath concentration and age in an age range between 7 and 18 years.[44] Acetone is produced by the liver during fatty acid metabolism which acts when glucose energy sources are not available. Higher levels of acetone in blood are therefore measured in humans during fasting and prolonged exercise.[45] The larger acetone emission rates from adults (13 percent higher) may be simply a function of their larger body mass. Further factors like the diabetic status of the attendees presumably leading to higher emissions rates of acetone cannot be excluded.[46]

Acetaldehyde was found to be age independent, so emission rates of children and adults are comparable despite differences in body mass. This is in agreement with previous studies.[44,47] Acetaldehyde is produced in the liver as an intermediate in the ethanol metabolism[48] and through the action of bacteria on ethanol in the mouth.[49] The aforementioned molecules all show a relatively small standard deviation compared to their emission rate and to the other compounds. This behavior may reflect the fact that they are predominantly endogenously produced and thus are less liable to influence by exogenous factors like food and drink consumption.

The average CO_2 emission rate for the different films and screening times can be seen in Figure 3. The CO_2 emission rates during each of the films ("Help, I've shrunk my teacher" in red screened at 11:30 and 17:20, "Star Wars" in green screened at 14:30,18:00, and 22:30, and "I'm off then" in blue screened at 17:30 and 20:00) are closely comparable for multiple screenings of the same film, but the three films exhibited significantly different emission rates and standard deviations, see Table 1. Interestingly, the emission rate for CO_2 as well as for acetone and isoprene (and many other species) gets higher during later screenings with a maximum at 22:30. This might be a result of a higher emission rate seen in the example of CO_2 or the underestimation of the emission rates during midday due to the error introduced by the measurement of the background during night. The CO_2 emission rate for the children's film, shown at 11:30 and 17:20 (only two screening times), lay well below that of the other two films.

When examining the data for trends in the emission rate as a function of time of day, it is important to note that all "Help, I've shrunk my teacher" films were screened in the morning and early afternoon whereas the "Star Wars" and "I'm off then" films had screening times distributed over the day, as shown in the Table S2. In Table 1, it can be seen that other VOCs like methanol, ethanol, and the monoterpenes show larger standard deviations compared to their emission rates than the main breath gases discussed above. Methanol is known to be produced endogenously by the consumption of fruit through the degradation of pectin.[50] The high standard deviation may stem from the different dietary habits between the viewers. Therefore, the high emission rate of methanol for the children's film "Help, I've shrunk my teacher" may be caused by the consumption of fruits and fruit juices during breakfast as this emission rate diminishes during the day. The middle panel in Figure 3 depicts the daily pattern of methanol which is clearly distinct from CO_2. The emission rate of methanol shows a maximum at 11:30 and again at 22:30 and a relatively constant emission rate during the rest of the day. Monoterpenes are ingredients of many fruits and can be also found in soft drinks like Cola. Additionally, monoterpenes like limonene are frequently used as fragrances in personal care and cleaning products. The use of personal care products and their effect on emission rates is discussed in detail using the example of decamethylcyclopentasiloxane below.

In the lower panel, the emission rates of decamethylcyclopentasiloxane (D_5) calculated at different screening hours is shown. This molecule belongs to a group of chemicals collectively called siloxanes or silicones that are commonly found in personal care products such as shampoo and deodorants as well as in cleaning and polishing products.[51] It is therefore an exogenous species and shows a temporal emission behavior similar to that reported by Tang et al. who measured

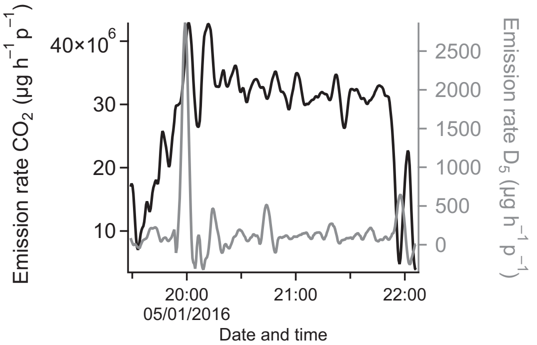

FIGURE 4 Emission rate of CO_2 (black curve) and decamethylcyclopentasiloxane (gray curve) in [$\mu g\ h^{-1}\ p^{-1}$] during the film "Star Wars" starting at 14:00 and ending around 16:30

the mixing ratio of different cyclic siloxanes in a classroom of engineering students.[22] In that study, D_5 was found to decrease over the course of day, likely due to evaporative losses of applied hygiene products. Indeed, the earliest and the latest screenings show the highest values. This may simply reflect that hygiene and cosmetic products containing siloxanes are applied in the morning then "refreshed" later on prior to late screenings. The emission rates of several different siloxanes were calculated in a study of Tang et al.[22] The calculated emission rates provided by Tang et al. were generally higher in the morning than in the evening due to outgassing from siloxanes of cosmetic products, ranging for D_5 from 9800 to 183 $\mu g\ h^{-1}\ p^{-1}$. In our study, such strong differences for D_5 could not be found, as shown in Figure 3, most of our reported average values lay close to the afternoon levels (between 14:10 and 16:00 pm) of 183 $\mu g\ h^{-1}\ p^{-1}$. This is despite the ventilation rates in both rooms being comparable. This discrepancy may reflect the fact that we used the average over the film to calculate VOC emission rates, whereas Tang et al. reported emission rates every minute. This is important because higher emission rates for D_5 were observed at the beginning and at the end of the film, when the audience undress and dress, respectively. This behavior is shown in Figure 4 along with the emission rate of CO_2. The peak emission of D_5 for the films screened in the morning was on average 2800 $\mu g\ h^{-1}\ p^{-1}$, and was therefore only slightly higher than measured for the films in the afternoon with an emission rate of 2500 $\mu g\ h^{-1}\ p^{-1}$. In general, we used only values during the film and not the peak emission at the beginning of the film since as the audience is entering the cinema we do not know the exact number of people present.

In Figure 4, the emission rate of D_5 decreases during the film while the audience remains seated as it is not emitted from breath and is probably emitted from skin at lower rates when the audience does not move. This indicates that they are not released from the human metabolism but from a "burst" source associated with ruffling of hair, clothes, and skin.[22] All other VOCs exhibit some emission source during the film that varies with time. The examples of D_5 show clear emission rate changes over the day. Determining differences between children and adults in our study is complicated by these temporal trends and by the fact that family films are screened earlier. The time of day can be an important factor for the release of VOCs due to temporally dependent habits and metabolic differences. Evaporative loss influences emission rates of chemicals which are applied or consumed only several times a day.

4 | CONCLUSION

In summary, a PTR-TOF-MS and a CO_2 instrument were plugged into the exhaust ventilation shaft of a movie theatre in order to characterize the emissions of VOC and CO_2 from a large number of seated people under real-world conditions. By sampling a crowd of people at different times of day rather than individuals, a representative average human VOC emission is obtained over a broad range of dietary and smoking habits, activity level, state of health, environmental exposures, age, stress level, or mood. This approach offers a statistically robust method for determining average emission rates of VOC from humans incorporating multiple sources including breath, skin, clothes, and some foodstuffs.[20]

The most abundant compounds were the endogenous breath compounds CO_2, acetone, and acetaldehyde, and the predominantly exogenous ethanol, monoterpenes, and decamethylcyclopentasiloxane (D_5). The emission rates of the VOCs measured from humans covered a range of five orders of magnitude, and CO_2 emission rates were a factor of 10^5 higher than the VOC emissions. Large variances were found between adults and children younger than 12 (for CO_2, acetone and isoprene), for time of day (methanol, siloxanes),[16,22] and between seated and moving crowds. The underlying reasons for the differences can be biological (result of metabolic processes as with isoprene and acetone) or behavioral (from hygiene or diet as with siloxanes and methanol). As this dataset represents average emissions from a wide cross-section of society, it can therefore be used for indoor air chemistry studies, comparison of source strengths, and building design.

REFERENCES

1. Molina MJ, Molina LT. Megacities and atmospheric pollution. *J Air Waste Manag Assoc*. 2004;54:644-680.
2. Lelieveld J, Evans JS, Fnais M, Giannadaki D, Pozzer A. The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature*. 2015;525:367-371.
3. Klepeis NE, Nelson WC, Ott WR, et al. The national human activity pattern survey (NHAPS): a resource for assessing exposure to environmental pollutants. *J Expo Sci Environ Epidemiol*. 2001;11:231-252.
4. Wolkoff P, Clausen PA, Jensen B, Nielsen GD, Wilkins CK. Are we measuring the relevant indoor pollutants? *Indoor Air*. 1997;7:92-106.
5. Levin H. Building materials and indoor air quality. *Occup Med*. 1989;4:667-693.
6. Hodgson AT, Beal D, McIlvaine JER. Sources of formaldehyde, other aldehydes and terpenes in a new manufactured house. *Indoor Air*. 2002;12:235-242.
7. Hodgson AT, Wooley JD, Daisey JM. Emissions of volatile organic compounds from new carpets measured in a large-scale environmental chamber. *Air Waste*. 1993;43:316-324.
8. Hites RA. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environ Sci Technol*. 2004;38:945-956.

9. Lamorena RB, Jung S-G, Bae G-N, Lee W. The formation of ultra-fine particles during ozone-initiated oxidations with terpenes emitted from natural paint. *J Hazard Mater*. 2007;141:245-251.
10. Corsi RL, Lin C-C. Emissions of 2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (TMPD-MIB) from latex paint: a critical review. *Crit Rev Environ Sci Technol*. 2009;39:1052-1080.
11. Nazaroff WW, Weschler CJ. Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmos Environ*. 2004;38:2841-2865.
12. Bernstein JA, Alexis N, Bacchus H, et al. The health effects of nonindustrial indoor air pollution. *J Allergy Clin Immunol*. 2008;121:585-591.
13. Weschler CJ. Changes in indoor pollutants since the 1950s. *Atmos Environ*. 2009;43:153-169.
14. Spengler JD, Sexton K. Indoor air pollution: a public health perspective. *Science*. 1983;221:9-17.
15. de Costello BL, Amann A, Al-Kateb H, et al. A review of the volatiles from the healthy human body. *J Breath Res*. 2014;8:14001.
16. Fenske JD, Paulson SE. Human breath emissions of VOCs. *J Air Waste Manag Assoc*. 1999;49:594-598.
17. Weschler CJ, Nazaroff WW. Dermal uptake of organic vapors commonly found in indoor air. *Environ Sci Technol*. 2014;48:1230-1237.
18. Ueta I, Saito Y, Teraoka K, Miura T, Jinno K. Determination of volatile organic compounds for a systematic evaluation of third-hand smoking. *Anal Sci*. 2010;26:569-574.
19. Herbig J, Müller M, Schallhart S, Titzmann T, Graus M, Hansel A. Online breath analysis with PTR-TOF. *J Breath Res*. 2009;3:27004.
20. Williams J, Pleil J. Crowd-based breath analysis: assessing behavior, activity, exposures, and emotional response of people in groups. *J Breath Res*. 2016;10:32001.
21. Rosbach J, Krop E, Vonk M, et al. Classroom ventilation and indoor air quality—results from the FRESH intervention study. *Indoor Air*. 2015;26:538-545.
22. Tang X, Misztal PK, Nazaroff WW, Goldstein AH. Siloxanes are the most abundant volatile organic compound emitted from engineering students in a classroom. *Environ Sci Technol Lett*. 2015;2:303-307.
23. Tang X, Misztal PK, Nazaroff WW, Goldstein AH. Volatile organic compound emissions from humans indoors. *Environ Sci Technol*. 2016;50:12686-12694.
24. Wang TC. A study of bioeffluents in a college classroom. *ASHRAE Trans*. 1975;81:32-44.
25. Shields HC, Fleischer DM, Weschler CJ. Comparisons among VOCs measured in three types of U.S. commercial buildings with different occupant densities. *Indoor Air*. 1996;6:2-17.
26. Veres PR, Faber P, Drewnick F, Lelieveld J, Williams J. Anthropogenic sources of VOC in a football stadium: assessing human emissions in the atmosphere. *Atmos Environ*. 2013;77:1052-1059.
27. Williams J, Stönner C, Wicker J, et al. Cinema audiences reproducibly vary the chemical composition of air during films, by broadcasting scene specific emissions on breath. *Sci Rep*. 2016;6:25464.
28. Risby TH, Solga SF. Current status of clinical breath analysis. *Appl Phys B*. 2006;85:421-426.
29. Pleil JD. Role of exhaled breath biomarkers in environmental health science. *J Toxicol Environ Health B Crit Rev*. 2008;11:613-629.
30. Amann A, Corradi M, Mazzone P, Mutti A. Lung cancer biomarkers in exhaled breath. *Expert Rev Mol Diagn*. 2011;11:207-217.
31. Filipiak W, Ruzsanyi V, Mochalski P, et al. Dependence of exhaled breath composition on exogenous factors, smoking habits and exposure to air pollutants. *J Breath Res*. 2012;6:36008.
32. IMDb – Movies, TV and Celebrities – IMDb. http://www.imdb.com/. Accessed June 3, 2016.
33. Jordan A, Haidacher S, Hanel G, et al. A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS). *Int J Mass Spectrom*. 2009;286:122-128.
34. Blake RS, Monks PS, Ellis AM. Proton-transfer reaction mass spectrometry. *Chem Rev*. 2009;109:861-896.
35. R Core Team. *R: A Language and Environment for Statistical Computing*. Vienna, Austria: R Foundation for Statistical Computing; 2013.
36. Nicas M. Estimating exposure intensity in an imperfectly mixed room. *Am Ind Hyg Assoc J*. 1996;57:542-550.
37. Amann A, Spaněl P, Smith D. Breath analysis: the approach towards clinical applications. *Mini Rev Med Chem*. 2007;7:115-129.
38. Persily A, de Jonge L. Carbon dioxide generation rates for building occupants. *Indoor Air*. 2017;27:868-879.
39. Wisthaler A, Weschler CJ. Reactions of ozone with human skin lipids: sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air. *Proc Natl Acad Sci*. 2010;107:6568-6575.
40. Smith D, Španěl P, Enderby B, Lenney W, Turner C, Davies SJ. Isoprene levels in the exhaled breath of 200 healthy pupils within the age range 7–18 years studied using SIFT-MS. *J Breath Res*. 2010;4:17101.
41. Lechner M, Moser B, Niederseer D, et al. Gender and age specific differences in exhaled isoprene levels. *Respir Physiol Neurobiol*. 2006;154:478-483.
42. Mendis S, Sobotka PA, Euler DE. Pentane and isoprene in expired air from humans: gas-chromatographic analysis of single breath. *Clin Chem*. 1994;40:1485-1488.
43. Stone BG, Besse TJ, Duane WC, Evans CD, DeMaster EG. Effect of regulating cholesterol biosynthesis on breath isoprene excretion in men. *Lipids*. 1993;28:705-708.
44. Enderby B, Lenney W, Brady M, Emmett C, Španěl P, Smith D. Concentrations of some metabolites in the breath of healthy children aged 7–18 years measured using selected ion flow tube mass spectrometry (SIFT-MS). *J Breath Res*. 2009;3:36001.
45. Laffel L. Ketone bodies: a review of physiology, pathophysiology and application of monitoring to diabetes. *Diabetes Metab Res Rev*. 1999;15:412-426.
46. Wang Z, Wang C. Is breath acetone a biomarker of diabetes? A historical review on breath acetone measurements. *J Breath Res*. 2013;7:37109.
47. Turner C, Španěl P, Smith D. A longitudinal study of ethanol and acetaldehyde in the exhaled breath of healthy volunteers using selected-ion flow-tube mass spectrometry. *Rapid Commun Mass Spectrom*. 2006;20:61-68.
48. Freund G, O'Hollaren P. Acetaldehyde concentrations in alveolar air following a standard dose of ethanol in man. *J Lipid Res*. 1965;6:471-477.
49. Wang T, Pysanenko A, Dryahina K, Španěl P, Smith D. Analysis of breath, exhaled via the mouth and nose, and the air in the oral cavity. *J Breath Res*. 2008;2:37013.
50. Lindinger W, Taucher J, Jordan A, Hansel A, Vogel W. Endogenous production of methanol after the consumption of fruit. *Alcohol Clin Exp Res*. 1997;21:939-943.
51. Horii Y, Kannan K. Survey of organosilicone compounds, including cyclic and linear siloxanes, in personal-care and household products. *Arch Environ Contam Toxicol*. 2008;55:701-710.

SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

How to cite this article: Stönner C, Edtbauer A, Williams J. Real-world volatile organic compound emission rates from seated adults and children for use in indoor air studies. *Indoor Air*. 2018;28:164–172. https://doi.org/10.1111/ina.12405