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The Indoor Chemical Human Emissions and Reactivity project (ICHEAR): Overview of experimental methodology and preliminary results

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ABSTRACT

With the gradual reduction of emissions from building products, emissions from human occupants become more dominant indoors. The impact of human emissions on indoor air quality is inadequately understood. The aim of the Indoor Chemical Human Emissions and Reactivity (ICHEAR) project was to examine the impact on indoor air chemistry of whole-body, exhaled and dermally emitted human bioeffluents under different conditions comprising human factors (t-shirts/shorts vs. long sleeve shirts/pants; age: teenagers, young adults, seniors) and a variety of environmental factors (moderate vs. high air temperature; low vs. high relative humidity; presence vs. absence of ozone). A series of human subject experiments were performed in a well-controlled stainless-steel climate chamber. State-of-the-art measurement technologies were used to quantify the volatile organic compounds emitted by humans and their total OH reactivity; ammonia, nanoparticle, fluorescent biological aerosol particle (FBAP), and microbial emissions; and skin surface chemistry. This paper presents the design of the project, its methodologies and preliminary results, comparing identical measurements performed with five groups, each composed of 4 volunteers (2 males and 2 females). The volunteers wore identical laundered new clothes and were asked to use the same set of fragrance-free personal care products. They occupied the ozone-free (< 2 ppb) chamber for 3 hours (morning) and then left for a 10-min lunch break. Ozone (target concentration in occupied chamber ~ 35 ppb) was introduced 10 minutes after the volunteers returned to the chamber and the measurements continued for another 2.5 hours. Under a given ozone condition, relatively small differences were observed in the steady state concentrations of geranyl acetone, 6MHO and 4OPA between the five groups. Larger variability was observed for acetone and isoprene. The absence or presence of ozone significantly influenced the steady state concentrations of acetone, geranyl acetone, 6MHO and 4OPA. Results of replicate experiments demonstrate the robustness of the experiments. Higher repeatability was achieved for dermally emitted compounds and their reaction products than for constituents of exhaled breath.

Key Words: Indoor emissions, human beings, VOC, OH reactivity, particles, ammonia, ozone

Practical Implications

- Human emissions and their oxidative chemical transformations can substantially contribute to indoor air pollution.
- Measurements of human emissions and their transformations using state-of-the-art instrumentation under controlled conditions in climate chambers can lead to novel findings of practical importance, including emission rates of volatile organic compounds, ammonia and nanoparticles.
- This study serves as a basis for future high-precision investigations of occupant related indoor chemistry under controlled conditions, including the separation of the impacts of exhaled breath and dermal emissions.

1. INTRODUCTION

The chemical composition of indoor air influences human exposures, health, and cognitive performance.^{1,2,3} Indoor living spaces typically contain multiple sources of chemicals including the building materials and the furnishings. The emission rates of chemicals from these sources are routinely measured.^{4,5,6,7,8,9} In contrast, emissions from occupants have received less attention, although humans are a mobile, potent, chemically diverse and highly variable source of reactive chemicals in indoor spaces. The impact of human beings remains a relatively inadequately quantified factor with respect to indoor air quality. As emissions from building products are gradually reduced (e.g. due to labelling schemes), the importance of human emissions for indoor air quality grows. To enable us to model and predict air composition and chemistry indoors, these human emissions must be well characterized under typical indoor climate conditions.

Humans emit hundreds of organic compounds originating from sweat and sebaceous glands, and from skin, breath, and intestinal gases (flatulence). Some studies have measured whole-body bioeffluents, others have analyzed bioeffluents emitted when breathing (exhaled bioeffluents) and through skin (dermally emitted bioeffluents) or bioeffluents from a particular part of the body.^{10,11} A recent chamber study investigated the influence of separated dermal emissions and exhaled air on perceived air quality and showed that dermally emitted pollutants contribute to sensory nuisance caused by human emissions.¹¹ Studies attempting to characterize the contribution of

occupants to indoor chemistry have only recently begun to emerge.¹² With improving measurement technology, new insights have been made (e.g. from skin and from breath).^{13,14,15,16} They have pointed out the paramount importance of reactions on the human-occupant interface, as well as the significant contribution from occupants to the composition of indoor air.^{17,18,19,20}

Human emissions can undergo chemical transformations and generate a suite of new compounds.^{12,21,22} A prime example of such transformations is the ozonolysis of skin lipid constituents, especially squalene. Ozonolysis is an important source of indoor volatile organic compounds (VOCs) and a sink for indoor ozone.^{13,14,23,24,25,26,27} These reactions also occur on clothing, which acquire skin oils during wear.^{20,28,29,30,31} The products partition between the gas phase and surfaces. Some of them stay on the skin, while others can deposit on other indoor surfaces and become precursors for subsequent secondary reactive chemistry.¹² Factors that modify this chemistry include number of occupants, room temperature, relative humidity (RH), ozone concentration and ventilation rate.^{20,32} Model simulations further indicate that the presence of occupants can reduce oxidant concentrations and affect the formation of new products,²² as was demonstrated for a fixed set of conditions in an earlier chamber study.³³ However, more extensive controlled chamber studies of human emissions, their constituents and chemical transformations are lacking.

A valuable new instrumental development, complementing traditional measurements of air composition, is the measurement of total OH reactivity. The total OH reactivity method determines the lifetime of OH radicals in the environment where the measurement is made, accounting for all reactive organic species in the air, even those not measured by the available analytical methods. Comparing the measured total OH reactivity (total oxidation capacity) to the summed reactivity anticipated from known individual trace gases reveals whether all relevant species are being measured. The comparative reactivity method for measuring total OH reactivity³⁴ has been successfully applied in numerous outdoor air measurements.^{35,36,37,38} However, the method has never been applied in indoor environments.

The aim of the Indoor Chemical Human Emissions and Reactivity (ICHEAR) project is to utilize advanced technologies to examine the role of humans and their emissions in indoor air chemistry. The ICHEAR project has investigated the impact on indoor air chemistry of exhaled and dermally

emitted human bioeffluents under different conditions comprising human factors (level of clothing/fraction of exposed skin, age) and a variety of environmental factors (air temperature, RH, ozone). The main specific objectives were to 1) quantify the volatile organic compounds, ammonia, CO₂ and nanoparticles emitted by humans under various environmental conditions within a climate chamber, 2) determine the impact of age and extent of skin coverage by clothing on human emissions and total OH reactivity, 3) quantify the contribution of exhaled and dermally emitted compounds to total emissions and OH reactivity, and 4) determine the most OH-reactive human emissions and the extent of “missing” indoor OH reactivity. This paper presents an overall introduction to the project, describes in detail its experimental design and methodologies and provides selected preliminary results, especially demonstrating the effect of age and the robustness and repeatability of the experiments.

2. METHODS

2.1 Climate chambers

The experiments were performed in two 22.5 m³ twin stainless-steel climate chambers (26.8 m³ including the underfloor plenum) at the Technical University of Denmark (Figure 1).³⁹ Each chamber is ventilated through a perforated floor and the air is exhausted through an outlet in the ceiling. The doors are sealed with a silicon rubber tube which is pressurized and depressurized when the doors are closed and open. All objective measurements were performed in the same one of the two chambers (primary chamber). The chamber was furnished with only a table, four wire mesh chairs, and two pedestal mechanical fans, to minimize any emissions other than from the human occupants. In order to remove reactive compounds from the indoor surfaces, the chamber underwent thorough cleaning, thermal treatment and ozone treatment prior to the first experiment. The chamber was cleaned by washing all surfaces first with a 10% solution of Extran[®] MA02 (Merck, Burlington, Massachusetts, USA) in water, then with demineralized water. During thermal treatment, the air temperature was maintained at ~40 °C and the chamber was ventilated with an air change rate (ACR) of 11 h⁻¹ over a period of 42 h. Subsequently, the ozone concentration was maintained at an average of 595 ppb (range 395-745 ppb) for 63 h. Finally, all surfaces were cleaned using a Kärcher SC3 steam cleaner (Alfred Kärcher SE & Co. KG, Winnenden, Germany). Steam cleaning was again performed right before each set of experiments (see “*Experimental conditions and procedures*”).

A moderate and a high air temperature level (set points 25 and 31 °C) and a low and a high RH level (set points 25 and 65 %) were used throughout the experimental conditions. The temperature was controlled by the chamber's HVAC system. However, the occupancy combined with the relatively warm outdoor air, sometimes exceeded the cooling capacity of the system and caused increases in indoor temperature above the set point, especially during the moderate temperature conditions. For the same reason the originally planned 21 and 27 °C set points were not feasible. The low nominal RH level was not controlled (humidifier off, no dehumidifying), while the high nominal RH level was achieved by operating a steam humidifier in the HVAC system. The chamber was ventilated with 100% outdoor air at an average ACR of 3.2 h⁻¹ (standard deviation SD 0.11, n=36), determined from the decay of the occupant generated carbon dioxide (CO₂) after each occupied period.⁴⁰ The same ACR was measured at the beginning of the experimental campaign with an Innova 1312 Photoacoustic Multi-gas Monitor (LumaSense Technologies A/S, Ballerup, Denmark) using Freon[®] 134a as tracer gas.

The incoming air was filtered with a newly installed F7 efficiency glass fiber particle filter (average efficiency for 0.4 µm particles between 80% and 90% according to EN779:2012, corresponding manufacturer-specified efficiency according to EN ISO 16890:2016 is ePM₁ 60%) and a high efficiency molecular filter (activated carbon in loose-fill canisters). The molecular filter ensured that ozone-free air was supplied to the chamber. During experiments investigating ozone-initiated reactions, ozone was generated in the HVAC system downstream of the activated carbon filter. Pure oxygen was delivered through a Jelight 600 UV ozone generator (Jelight Company Inc., Irvine, CA, USA). The target ozone concentration was ~100 ppb in the unoccupied chamber. Ozone dosing was initiated i) after reaching steady-state CO₂ concentration (following a short lunch break) or ii) the evening before the experimental day, ensuring steady-state target ozone concentrations in the chamber before the volunteers entered in the morning. Thus, i) steady-state was achieved from an ozone-free state during occupancy or ii) the ozone concentration was at steady-state when the volunteers entered the chamber (see "*Experimental conditions and procedures*"). After each experiment, with the chamber empty, the ozone concentration was allowed to approach near steady-state before the next experimental condition was established (average 94 ppb, SD 6 ppb). This served to clean/passivate the chamber surfaces prior to the next experiment.

Mixing of the air in the chamber was ensured by operating two pedestal fans, both pointing away from the volunteers towards the chamber walls. To isolate dermally emitted and exhaled bioeffluents, when applicable, the identical second chamber (auxiliary chamber) was used. The volunteers sat in one of the chambers and wore breathing masks covering their mouth and nose (Sperian ValuAir Plus 6100V series RP155). One-way valves in the mask ensured that the volunteers inhaled air from the chamber where they were seated, and exhaled into the adjacent twin chamber (Figure S1). The air temperature and RH were set to be identical in both chambers. The masks were attached to Teleflex medical tubes made of clear vinyl with an outer diameter of 22 mm. The tubes were connected to a polyurethane plate tightly mounted on the door-passage connecting the two chambers using wooden boards wrapped in aluminum tape. A miniature fan mounted in the end of each tube facilitated the movement of all exhaled air through the tube into the second chamber. The fan operated at a low speed in order not to extract additional air from one chamber into the other. It only operated when the mask was worn. Both the measured CO₂ concentrations and tracer gas measurements confirmed the functioning of the breathing arrangement; no leakage from the mask or the other chamber into the occupied chamber was detected (see also *Results and Discussion*). The volunteers were instructed to breathe normally through the masks.

2.2 Volunteers

Five groups with four volunteers each were recruited to participate in five distinct sets of experiments. Groups were used in order to reduce the influence of individual variability in the emissions on the results. Three of the five groups consisted of young adults (A1, A2, A3, referred to as “adults”), primarily students at the Technical University of Denmark. This allowed us to examine the variability between different groups of volunteers of similar age and thus get an insight into intra-person variability. The average age of the adults was 25 years (range 19-30), the average BMI was 21.6 (range 20.0-23.9). The fourth group consisted of teenagers (T4) with average age 13.8 years (range 13-15) and BMI 19.5 (range 19.1-20.4). The fifth group consisted of seniors (S5) with average age 70.5 years (range 68-72) and BMI 25.6 (range 22.5-28.1).

There were two males and two females in Groups A2, A3 (except for Experiments 14+15 in Table 1), T4, and S5. There were three males and one female in Group A1 and Group A3 for Experiments 14+15. All volunteers were Caucasian, non-smokers, not living with a smoker and

did not suffer from asthma, allergies or any chronic disease. To address potential dropouts during the experiments, two additional volunteers (one male and one female) were recruited for each experimental set to stand-by and substitute for a primary volunteer if needed on any of the experimental days. They were asked to follow the same requirements and come to the lab in the morning of each experimental day. They were allowed to leave once all primary volunteers for the day had arrived. Only one stand-by volunteer on one experimental day was used due to illness of a primary volunteer (Experiments 14+15; a male volunteer was substituting a female volunteer).

The volunteers were instructed not to drink alcohol or eat spicy food, garlic, lozenges, chewing gum or mint drops one day prior to and during the days of the experiments. They were asked to keep a somewhat consistent diet and mode of morning-transport to the laboratory throughout the entire experimental session. They received paraben-, perfume- and colorant-free liquid soap and shampoo (Neutral, Unilever Danmark, Copenhagen, Denmark) as well as toothpaste (Zendium Classic, Unilever). No other personal care products were permitted. They were asked to shower in the evening, but not in the morning, prior to each experiment. On every experimental day they filled out a questionnaire indicating the food items they had consumed the preceding 24 hours, overall thermal comfort and perceived air quality during the experiments, as well as whether they had menstruation, ovulation or taken oral contraceptive the past 24 hours (voluntary questions for females).

On each experimental day, the volunteers wore a brand-new set of clothing provided by the experimenters, except their own underwear. They did not wear shoes in the chamber. To test the influence of exposed skin area, participants either wore “long” or “short” black clothing. “Long” clothing consisted of 100% cotton sweatpants, 100% cotton long-sleeve shirts and calf socks of 80 % cotton, 15% polyester, 5% elasthan. “Short” clothing consisted of 100% polyester shorts, 100% cotton t-shirts and ankle socks of the same material composition as the calf socks. The clothing was washed once after purchase with odor-free detergent (Tex Liquid Enzyme 758, Novadan, Kolding, Denmark) at 40 °C, tumble dried and packed in individual zip-lock bags using nitrile gloves. The volunteers were provided with perfume- and colorant-free liquid washing detergent (Neutral, Unilever Danmark, Copenhagen, Denmark) to wash a set of underwear to be worn during the experiments.

2.3 Experimental conditions and procedures

Five sets of experiments, each with their respective groups of volunteers, were designed to address five specific research questions (Table 1). The first set examined the effect of temperature and RH with “long” clothing in a 2x2 experimental design (Experiments 1-4). In an additional experiment, the measurements under high temperature and high RH were repeated with “short” clothing (Experiment 5). In three of the experiments (1, 2 and 4), ozone was added to the chamber air after lunch break when the primary emissions from humans had reached steady-state, i.e. after 3 hours of exposure.

The second set of experiments examined the impact of ozone-initiated reactions on reactivity and indoor chemistry in two types of experimental designs. In the first type (Experiments 6 and 8), the volunteers occupied the ozone-free chamber for 3 hours, left for a 10-min lunch break, and ozone was added 10 minutes after the volunteers returned to the chamber. Another 2.5 hours of measurements were then performed (marked as “from SS” in Table 1). In the second type of experiments (Experiments 7 and 9), the target ozone concentration was established before the volunteers entered the chamber. In this case the dynamics of the chemistry, especially those of secondary and tertiary products, is expected to be different, as the products of human emissions do not reach steady-state before ozone-initiated reactions commence (marked “from start”).²⁰ Both types of experiments were performed at the lower air temperature and RH, with both “long” and “short” clothing.

The third set examined the chemical composition of exhaled and dermally emitted human bioeffluents as well as their chemical transformations. All measurements were performed in the primary chamber, which contained either dermal emissions (Experiment 11) or exhaled breath (Experiment 12). These measurements were done with “short” clothing, at high temperature and RH. The measurements with dermal emissions were repeated under moderate temperature and low RH (Experiment 13). In all cases, ozone was added in the primary chamber after 3 hours of exposure. A separate experiment (14+15) probed whether the presence of ozone affects the composition of exhaled breath and the OH reactivity of indoor air. The volunteers were seated in the auxiliary chamber, inhaling ozone-free chamber air and exhaling into the primary (measured) chamber via the breathing masks. After 3 hours, they exited the chamber for a 20-min break. During the break, the primary chamber was flushed at an ACR of $\sim 7 \text{ h}^{-1}$ (CO_2 concentration

decreased from ~1230 pm to ~500 ppm). To rapidly increase the ozone concentration in the auxiliary chamber to ~100 ppb, a corona discharge ozone generator was used. The corona discharge generator was then turned off and the experiment continued with the usual UV ozone generation in the HVAC system, at which point the volunteers returned to the auxiliary chamber and the experiment continued for another 3 hours.

The fourth and fifth sets of experiments repeated earlier experiments (lower temperature and RH, “long” clothing and both types of ozone dosing described under the second experimental set) with volunteers from two additional age groups: teenagers and seniors. Together these experiments were designed to provide information on the emissions from three different age groups. Full benchmarking of the five groups was achieved by performing one experiment identically with all groups. Additionally, in order to assess the precision and repeatability of the results with a specific focus on analytical errors and day-to-day variations in bioeffluents emitted by the volunteers, seven experiments were replicated. Experiments 20-26 replicated Experiments 3, 6, 7, 8, 9, 16 and 18, respectively.

Time was reserved in the planning stage to repeat any experiments in which technical problems prevented completion. Since no experiments needed to be repeated, the reserved time could be used for additional experiments. These were designed to test the effect (on emissions and related chemistry) of i) showering, ii) bare-skinned vs. clothed volunteers, and iii) new vs. used clothing. Two other experiments looked at iv) the impact of human bioeffluents in the inhaled air on exhaled breath, and v) the human emissions, OH reactivity and chemical transformations while a volunteer slept in the controlled climate chamber. One experiment looked at vi) emissions from used carpet under different conditions of ozone and light. These experiments will be described in detail in future publications.

The experimental conditions in the chambers were established the evening before, ensuring sufficient time to reach steady-state before the commencement of the experiments in the morning. The volunteers were asked to arrive in the assembly area at least 30 minutes prior to entering the chamber. Skin wipe samples (see below) were collected from the volunteers’ right forearm, after which they rinsed their forearm with warm running water for at least 1 minute and then put on the clothes assigned for the experiment. This occurred about 15 minutes before entering the chamber.

They were encouraged to use the restroom before they entered the chamber, which remained undisturbed and closed during measurement periods.

The volunteers sat around a table, mostly performing activities on their smartphones or the provided tablets, which remained in the chamber during the entire campaign. They were not allowed to bring books, papers, food or their own computers. Tap water was provided. They were asked once every hour to record their skin water and skin oil content measured by a low-cost Neon SK-5D skin analyzer (range 0-99.9 %, accuracy ± 0.1 %) on the back of the hand and stand up and stretch for a few minutes; they were otherwise sedentary. The exposure in the chamber lasted either 3 hours when ozone was present in the chamber from the start, or 3 hours in the morning (ozone-free) and 2.5 hours (2 hours in Experiments 1, 2 and 4) in the afternoon (ozone present). During the latter (long experimental days), the volunteers took a 10-min lunch break outside the chamber. Identical lunches consisting of bread, butter and sliced cheese were provided during the breaks. Ozone generation began 10 minutes after the volunteers returned into the chamber following the lunch break. This was done to partially compensate for the short decay in the bioeffluent concentrations during the break. After exiting the chamber at the end of the experiment, another skin wipe sample was collected, this time from the volunteers' left forearm, after which the volunteers changed into their own clothes. Measurements of chamber air continued for another 30 minutes to monitor the decreasing concentrations of gases and particles. Sampling of the chamber surfaces was then carried out (see below). Finally, ozone was dosed in the chamber until it reached near steady-state, as described earlier, before changing the conditions for the next experimental day. The experimental procedure is summarized in a flow chart in Figure S2.

2.4 Measurements and sampling

Ozone concentration inside the chamber was continuously monitored with a 2B Technologies Model 205 ozone monitor (2B Technologies, Boulder, CO, USA) with a time resolution of 10 seconds (accuracy: 1.0 ppb or 2% of reading). Occasionally the monitor was switched to sample inlet air in the HVAC duct immediately before it entered the chamber. NO and NO_x inside the chamber were measured with a chemiluminescence NO/NO_x analyzer (ECO PHYSICS, model CLD 700 AL) with a time resolution of 1 minute (minimum detectable 1.0 ppb, linearity 1% of reading in range). These instruments were placed outside the chamber and sampled the chamber air via 3 m long Teflon sampling lines. Air temperature, RH and CO₂ concentrations were

continuously monitored with 1-minute time resolution using Vaisala GMW90 (accuracy: temperature ± 0.5 °C, RH $\pm 2.5\%$ below 60%, $\pm 3\%$ between 60-80%, CO₂ ± 30 ppm + 2 % of reading; Vaisala Corporation, Helsinki, Finland) connected to a HOBO® UX120-006M 4-channel analog data logger (Onset Computer Corporation, Bourne, MA; USA). This measurement station was placed on the table in the middle of the chamber. These instruments were newly calibrated before the experiments. All other instruments measured the chamber's exhaust air, either directly at the air outlet in the chamber's ceiling (VOCs and reactivity) or approximately 0.3 m into the duct exhausting the air from the chamber (ammonia and particles). CO₂ was also measured in the exhaust air using a cavity ring-down spectrometer (see below).

Gas phase VOCs were measured online using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS 8000, Ionicon Analytik GmbH, Innsbruck, Austria), which has been widely used in VOC measurements.⁴¹ Protonated water (H₃O⁺) was used as the primary ion during ICHEAR under conditions of drift tube pressure (P_{drift}) 2.2 mbar, temperature (T_{inlet}) 60°C and $E/N=137$ Td (1 Td= 10^{-17} Vcm⁻¹) with time resolution of 20 s. VOCs with a proton affinity higher than water (691 kJ mol⁻¹) are protonated via proton transfer reaction by H₃O⁺ and then transferred to the detector (time-of-flight mass spectrometry). The mass resolution was 4000 at mass 96 amu. A flow of 100 mL min⁻¹ was set to draw the air from the main inlet line to the instrument. 4-point calibrations were performed three times throughout the whole campaign using a standard gas mixture (Apel-Riemer Environmental Inc., Broomfield, USA) containing 14 compounds (methanol, acetonitrile, acetaldehyde, acetone, dimethyl sulfide, isoprene, methyl vinyl ketone, methacrolein, methyl ethyl ketone, benzene, toluene, xylene, 1,3,5-trimethylbenzene and α -pinene). The mixing ratios of masses not included in the gas standard were calculated using the theoretical method assuming a constant proton transfer reaction rate constant (2.0×10^{-9} cm³ s⁻¹) with an accuracy around 50%.⁴² The PTR-ToF-MS data was initially processed by PTRwid,⁴³ in which correction of mass-dependent transmission efficiency was considered, as suggested by Cappellin et al.⁴⁴ The detection limit for the species reported in this study were 84 ppt for acetone, 7 ppt for geranyl acetone, 17 ppt for 6MHO and 43 ppt for 4OPA.

Total OH reactivity was measured using the comparative reactivity method (CRM),³⁴ which consists of a home-built glass flow reactor coupled to a commercial PTR-MS (Ionicon Analytik GmbH, Austria).⁴⁵ Briefly, the CRM is based on the competitive reaction between a reference

molecule, whose reaction with OH is well established and whose concentration can be unambiguously detected (here pyrrole, C₄H₅N) and ambient reactive molecules with OH radicals. Pyrrole (Westfalen AG, Germany) is alternatively introduced inside the reactor with clean air (C2 in Equation 1) or ambient air (C3), while the OH radicals are generated in-situ through photolysis of water vapor. The PTR-MS was operated at standard conditions ($P_{\text{drift}} = 2.2$ mbar, $E/N = 130$ Td, $T_{\text{inlet}} = 60$ °C) and used to monitor pyrrole concentration at the protonated fragment m/z 68 with a dwell time of 20 s throughout sequential experimental stages. Switches between C2 and C3 were programmed to occur every 5 minutes, while C1 was recorded occasionally.⁴⁶ Assuming a pseudo first order kinetics regime ($[\text{pyrrole}] \gg [\text{OH}]$), we quantified the total OH reactivity (R_{air}) as follows:

$$R_{\text{air}} = \frac{(C3 - C2)}{(C1 - C3)} \cdot k_{\text{pyrrole}+\text{OH}} \cdot C1 \quad (1)$$

where C1 is the initial concentration of pyrrole diluted in clean air, quantified after its photolysis and when the OH radicals are scavenged, $k_{\text{pyrrole}+\text{OH}}$ is the rate constant of the reaction between pyrrole and OH, which equals $(1.20 \pm 0.16) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.^{47,48} Pyrrole/OH was between 2.5 - 3.5, therefore the reactivity calculated in Equation 1 was corrected for the experimental kinetics regime by using calibration with different test gases.⁴⁹ Corrections for interferences with changing RH and ozone concentration were taken into account (see Fuchs et al.⁵⁰ for more details). The time resolution of the CRM was 1-10 minutes and the limit of detection is $\sim 3\text{s}^{-1}$.

A custom-made fast gas chromatograph – mass spectrometer (SOFIA – System for Organic Fast Identification Analysis) with a cryogenic preconcentration system and a time resolution of 3 min was used to detect nonmethane hydrocarbons and organohalogens.⁵¹ Air was drawn into the instrument with an inlet flow of 200 mL/min. To avoid ozone induced oxidation during trapping, a sodium thiosulfate ozone scrubber was installed in the instrument's inlet line. The sampling volume was between 20 and 40 mL. A separate calibration with a standard gas mixture containing the measured analytes (Apel-Riemer Environmental Inc., Broomfield, USA) was performed every day. The detection limit for isoprene was between 1 and 25 ppt.

A cavity ring-down spectrometer (Picarro G2401; Picarro Inc., Santa Clara, California, USA) was used to measure CO₂, CO, CH₄ and H₂O. The CO₂ data (accuracy 0.2 ppm) were corrected using the relationship between measured and known concentrations at five levels (~500, 1000, 1500, 2000, 2500 ppm) injected into the instrument using a calibration gas, synthetic air and mass flow controllers (dosed conc. = 1.009 x measured conc.; R²>0.99999). This instrument together with the PTR-ToF-MS, OH reactivity system and the fast GC-MS shared a common sampling inlet using a 5 meter long ½" (outside diameter 1.27cm) fluorinated ethylene propylene tubing with a flow of around 7 L min⁻¹. It could be manually switched between sampling supply air and exhaust air in the chamber's outlet via a 3-way valve (Galtek® Solenoid Valves, Entegris, Inc.). Sub-stream air was taken from the main inlet for the four different instruments. All the inlet tubing except the sub-stream line for Picarro was insulated and heated to 40-45 °C to avoid condensation during high humidity conditions. Another manufacturer-calibrated cavity ring-down spectrometer (Picarro G2103) was used to measure NH₃ in the chamber's exhaust air. The instrument was placed directly next to the exhaust air duct, and the sampling line had a length of ~0.2 m. Data from both cavity ring-down spectrometers were corrected for water and reported in dry-air mole fraction.

Particles with diameters between 1 and 4 nm were measured in real-time with a state-of-the-art Nano Condensation Nucleus Counter (Airmodus A11-nCNC system).⁵² Prior to the campaign, it was fully serviced and calibrated using monodisperse NiCr-oxide particles for the 1-4 nm size range (Particle Size Magnifier). Additional monitoring of time-resolved particle levels was done using an aerosol spectrometer (size range 0.01 – 35 µm divided into 40 size channels, Mini-WRAS, Grimm Aerosol Technik). Data from the 0.01 – 0.5 µm size range was neglected, as human body emissions are typically not associated with significant particle emission rates in this size range,⁵³ and small changes are difficult to discern under relatively high background concentrations, which was the case in our chamber. Concentrations of fluorescent biological aerosol particles (FBAPs), proxy for aerosol particles of biological origin, were measured with a Waveband Integrated Bioaerosol Sensor (WIBS) using an embedded UV light-induced fluorescence (UV-LIF) technique (WIBS-NEO, Droplet Measurement Technology, Inc.). Fluorescent particle concentrations were resolved in 6 size channels within the particle size resolution 1-10 µm. Maintenance and zero count checks for Mini-WRAS and WIBS instruments were performed before and after the campaign. Size calibration was checked using monodispersed

1.005 μm and 2.005 μm polystyrene latex (PSL, Thermal Scientific, US), and showed < 10% error.

Gas phase VOCs were also sampled on sorbent tubes containing Tenax adsorbent. 5 L of chamber air was collected on the adsorbent tubes in the chamber's exhaust air outlet at a flow of 150 mL/min using a Gilian GilAir® Plus sampling pump (Sensidyne LP, St. Petersburg, Florida, USA). One sample was taken each morning immediately before volunteers entered the chamber (chamber air background), duplicate samples were taken right before the volunteers left the chamber (last 33 minutes of the occupancy), which was assumed to represent steady-state. On long exposure days an additional sample was taken right before the short lunch break. Ozone scrubber was not used upstream the tubes during sampling. The Tenax tubes were thermally desorbed (Markes International, Unity 1 and Ultra) and the VOCs were analyzed by gas chromatography/mass spectrometry (Agilent 6890 GC, Agilent 5973N MS).

To improve our understanding of the surface chemistry occurring along with the emissions and their chemical transformations, wipe samples from the volunteers' skin and from surfaces of the chamber were collected. Pre-cleaned sterilized cotton pads wetted with 2-propanol were used to thoroughly wipe (7 strokes) an area of 100 cm² on each volunteer's right forearm before exposure and on the left forearm after exposure. The sampling area was marked by holding a plastic sheet with a 100 cm² hole to the forearm. The sheet was cleaned with disposable wipes (Kimtech Science™ Kimwipes™; Kimberly-Clark Worldwide, Inc.) wetted with 2-propanol after each use. To prevent any 2-propanol from contaminating the chamber when the volunteers entered, the sampling was done in a dedicated room. Additionally, a 10 cm x 10 cm sample from the shoulder area of each volunteer's shirt was cut after exposure. For background measurements, each experimental day one sample of the same size was cut from the lower back area of one of the volunteers' shirt before it was worn. The samples were wrapped in aluminum foil and frozen until analyses. The same 1 m² of chamber wall area was wiped after each day's exposure with pre-cleaned (by heating, 400 °C) glass wool wipes soaked with 2-propanol. The samples were then stored in sealed glass vials, frozen at -18 °C until analyses. Morning background samples on the chamber surface were not taken, in order not to disrupt the established experimental condition. The samples were analyzed with solvent extraction followed by GC-MS (Thermo Scientific; TRACE 1310 GC, TSQ 800 Evo MS) and LC-MS (Thermo Scientific Ultimate 3000 ultra-high-

performance liquid chromatograph (UHPLC), Q-Exactive Orbitrap mass spectrometer (MS)). Finally, skin temperature and in some cases skin humidity were continuously measured on each volunteer's back of hand, forearm and forehead (temple) with iButtons (Thermochron or Hygrochron, Maxim Integrated, San Jose, CA, USA); in Experiments 6-9 and 21-24 the measurements were taken only on forehead (temple).

Chamber surface swab samples and shirts samples were also collected for later microbiota analysis to provide information on microbial contamination on the chamber surfaces under the different experimental conditions and to link this information with the gas-phase and surface chemistry assessment. Sampling was done by swabbing a 25 cm x25 cm area with a sterile cotton swab wetted with sterile ultraclean water. Each surface was swabbed over 15 seconds in one direction while rotating the swab tip, and over another 15 seconds in 45° rotated direction. Cotton tips of the swabs were cut into a DNA extraction tube and stored frozen until shipment. The surface of the chamber wall and table were sampled. Two sampling areas were marked on the wall and table, and these were sampled on alternate experimental days. Shirt samples, identical to those described above for chemical analyses, were saved for later microbial analyses. All sampling was performed wearing sterile gloves, and the tools were cleaned with wipes wetted with 2-propanol after each sampling.

3. RESULTS AND DISCUSSION

To assess the robustness and repeatability of the methods, ACR, ozone, air temperature, RH, CO₂ concentrations and skin water content are compared across all experiments (Table S1). For the five benchmarks and their three replicate experiments (Table 2), additional analyses are presented in Figure 2.

The ACRs were calculated from the decay of the occupant generated CO₂ concentrations after each occupied period. On long experimental days, the ACR was also calculated from the CO₂ decay during lunch breaks. The ACRs in Table S1 for the long days are thereby the averages of the two ACRs; the average difference in ACR between morning and afternoon was 0.05 h⁻¹ (from CO₂ in the exhaust). The calculations were made using CO₂ concentrations measured both in the ventilation exhaust (Picarro G2401) and in the middle of the chamber (Vaisala CO₂ monitors); the average difference in the ACR determined using the two datasets was 0.01 h⁻¹. The ACR was

stable during the entire campaign. The standard deviation across all experiments was 0.1 h^{-1} . Same ACR (3.2 h^{-1}) was measured using a photoacoustic multi-gas monitor and Freon[®] 134a as tracer gas.

The steady state ozone concentrations were similar for all experiments when ozone was present in the chamber. With the chamber occupied, the average steady state ozone level when the experiments began with elevated ozone (mornings) was 39.1 ppb (SD 3.8 ppb), while it was 36.9 ppb (SD 2.3 ppb) when ozone was dosed after the volunteers reentered following lunch break (afternoon). For experiments that started with elevated ozone, the average initial steady-state ozone concentration before occupancy was 102 ppb (SD 3 ppb). The steady state level was thus on average 38% (SD 3%) of the corresponding initial value. The average ozone concentration in the inlet air across all experiments with ozone dosing was 107 ppb (SD 8 ppb). The steady state ozone concentrations during occupancy were similar regardless of the volunteer group and whether the exposure was whole body or dermal only (Experiments 11 and 13). The average ratio of steady state to inlet air ozone concentration, without Experiment 12 (breath only) was 0.35 (range 0.31-0.40). When the chamber contained only exhaled breath (Experiment 12), the steady state ozone concentration was 96.5 ppb and it did not change meaningfully after the volunteers exited the chamber. This indicates that ozone reactive chemicals in exhaled breath (e.g., isoprene) do not react fast enough to compete with the air change rate.

Ozone measurements in the supply air were available for two of the experiments with high initial ozone concentrations. During two additional experiments, the ozone concentrations were allowed to reach steady state after the volunteers left the chamber. In these four experiments the rate at which ozone was removed by the empty stainless steel chamber (k_{chamber}) was determined from the ratio (R) of the steady state ozone concentration in the chamber to that in the supply air and the ACR ($k_{\text{chamber}} = (\text{ACR}/R) - \text{ACR}$). The average value for k_{chamber} was 0.17 h^{-1} (range $0.092 - 0.29 \text{ h}^{-1}$), which is very close to the value reported by Salvador et al.²⁰ for the same chamber (0.15 h^{-1}). The chamber surfaces were thus relatively clean and were responsible for only a small fraction of the total ozone removal relative to the ozone in the supply air.

The nominally moderate chamber air temperature was difficult to maintain during the experiments. This was caused by the relatively high outdoor air temperatures, heat generated by

the volunteers, ventilation with 100% outdoor air and an underperforming cooling system. Recirculation of chamber air would have allowed for more efficient temperature control. However, this was not done in order to avoid influencing the measurements by chemical transformations of human emissions in the ventilation system. The average background temperature before volunteers entered was 24.8 °C (SD 1.4 °C). This increased to an average of 27.9 °C (SD 1.4 °C) before the volunteers left the chamber in the morning and it continued to increase to 28.7 °C (SD 1.1 °C) during the afternoon exposure. The nominally high temperature was more stable. The average background temperature before volunteers entered was 31.6 °C (SD 0.9 °C) and it changed little during the course of the experiments (32.3 °C, SD 0.7 °C before the volunteers left the chamber in the morning; 31.8 °C, SD 0.7 °C before the end of experiments in the afternoon). Occasionally the temperature during an experiment with nominally moderate temperature reached nearly 30 °C, similar to the nominally high temperature experiments (Table S1). However, the temperature during occupancy was on average 5.4 °C lower on moderate setpoint days compared to high setpoint days in the mornings and 3.6 °C in the afternoons.

The RH in the chamber was relatively constant throughout each experimental day, although small differences were observed between days, as indicated by the wider standard deviations compared to the other parameters. The low and high nominal RH were, however, distinctly different. The average background RH before volunteers entered was 23% (SD 5%) and 64% (SD 4%), corresponding to the low and high nominal values, respectively. It increased slightly during nominally low RH days to an average of 27% (SD 5%) before the volunteers left the chamber in the morning and remained the same during the afternoon exposure. The average RH remained virtually unchanged during nominally high RH days (62 % (SD 5%) morning steady state; 63 % (SD 7%) afternoon steady state). However, due to the on/off control of the humidifier (relatively consistent 15-20 min periods of each), the RH oscillated on average $\pm 15\%$ of the average RH (average min. 55%, average max. 73%).

The average skin water content for all volunteers during an entire experiment (morning, afternoon and combined) was calculated. Morning and afternoon averages were similar (Table S1). The grand average (mornings and afternoons combined) was 29.4% across all experiments with moderate temperature and low RH (n=17) and 45.8% under high temperature and high RH (n=3). There were two conditions with moderate temperature and high RH (skin water content 31.5% and

41.3%) and one experiment with high temperature and low RH (skin water content 36.7%). The relationship between skin water content and enthalpy of moist air and that between skin water content and predicted mean vote (PMV) calculated for chamber air, are shown in Figures S3 and S4, respectively. Enthalpy was calculated using the HumidAir psychrometric calculator (Megawatsoft Inc., www.psychrometric-calculator.com/HumidAirWeb.aspx) assuming absolute pressure of 1 bar. PMV was calculated using the CBE Thermal Comfort Tool (Center for the Built Environment, University of California Berkeley, <https://comfort.cbe.berkeley.edu/>) assuming an air speed of 0.25 m/s, metabolic rate of 1 met and a clothing level of 0.4 clo for “short” clothing and 0.7 clo for “long” clothing. It should be noted that despite the high accuracy of the low-cost skin water content sensor reported by the manufacturer, such instruments may have limited accuracy and reproducibility.

Ammonia results have been presented in detail in a related publication.⁵⁴ In summary, background NH_3 concentrations in the unoccupied chamber were low (typically < 10 ppb) and began to increase as soon as volunteers entered, rising to between 50 and 450 ppb by 12:30 pm. The NH_3 concentrations were higher on days with high temperature/high RH and on days with “short” clothing. Ozone and RH had a smaller impact on NH_3 concentrations than temperature and amount of exposed skin. On experimental days with an afternoon ozone exposure, NH_3 concentrations were higher in the afternoon than in the morning. This was presumably due to the light lunch prior to the afternoon exposure as opposed to the introduction of ozone, since ozone in morning experiments had little impact on NH_3 concentrations. For young adults and seniors, the NH_3 emission rates derived from the morning measurements ranged from 0.35 $\text{mg h}^{-1} \text{ person}^{-1}$ at moderate T, low RH and “long” clothing to 5.2 $\text{mg h}^{-1} \text{ person}^{-1}$ at high T, high RH, and “short” clothing. The NH_3 emission rate increased strongly with temperature in a predictable fashion. Under otherwise similar conditions, NH_3 emission rates were highest for teenagers, while young adults and seniors had comparable emission rates.

The average background CO_2 concentration before volunteers entered the chamber was 425 ppm (SD 6 ppm). The morning and afternoon exposure periods were sufficiently long for CO_2 to reach steady state. The average steady state CO_2 concentration measured in the chamber exhaust was 1277 ppm (excluding “dermal only” Experiments 11 and 13). The steady state concentrations were consistent across all experiments (SD 56 ppm). During the lunch break the concentrations slightly

decreased. After the volunteers returned to the chamber, the newly established steady state was slightly higher than that in the morning (average 1344 ppm, SD 54 ppm). When volunteers were seated in the primary chamber and breathing through a mask into the auxiliary chamber, the CO₂ concentrations increased very little (steady state ~465 ppm in Experiment 11, ~445 ppm in Experiment 13). When they were seated in the auxiliary chamber and breathing into the primary chamber, the CO₂ concentrations were comparable to all other experiments. This demonstrates that the breathing apparatus was tight and performed as intended.

Figure 3 shows an example of time series profiles of CO₂, O₃, acetone, geranyl acetone, 6-methyl-5-hepten-2-one (6MHO) and 4-oxopentanal (4OPA) for Group S5 (seniors). Figure 4 and Figure 5 (and Figure S5 using a log scale) depict mean morning and afternoon steady state concentrations of CO₂, acetone, geranyl acetone, 6MHO and 4OPA for the five benchmark experiments and the three replicate measurements for different age groups. The consistently higher steady state CO₂ concentrations in the afternoon compared to morning have been observed for all benchmark experiments and their replicates (Figure 4). This may have been caused by increased metabolic rate of the volunteers following lunch coupled with the continuously increasing temperature in the chamber.^{55,56} Since the experiments that began with elevated ozone in the morning did not demonstrate higher morning CO₂ steady state concentrations, it is unlikely that the presence of ozone had any physiological effect leading to elevated CO₂ emissions. The differences between the groups were very small, while results of replicate experiments indicate good repeatability. The relationship between CO₂ emission rates and the different experimental variables (temperature, RH, clothing, ozone) will be reported in detail elsewhere.

The background acetone concentrations were always around 1 ppb (average 1.14 ppb, SD 0.18 ppb). Acetone concentrations increased with occupancy (Figure 3), typically reaching a steady state between 8 and 12 ppb before the volunteers left the chamber (Figure 4). It further increased with the addition of ozone in the afternoon, reaching a new steady state between 18 and 25 ppb before the end of the afternoon exposure. The exception to these typical values were Experiments 1 (adult group 1) and 6 (adult group 2), whose morning and afternoon steady states were substantially higher. It is noteworthy that Experiment 21, the replicate to Experiment 6, had “typical” acetone concentrations. Afternoon steady state concentrations tended to be approximately twice the concentrations in the morning for adult group 3, teenagers and seniors

(Figure 4). The difference between the morning and afternoon steady states was around 10 ppb except for Experiment 6 (3.7 ppb).

Acetone is one of the major VOCs in the exhaled breath of healthy individuals.^{57,58,59} Breath emissions of acetone are influenced by sex and age.^{60,61} The differences between the groups were however small. The differences between replicate measurements for teenagers and seniors were also small, although slightly lower steady state concentrations were measured with seniors the second time (Experiment 25). This may be due to day-to-day variations in diet and metabolism. The atypically large acetone concentrations in Experiments 1 and 6 do not appear to have been caused by differences among the volunteer groups, since the same volunteer group (adult 2) participated in Experiment 6 (atypical value) and Experiment 21 (typical value). The reason for the larger acetone concentrations in Experiments 1 and 6 are not known but may reflect a dietary influence. The higher acetone concentrations in the afternoon are presumably caused by ozonolysis of squalene and certain squalene oxidation products (e.g., geranyl acetone and 6-MHO) on surfaces or in the gas phase.^{13,23,24,25} Additionally, acetone can be formed by reaction of ozone with 2-methyl-2-docosene.⁶²

Background concentrations of geranyl acetone (average 0.003 ppb) and 6MHO (average 0.03 ppb) were negligible, that of 4OPA was also very low (average 0.16 ppb) (Figure 5). Morning steady states were an order of magnitude higher, yet still low for geranyl acetone (range 0.036-0.072 ppb) and 6MHO (range 0.17-0.36 ppb). For 4OPA they remained similar to background levels (range 0.20-0.32 ppb). The slightly elevated morning concentrations (no ozone) may be caused by emissions of these compounds available on the skin of the volunteers as a result of squalene-ozone reactions that occurred prior to entering the chamber. Moreover, geranyl acetone has been reported to be one of the major dermally emitted compounds.^{63,64,65,66} It has high molecular weight and is a relatively sticky compound.

As expected, the concentrations of all three compounds were elevated when ozone was present in the chamber. Steady state levels of geranyl acetone in the afternoon (with O₃) were an order of magnitude lower than those of 6MHO and 4OPA. This is consistent with the fact that geranyl acetone further reacts with ozone to produce the other two compounds. The highest concentrations were measured for 6MHO, which is the primary reaction product of ozone/squalene reactions and

the secondary reaction product as ozone reacts with geranyl acetone. Slightly lower concentrations were obtained for 4OPA, which is the major secondary reaction product as 6MHO and geranyl acetone further react with ozone. It should be noted, however, that 4OPA did not reach steady-state before the end of the experiments, although its rate of change in concentration during the last 15 minutes was small compared to the beginning of the afternoon session. Steady state concentrations are a result of balance among primary ozone-skin oil reactions (source), secondary and tertiary reactions (sources of some compounds, sinks for others) and ventilation (sinks). Salvador et al.²⁰ measured oxidation of human skin oil constituents on used t-shirts at two ACRs and two initial ozone mixing ratios in the same climate chamber as was used in this study. A series of mass balance models demonstrated that geranyl acetone, which was generated by ozone-squalene reactions on the t-shirts, was removed almost equally by ventilation and further reaction with ozone. More than half of the 6MHO and 4OPA were generated on the t-shirts and the rest was the result of gas-phase chemistry. Most of the 6MHO and all of the 4OPA was removed by ventilation.

Steady state concentrations of the three compounds were similar among the groups. Comparing afternoon measurements with ozone present, slightly higher geranyl acetone concentrations were observed for the adult groups, compared to teenagers and seniors. 6MHO concentrations were highest for adult groups 2 and 3, lowest for adult group 1 and seniors. The highest 4OPA concentrations were reached with teenagers and the lowest with adult group 1 and seniors. The overall between-measurement variances are dominated by the variances obtained for the three adult groups (Table S2). We do not know the reasons for the slightly lower steady state 6MHO and 4OPA concentrations obtained for group A1 (three males and one female) compared with the other two adult groups (two males and two females), although it may reflect the difference in the male/female composition of the groups. If so, the seemingly insignificant differences among age groups warrant further investigation.

The small differences in concentrations are not reflected in the measured ozone steady state concentrations, since the rate of ozone removal to skin is dominated by the resistance to mass transport across the boundary layer of air adjacent to the skin.⁶⁷ The negligible differences in the concentrations of geranyl acetone, 6MHO and 4OPA measured in replicate measurements compared to differences between groups indicate good repeatability and robustness of the applied

methodology. Between-replicate variances were one to two orders of magnitude lower than the overall between-measurements variances, except for geranyl acetone, for which they were however also lower (Table S2). The steady state concentration ratios of “6MHO / geranyl acetone” and “(geranyl acetone + 6MHO) / 4OPA” (Figure S6) further indicate that the complex ozone/skin oil chemistry occurring in these experiments was relatively consistent among the different groups, as well as with the same group on different days.

Background isoprene levels were below or near the limit of detection. Isoprene concentrations increased with morning occupancy (Figure S7). The effect of ozone in the afternoon was inconsistent across the experiments. While steady state isoprene concentrations decreased in four experiments (6, 10, 16 and 18), they increased in two experiments (21, 25) and remained unchanged in experiment 26. Replicate measurements indicated poorer repeatability than for other compounds and the differences between the groups are also less pronounced. Isoprene is a major VOC constituent of exhaled breath.⁵⁹ Isoprene breath concentrations exhibit large variability with age and sex, although they may become reasonably stable in central tendency after reaching adulthood.^{68,69,70,71} Cardiac output, breathing pattern, sleep/wakefulness, physical activity as well as clinical conditions can further influence emission rates.^{70,72} Exhaled isoprene reacts slowly with ozone, but reacts more quickly with hydroxyl and nitrate radicals.¹²

4. CONCLUSIONS

The Indoor Chemical Human Emissions and Reactivity (ICHEAR) project is the first attempt to comprehensively determine the effects of human emissions on indoor air quality. Using extremely sensitive, high resolution, real-time measurements of volatile organic compounds, total OH reactivity, non-methane hydrocarbons, nanoparticles, fluorescent biological aerosol particles, ammonia and CO₂, supplemented with traditional air sampling, surface sampling and analyses of clothing samples for both chemical and microbiological contaminants, the project aims to provide new insights on the influence of air temperature, RH, ozone, age and skin-coverage with clean clothing on human chemical, particulate and microbial emissions and their transformations in indoor air. In a set of specially designed experiments, the contribution of oral and dermal emissions are isolated from one another. The experimental campaign was designed to address potential analytical errors and day-to-day variations in bioeffluents through a number of replicate experiments, which demonstrated the robustness and repeatability of the measurements, especially

for the dermally emitted compounds. Ammonia results, including the impact of the investigated variables, have been reported in a related publication. Future publications will present, in detail, the effect of the investigated variables on CO₂ emissions, VOC emissions, total OH reactivity, fluorescent biological aerosol particle emissions, nanoparticle formation and skin surface chemistry.

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Table 1. Experimental matrix for ICHEAR.

Experimental set – objectives (volunteer group)	Experiment No. (replicate)	Condition [†] (T/RH/O ₃ present)	Clothing	Date	Note
1 – Effect of temperature, relative humidity and clothing (A1)	1	moderate / low / from SS	long	26.4.	group benchmark
	2	high / high / from SS	long	30.4.	
	3 (20)	moderate / high / none	long	23.4.(25.4.)	
	4	high / low / from SS	long	29.4.	
	5	high / high / none	short	24.4.	
2 – Effect of ozone and clothing (A2)	6 (21)	moderate / low / from SS	long	12.4.(15.4.)	group benchmark
	7 (22)	moderate / low / from start	long	8.4.(10.4.)	
	8 (23)	moderate / low / from SS	short	16.4.(17.4)	
	9 (24)	moderate / low / from start	short	9.4.(11.4.)	
3 – Contribution of dermal emissions and exhaled breath (A3)	10	moderate / low / from SS	long	8.5.	whole body; group benchmark
	11 [‡]	high / high / from SS	short	2.5.	dermal only
	12 [‡]	high / high / from SS	short	3.5.	breath only
	13 [‡]	moderate / low / from SS	short	7.5.	dermal only
Effect of inhaled ozone on exhaled breath (14+15) (A3)	14+15 [§]	moderate / low / none (14), from start (15)	long	6.5.	breath only
4+5 – Effect of age (T4+S5)	16 (25)	moderate / low / from SS	long	13.5.(15.5.)	seniors; group benchmark
	17	moderate / low / from start	long	14.5.	seniors
	18 (26)	moderate / low / from SS	long	17.5.(19.5.)	teenagers; group benchmark
	19	moderate / low / from start	long	18.5.	teenagers

[†] Ozone dosing was started either after ~3 hours of exposure (“from SS”) or the evening before the experimental day, ensuring steady-state ozone concentrations before the volunteers entered (“from start”).

[‡] Volunteers occupied one chamber and breathed through breathing masks into another chamber. All measurements were performed in the primary chamber.

[§] Volunteers sat in the auxiliary chamber wearing a breathing mask, exhaling air into the primary chamber.

They first inhaled ozone-free air (Experiment 14), then ozone-laden air (Experiment 15). The volunteers were 3 males (including a stand-by) and 1 female.

Table 2. Experiments addressed in the present paper.

Volunteer group	Experiment	Replicate experiment
Adult 1 (A1)	1	
Adult 2 (A2)	6	21
Adult 3 (A3)	10	
Seniors (S5)	16	25
Teenagers (T4)	18	26

Figure 1. Experimental set-up in the twin chambers

Figure 2. Mean temperature and RH (during exposure period), and steady state (SS; last 15 min) ozone, air temperature, RH and CO₂ across all experiments (1-26), both for morning (M) and afternoon (A) periods (when applicable). Temperature and RH are grouped by their respective nominal values (moderate/high; low/high). The dots represent means and the error bars indicate standard deviations.

Figure 3. Example of time series profiles for CO₂, acetone, ozone, geranyl acetone, 6MHO and 4OPA for replicate experiments 16 (left) and 25 (right) with seniors.

Figure 4. Mean morning and afternoon steady state (last 15 min) CO₂ and acetone concentrations for the selected experiments (1, 6+21, 10, 16+25, 18+26) without ozone (open circles) and with ozone (full circles) in the chamber. Five volunteer groups and three sets of two replicate measurements are compared. Error bars denote standard deviations. Average temperature and RH during each measurement period are indicated at the top of the figure. Background data before volunteers entered the chamber are based on combined data for all presented experiments (except for acetone in Experiment 6, which was missing due to a malfunctioning sampling pump).

Figure 5. Mean morning and afternoon steady state (last 15 min) geranyl acetone, 6MHO and 4OPA concentrations for the selected experiments (1, 6+21, 10, 16+25, 18+26) without ozone (open circles) and with ozone (full circles) in the chamber. Five volunteer groups and three sets of two

replicate measurements are compared. Error bars denote standard deviations. Average temperature and RH during each measurement period are indicated at the top of the figure. Background data before volunteers entered the chamber are based on combined data for all presented experiments (except Experiment 6, which was missing background data due to a malfunctioning sampling pump).