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VOC sources and exposures in nail salons: a pilot study in Michigan, USA

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Abstract

Purpose—Exposures of nail salon technicians have received attention due to the potentially toxic materials used in nail products, which include volatile organic compounds (VOCs) such as formaldehyde and methyl methacrylate (MMA). This study characterized area and personal concentrations and other indoor air parameters in 17 nail salons in fall and winter seasons in three areas of Michigan.

Methods—VOC samples were analyzed using thermal desorption, gas chromatography and mass spectroscopy, and the VOC composition of 35 nail products (e.g., polish, top coat, base coat) was measured using headspace sampling. Ventilation rates were derived using CO2 concentrations, occupancy and building information, and VOC sources were apportioned by a novel application of chemical mass balance models.

Results—We detected ethyl acetate, propyl acetate, butyl acetate, MMA, n-heptane and toluene in most salons, and benzene, d-limonene, formaldehyde, and ethyl methacrylate (EMA) in some salons. While MMA was not measured in the consumer and professional products, and the use of pure MMA in salons has been not been permitted since the 1970's, MMA was found in air at concentrations from 100 to $36,000 \mu g/m3$ in 15 of 17 salons; thus, its use appears to be commonplace in the industry. Personal measurements, representing exposures to workers and clients, were about twice those of the area measurements for many VOCs.

Conclusion—This study identifies the products responsible for emissions, shows the widespread presence of MMA, and documents low ventilation rates in some salons. It also demonstrates that "informal" short-term sampling approaches can evaluate chemical exposures in nail salons, providing measurements that can be used to protect a potentially susceptible and vulnerable population. Additional controls, including restrictions on the VOC compositions and improved ventilation, can reduce exposures to salon workers and clients.

Conflict of interest The authors declare that they have no conflict of interest.

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Compliance with ethical standards

Ethical approval The visits were conducted as routine nail services without notification of the research purpose. Our procedures were vetted by our institutional review board (IRB). We neither requested nor collected personal information or business information from salon staff or clients, and no interventions were attempted. IRB staff at the University of Michigan confirm our reasoning.

Keywords

Occupational health; chemical exposures; ventilation; indoor air quality (IAQ); methyl methacrylate (MMA)

1 Introduction

Nail salons and nail salon technicians (NSTs) routinely use a number of chemicals and may represent an exposed and vulnerable worker population. In 2014, 42% of NSTs were reported to be immigrants; the undocumented fraction is unknown but believed to be substantial (Switalski 2016). These workers may be at additional risk as they may not comprehend warning labels or instructions for safe practices that are printed only in English (NM 2013). Most NSTs are women, and many are of child-bearing age. The NST population is large and growing, e.g., in 2015, there were an estimated 129,682 nail salons in the US and 3,300 in Michigan alone (9th highest among US states) (NM 2014; NM 2015); and the industry is estimated to have revenues of \$8.5 billion in 2015 (NM 2015).

Chemical exposures to NSTs include volatile organic compounds (VOCs), which form components of nail polishes, nail polish removers, artificial nails, nail tip adhesives, glues, nail hardeners, and other materials. VOCs measured in salons include acetone, toluene, ethyl acetate, isopropyl alcohol, methyl methacrylate (MMA), ethyl methacrylate (EMA), and formaldehyde (Alaves et al. 2013; Garcia et al. 2015; Quach et al. 2011). Several of these VOCs have known or suspected adverse effects, including: irritation to eye, skin and nose; damage to the respiratory system, liver and kidney; reproductive effects; and breast cancer. Several studies have indicated potentially harmful exposure levels (Alaves et al. 2013; Quach et al. 2011; Quach et al. 2008; Quach et al. 2013; Roelofs et al. 2008; Roelofs and Do 2012; Tsigonia et al. 2010), e.g., formaldehyde levels exceeded the National Institute for Occupational Safety and Health recommended exposure limits (NIOSH RELs) in 58% of samples collected in a California study (Alaves et al. 2013). Adverse health effects observed among NSTs include asthma, dermatitis, and neurological symptoms (Quach et al. 2014; Roelofs et al. 2008). In addition, some VOCs can form less volatile carbonyls, acids, and oxygenated products that may condense to form secondary organic aerosols that may affect health (Goldin et al. 2014).

Several factors can increase NST exposure. Many salons appear to be poorly ventilated based on high concentrations of CO_2 (Alaves et al. 2013; Goldin et al. 2014; Gorman and O'Connor 2007); although few studies have reported ventilation rates. Potentially many NSTs are exposed for over 8 hours per day (NM 2014). Most NSTs (over 60%) fail to use any personal protective equipment (PPE) (NM 2014). Finally, immigrant or undocumented NSTs, who constitute a large share of the workers, are unlikely to express concerns over poor working conditions due to employment pressure (Nir 2015).

The objectives of this study are to estimate inhalation exposures of technicians and clients in nail salons, specifically to VOCs found in nail care products, including polishes, nail polish remover and other materials, and to provide an initial assessment of ventilation and other factors that may influence exposures. We examine conditions in 17 nail salons in two

seasons, and identify the composition of chemicals currently in use. We investigate occupational inhalation exposures among Michigan NSTs, an unstudied cohort; explore whether VOC concentrations are amplified due to the lower ventilation rates expected in Michigan, especially in winter, as compared to the California studies (Alaves et al. 2013; Quach et al. 2008; Quach et al. 2013); use quasi-personal breathing zone measurements to better reflect exposure than the area measurements used in most previous studies; and take repeated measurements to examine variability over time and across salons, which has not been reported in previous studies. Lastly, the study is unique in measuring the composition of 35 common products used by NSTs and using this "fingerprint" information to identify emission sources that contribute to VOC exposure, providing key information needed to formulate practical control measures.

2 Methods

Indoor air quality (IAQ) parameters, including personal and area VOC concentrations, CO2 concentration, air change rate (ACR), temperature, and relative humidity (RH), were obtained at 17 nail salons in Michigan, and the VOCs composition of 35 consumer and professional nail products was analyzed using a head-space method to track down air pollution sources in nail salons.

2.1 Selection and characterization of nail salons

An initial survey conducted in summer 2016 indicated that many or most owners, managers and staff of nail salons were reluctant to participate in a research study, mainly due to language barriers; those who seemed amenable to participation may not have been representative of the salon population. After confirming the sampling approach with our institutional review board, we implemented a program in which salons were visited by two people (a researcher and a volunteer) for routine nail services and data collection without notification of the research purpose of the study. In fall 2016 and again in winter of 2017, 17 nail salons were visited. Salons were located in three Michigan cities that had different racial or ethnic demographics: Ann Arbor with a primarily white clientele (13 nail salons); Dearborn with a primarily Arab-American clientele (2 nail salons); and Detroit with a predominantly Africa-American clientele (2 nail salons). (Supplemental Figure S1 maps the study sites.) Each salon provides predominantly nail-related services, thus pollutants associated with other beauty products should be minimized. All of the salons were in shopping centers near parking lots and large roads.

During each visit, the number of NSTs, clients, work being performed, apparent ventilation system types, number of opened windows and doors, and other observations that might affect exposures and ACRs were recorded. The room dimensions were measured using a laser measuring tape. The type of products being used or provided was noted. Few NSTs utilized personal protective equipment (PPE), such as gloves, during our visits.

2.2 Personal and area air monitoring

Air quality parameters, including VOC, formaldehyde and CO₂ concentrations, temperature, and RH, were measured during each visit (during working hours). Personal VOC samples

(near or in the breathing zone) were collected by volunteers undergoing a nail service using a passive sampler (10 cm long stainless tubes packed with 60/80 mesh Tenax-GR with a 0.5 cm diffusion gap) pinned to their shirt or blouse collar. Prior to sampling, tubes were cleaned and conditioned at 325 °C for 6 h with a 30 mL/min flow of high purity N2. The distance between the samplers to the nail services being performed was comparable to that between the NSTs and the service area, thus, these samples were expected to reflect the personal exposures of the NSTs. Passive samples were deployed just prior to entering the salon, maintained for the duration of the nail service (typically 30 to 60 min for a single client) and then capped and stored upon exiting the salon. The sampling duration was recorded. The short-term sampling approach was designed on the assumption that the numbers and types of nail services performed during our randomly scheduled visits were typical of those in each nail salon. The passive sampling uptake rate was calculated using a diffusion model as a function of temperature, tube configuration, and the diffusion coefficient of each target compound (Batterman et al. 2002). Sampling protocols, including tube preparation, transport, storage and analysis, are well developed (Batterman et al. 2006; Batterman et al. 2007; Du et al. 2012; Jia et al. 2008; Jia et al. 2010; Jia et al. 2012), e.g., tube storage involves capping each tube, wrapping in baked aluminum foil, and placing it in a sealed glass jar with an activated carbon pack. Field blanks, collected and analyzed at each salon, showed negligible VOC levels, confirming that transport, storage, and handling activities did not contaminate the tubes.

Area measurements of temperature, RH, CO2, formaldehyde and VOC concentrations were conducted during the nail service using instruments placed in a backpack of the researcher (accompanying the volunteer) sitting in the salon's waiting area. An integrated logger (HOBO MX CO₂ Data Logger, Onset Computer Corporation, USA) recorded nearcontinuous (5-second) measurements of CO₂, temperature and RH. CO₂ calibrations used 0 ppm (pure N₂) and 1003 ppm CO₂ gases (certified standards, Scott Specialty Gases, Troy, MI, USA). Temperature was calibrated at 0 and 25 °C. RH was calibrated using saturated salt solutions at 75% (sodium chloride), 33% (magnesium chloride), and 11% (lithium chloride). The exposure time of the area VOC measurements were the same as the personal VOC air monitoring (30-60 min), and the time was recorded at each salon. Formaldehyde was measured using a colorimetric/photoelectric sensor (FM-801, GrayWolf Sensing Solutions, Shelton, USA) for at least 30 min inside the salons; this instrument has a limit of detection (LOD) of $6 \mu g/m^3$. The area measurements were initiated after entering the salon and stopped just prior to exiting the salon. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit values (TLV) and Michigan Air Toxics System (MATS) Initial Threshold Screening Level (ITSL) (MDEQ 2017), which are healthbased screening levels used by the State of Michigan for air quality permit applications, were used as benchmark values to evaluate occupational exposures from the personal and area air samples in nail salons. Because we did not collect 8-hour samples, our results are not directly comparable to ACGIH TLV or MATS ITSL concentrations; similarly, the average across salons is not directly comparable to the benchmarks (especially considering the variability found among salons as discussed in Section 3.4). Our comparisons to those standards and guidelines are used only to suggest the potential for exposures that may

approach or exceed levels that may be of concern, and thus high 30–60 min measurements do not necessarily indicate that occupational standards are exceeded.

Outdoor measurements (temperature, RH, CO₂, VOCs formaldehyde) were also collected during each visit, within 50 m of the salon and 150 m from major roads. Similar methods to those just described were used, except that active (rather than passive) VOC samples were collected. (Short-term passive sampling is not suitable given the low outdoor concentrations.) The outdoor VOC samples were collected using the same indoor samplers with a sampling pump (SKC Universal PCXR8 pump, Eighty Four, PA, USA) at 200 mL/min for 10 to 15 min (each time recorded).

2.3 Nail product selection and sampling

A total of 35 nail products were selected based on their availability to professional (licensed) NSTs and the general public (via retail or on-line purchase), and expected levels of VOCs. The final sample included 15 nail polishes (lacquers that decorate and protect the nail), 4 top coats (varnishes that preserve the polish), 7 base coats (varnishes that help the polish adhere to the nail), 2 nail powders (components of artificial nails), 5 monomers (components of artificial nails), 1 nail polish remover, and 1 cuticle oil (moisturizes the cuticle, skin and nail). The products are listed in Supplemental Table S1.

Samples for compositional analyses were collected using static headspace gas sampling. A 1 mL liquid aliquot of each product was transferred using a pipette to a 2-mL glass vial, which was immediately sealed using a Teflon septum and screw cap. After 1 h equilibrium at lab temperature (22 - 23 °C), a 50 µL gas-tight syringe was inserted through the septum into the middle of the headspace, a 10 µL of sample was extracted, and then immediately injected into the chromatography/mass spectroscopy (GC/MS, described below.) To prevent sample carryover, syringes were flushed with air three times after each injection. QA standards of each VOC detected in the headspace of nail products were prepared individually and included reagent grade ethyl acetate (99.8%), iso-propyl acetate (99.6%), n-propyl acetate (98.5%), n-butyl acetate (99.5%), methyl methacrylate (MMA, 99%), ethyl methacrylate (EMA, 99%), toluene (99.8%) and n-heptane (99%), all obtained from Sigma- Aldrich, St. Louis, USA; these were prepared and analyzed identically to the nail products.

2.4 VOC analysis

After sampling, VOC tubes were returned to the laboratory, refrigerated, and analyzed within one week. Prior to analysis, 2 ng internal standards (fluorobenzene, p-bromofluorobenzene, and 1,2-dichlorobenzene-d4) were injected into each tube (samples and blanks). Tubes were then loaded into a short-path automated thermal desorption system (ATD, Scientific Instrument Services, Inc., Ringoes, NJ, USA) coupled to a GC/MS (Model 6890/5973, Agilent Technologies, Santa Clara, USA). The ATD cryotrap/focuser was set to $-140 \,^{\circ}$ C (Zhong et al. 2017b). Chromatographic separation was performed using a DB-VRX capillary column (60 m x 0.25 mm, 1.4 µm film thickness) with the following temperature program: 45 $^{\circ}$ C (hold for 10 min), ramp at 8 $^{\circ}$ C/min to 140 $^{\circ}$ C (hold 10 min), ramp at 30 $^{\circ}$ C/min to 225 $^{\circ}$ C (hold 13 min). The MS detector transfer line, ion source, and quadrupole temperatures were set to 300, 230, and 150 $^{\circ}$ C, respectively. The MS was

operated in full scan mode from 29–270 atomic mass unit (AMU). Peak areas were extracted by a ChemStation macro program, adjusted for internal standards and transferred electronically to a spreadsheet. Analyte masses (ng) were converted to concentrations by dividing by sampling volume (m³) (Batterman et al. 2012; Chin et al. 2014; Jia et al. 2012).

Ventilation and air change rates (ACRs) were determined using CO_2 as a "natural" tracer gas, the steady-state mass balance model, field-measured CO_2 concentrations (20-min average from 5-sec measurements), observed occupancy (20-min average), measured salon volume, and CO2 emission rates for adult women (Batterman 2017). While the derived ACRs are approximate due to possible changes in occupancy, accuracy of the steady- state assumption, and the representativeness of measurements, ventilation parameters can provide key information to interpret the significance of emission sources and to support engineering controls to reduce exposure.

2.5 VOC calibrations and quality assurance

Multipoint calibrations for 100 VOCs from pentane to n-hexadecane were performed using authentic standards (Peng and Batterman 2000). Recovery rates for most compounds ranged between 80 and 120%. Method detection limits (MDLs) were determined as the standard deviation of seven replicate low concentration injections multiplied by 3.14 (USEPA 1996). MDLs ranged from 0.06 to 0.50 μ g/m³ for most of the target VOCs, higher than normal for the method due to the short sampling time. Non-detects were set to one-half of the MDL. Supplemental Table S2 lists the target compounds, MDLs, and detection frequencies (DFs).

Quality control (QC) and quality assurance (QA) activities for personal, area and outdoor measurements included field blanks (10% of samples) and duplicates (15% of samples) for personal, area and outdoor VOCs, respectively. A calibration/QA sample, consisting of a freshly-loaded adsorbent tube containing 10 ng of target compounds, was analyzed daily. Differences between the daily checks and calibration results were within 30%. No target VOC was detected above the MDL in the field blank. All duplicate samples were within acceptance criteria (relative percent difference below 20%).

2.6 Data analysis

Duplicate VOC measurements were averaged. TVOC was defined as the total of detected VOCs in each nail salon. Analysis focused on those VOCs with DFs exceeding 15% and included descriptive statistics, graphical displays, analysis of variance, and probability plots. Paired t- and signed rank tests were used to investigate differences between personal and area VOCs. Associations between VOCs themselves, ACRs, and other variables were evaluated using Spearman correlation coefficients. Ratios of personal to area concentrations were calculated for each nail salon and VOC. The variability of VOC concentrations, specifically within- and between-salon variability, was evaluated using nested random effects analyses. Spatial and seasonal differences in concentrations were evaluated using independent t and Kruskal-Wallis (K-W) tests, and displayed using box and distribution plots; these analyses are explorative given the small sample.

A source apportionment of VOCs in salons was conducted using the chemical mass balance receptor model approach (Watson et al. 2001). This used regression models to fit source

fractions to observed VOC levels and VOC source profiles derived from the headspace analyses of nail products. Only those VOCs detected in the headspace tests were included. Model fit was considered to be acceptable when source fractions were between 0 and 1, and the sum of the fractions approached unity. In most cases, the R^2 from the regression exceeded 0.8.

Excel (Microsoft 2013, Seattle, WA, USA) and SPSS Statistics v. 24 (SPSS Corporation, Chicago, IL, USA) were used for statistical analysis.

Results and discussion

3.1 Composition of nail products

VOC profiles from the headspace tests for the tested nail products are presented in Figure 1. (Supplemental Table S3 lists headspace VOC concentrations in each nail product, and Supplemental Table S4 summarizes VOC concentrations by the nail product type.) Ethyl acetate (EA) comprised a large share of VOCs in the headspace of many products, specifically, $57 \pm 20\%$ of nail polish (headspace concentration of 113 ± 84 g/m³), $67 \pm 18\%$ of the top coats (111 ± 64 g/m³), $63 \pm 8\%$ of the base coats (67 ± 4 g/m³), and $1 \pm 3\%$ of the monomer (1 ± 2 g/m³). n-Butyl acetate (NBA) was found at lower levels: $24 \pm 14\%$ of nail polish (36 ± 17 g/m³), $31 \pm 17\%$ of top coat (47 ± 43 g/m³), and $25 \pm 20\%$ of base coat (29 ± 23 g/m³). Nail polish included iso-propyl acetate (IPA, $7 \pm 10\%$), n-propyl acetate (NPA, $8 \pm 9\%$), and toluene ($4 \pm 8\%$). N-heptane was only found in the base coat ($12 \pm 12\%$, 12 ± 12 g/m³). The monomer was essentially pure ethyl methacrylate (EMA, $99 \pm 3\%$). None of the consumer and professional nail products contained MMA.

The headspace above the nail powder products did not contain significant levels of VOCs. As noted, the headspace tests were performed at lab temperature. However, these powders contain acrylic polymers and, if aerosolized and collected in the VOC sampler during the field tests (described below), the powder might produce VOC artifacts during the thermal desorption of the sampling tubes. Significant uptake of powder into the VOC sampling tube is unlikely given that passive samplers were used. Nevertheless, we conducted headspace tests of the powder at 150 °C that showed EMA at 1.0 ± 0.6 g/m³. This concentration was much lower than EMA levels found in the liquid monomers (46 ± 30 g/m³). The liquid monomers have a much stronger odor than the powders, providing some qualitative confirmation of the laboratory tests.

3.2 Salon characteristics and VOC levels

The salons contained an average of 10 ± 6 women and 2 ± 1 men, and included 7 ± 4 NSTs and 6 ± 3 clients (n=34; 17 salons visited in two seasons each). These counts exclude children, including a baby found in 3 instances (9%). About a third of the NSTs wore non-filtering surgical masks; and somewhat fewer wore gloves, otherwise no other personal protective equipment (PPE) was used.

The salon volumes ranged from 154 to 741 m³. Temperature and RH in the salons in fall averaged 20.2 ± 2.7 °C and $49 \pm 10\%$, respectively, and slightly cooler and more humid in

winter, 17.8 ± 2.9 °C and $49 \pm 18\%$. Outdoor temperature and RH averaged 11.2 ± 8.2 °C and $49 \pm 17\%$ in the fall, and 4.6 ± 5.6 °C and $53 \pm 19\%$ in the winter.

Across the two seasons, indoor CO_2 concentrations averaged 945 ± 449 ppm (range: 560 – 2905 ppm). The outdoor CO_2 concentration was relatively constant at 413 ± 20 ppm. Indoor CO_2 levels increased in winter (982 ± 533 ppm) compared to fall (908 ± 340 ppm), although this difference is not statistically significant.

As shown in Table 1, VOC levels in the personal and area samples varied widely. Probability plots of individual VOC suggest that EA, NBA, MMA and TVOC concentrations were approximately lognormal distributed (Figure 2). These plots also display how concentrations of personal samples tend to exceed area samples. Among the VOCs in the salons, EA and NBA were ubiquitous (100% detection frequency, DF) with median personal area concentrations of 1100 and 297 μ g/m³, respectively. VOCs with DFs exceeding 50% in both personal and area samples also included IPA, NPA, MMA, n-heptane, and toluene; less common VOCs included benzene, d-limonene, formaldehyde, and ethyl methacrylate (EMA). Additional VOCs found in personal and area sampling with DFs below 10%, including 2-butanone, methyl acrylate, tetrachloroethylene, p,m-xylene, and naphthalene, generally had low concentrations. These VOCs likely represent common indoor and outdoor contaminants, e.g., tetrachloroethylene in nail salon NS-3 may have originated from a nearby dry- cleaning facility (possibly due to air entrainment or cleaned clothes brought into the salon). Overall, VOC concentrations in the salons were comparable to levels measured in other nail salons (Supplemental Table S5).

Formaldehyde in the area samples was detected in about half of the salons (2 salons in fall and 6 salons in winter) at concentrations from 15 to 40 μ g/m³. (Personal measurements did not include this VOC.) Formaldehyde has not been found in consumer and professional nail products in the Michigan market, although it has been reported to be an ingredient of some nail hardeners (Alaves et al. 2013). Potentially, the formaldehyde measurements reflect relatively constant emissions from building materials and other indoor products, with seasonal differences attributed reduced ventilation and possibly higher humidity.

Chemicals in nail care products are regulated unevenly. Occupational Safety and Health Administration permissible exposure limits (OSHA PELs) have been established for several of the chemicals used in the industry, e.g., toluene, xylene and acetone (OSHA 2017), however, many of the PELs are outdated (most are from the 1960s) and few are intended to protect women of child-bearing age (Gorman and O'Connor 2007). ACGIH more frequent updates to its TLVs that guide evaluations and controls of workplace exposures, several chemicals found in salons do not have TLVs, such as EMA, which is now widely used in artificial nail systems that have contributed to the industry's recent growth. Some of the toxics in nail products, such MMA, have been recognized by the US Food & Drug Administration (FDA) (USFDA 2016). However, no regulation specifically prohibits the use of MMA in cosmetic products.

Table 1 lists ACGIH TLVs and the MATS ITSLs for the target VOCs. Concentrations in the salons fell well below TLVs, however, EA and MMA exceeded ITSLs for 12% and 50% of

the measurements, respectively (including both personal and area samples). For MMA, the ITSL is equivalent to the U.S. Environmental Protection Agency reference concentration for chronic inhalation exposure (700 μ g/m³) (USEPA 2016). In a few salons (NS-4, NS-25, and NS-28), MMA concentrations ranged from 8200 to 36000 μ g/m³, far above the reference level, and area and personal samples were similar, suggesting a potential health concern, although not necessary indicating that occupational standards are exceeded. The mean concentrations of EMA were 65–73 μ g/m³ for personal and area samples.

Measured concentrations could be sensitive to the location of samplers in the salon, as well as air-mixing and ventilation. Personal samplers placed in or near the breathing zone should better portray occupational exposures than the area samplers, which were placed in the salon's waiting area. Ratios of personal to area concentrations (P/A ratios), computed for each salon and VOC, are summarized in Figure 3. While individual P/A ratios varied considerably, median P/A ratios were between 1.0 and 2.0. NBA had the highest ratio, 2.0. Figure 2-d shows that the distribution of personal NBA measurements is uniformly shifted to right compared to the area measurements. This VOC is widely used in base coats, polishes and top coats (Figure 1). EA is also used in these products, and this VOC showed the second highest median P/A ratio, 1.4. The personal samples showed more modest but statistically significant increases of other salon-associated chemicals, including IPA, MMA, n- heptane, and TVOC, in both paired-t and signed rank tests (Table 1). In contrast, common indoor VOCs (benzene, toluene and d-limonene) had median P/A ratios near 1, indicating that personal and area exposures were comparable and likely not associated with salon products. Overall, our results suggest that personal exposures to VOCs in nail salon products exceed area measurements by a factor of 1.2 to 2.0. This factor tended to increase as the separation distance between personal and area sampling increased (R = 0.2; Supplemental Figure S2).

Concentrations of EA, IPA, NPA, NBA, MMA, d-limonene and TVOC across the salons were highly correlated (Spearman correlation coefficients of area measurements ranged from 0.38 to 0.95; Supplemental Table S6). Other VOCs had lower correlation, likely due to low DFs (EMA, benzene, formaldehyde) and the diversity of VOCs in building materials and consumer products (n-heptane, toluene).

In most cases, the VOCs detected indoors were not found outdoors, with the exceptions of benzene, toluene, n- heptane, and d-limonene (mean concentrations of 1.4, 1.6, 1.3, and 0.9 $\mu g/m^3$, respectively). Other VOCs detected outdoors included hexane, ethylbenzene, *p,m*-xylene, *o*-xylene, α -pinene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, and naphthalene. Outdoor TVOC concentrations ranged from 1.4 to 20.5 $\mu g/m^3$, much lower than the indoor levels, 370 to 48,400 $\mu g/m^3$.

Seasonal variability in personal and area measurements was not significant for most VOCs (one-way ANOVAs, K-W tests; Supplemental Table S7). The number of nail service operations, which were highly correlated with occupancy (r=0.93), tended to decline in winter in a number of salons (e.g., NS-1, NS-3, NS-19, and NS-25), which likely lowered VOC emissions and concentrations. However, this may have been offset with the lower ventilation rates deduced in winter (see below).

3.3 Ventilation

Table 2 presents the ventilation parameters in each nail salon for fall and winter seasons. As noted earlier, CO_2 levels increased slightly in winter. CO_2 levels exceeded 1000 ppm in 8 cases (24%) and 1500 ppm in 3 cases (9%), an indicator of low ventilation rates. ACRs across the 17 salons averaged 2.0 ± 0.9 h⁻¹ in the fall and fell slightly to 1.7 ± 0.7 h⁻¹ in the winter, possibly reflecting energy conservation measures taken during Michigan's cold winter, e.g., closing doors and air recirculation. Using the observed occupancy rate during the visits, most (76%) salons met the ASHRAE minimum recommended rate (12.4 L/s-person) (ASHRAE 2016). Using the default occupant density suggested by ASHRAE (25 persons per 100 m²), only 12% of nail salons met the recommended rate, including three that had open doors during visits (NS-2 in both visits, NS-14 in fall). ACRs were negatively correlated with CO_2 levels (r=-0.37).

The salons contained a variety of stand-alone and ventilators built into the manicure tables. In most cases, each manicure table had a small fan that was used for nail drying (not lowering exposures). One salon (NS-15) had a wall-mounted local exhaust system near three manicure tables, however, it was not turned on during our visits.

3.4 Variation of VOC levels

Area concentrations of EA, NPA, NBA MMA, and TVOC were positively correlated with CO2 levels, salon occupancy, and salon services (Supplemental Table S6). Surprisingly, VOC levels were not significantly correlated to ACRs. As noted earlier, some salons were less busy in winter.

The variance analyses showed that VOC levels differed between salons (p <0.01 for most VOCs), that between- salon variation was dominant for EA, NPA, MMA, n-heptane, d-limonene and TVOC, and that within-salon variability was dominant for IPA, NBA, EMA, benzene and toluene (Table 3). Between-nail salon variation results from factors that alter VOC levels in different salons, e.g., differences in the products used, services provided, ventilation rates and practices such as open or closed waste bins (salons NS-9 and NS-15 had open bins during our visits), while within-salon variation may result from the location of emission sources (nail services) and the degree of air mixing. Given that only two locations were studied in each salon, results of the variance analysis are preliminary. Additional measurements and more information on HVAC systems in each salon (e.g., locations of vents and air flows) would be helpful.

Concentrations of three VOCs (EA, NPA and MMA) varied between the three cities (ANOVA, p-value = 0.001–0.012; K-W test, p-value = 0.005–0.044), and salons in Dearborn and Detroit were several to many times higher than levels in Ann Arbor; this applied to both personal and area samples (Supplemental Table S8). Only one difference in the types of products by city were found: one of the Detroit salons (NS-25) had as its major business artificial nails, which might lead to VOC composition or concentration differences. Study limitations, including the small sample size in Dearborn and Detroit and the lack of comprehensive inventories in products and services, preclude a more definitive analysis.

3.5 MMA

MMA monomer is used as an adhesive for artificial nails, although products containing 100% MMA have not been permitted in the U.S market since the 1970s (USFDA 2016) due to health concerns of fingernail damage and dermatitis, especially for people allergic to methyl methacrylate. However, MMA monomer can be used as a component of cosmetic products. The head-space results confirmed that the consumer and professional nail products did not contain MMA. However, MMA was detected in 15 of 17 salons (88%), and the highest concentration 36,000 μ g/m⁻³ (fall measurement in NS-25) exceeded the reference concentration for chronic inhalation exposure (700 μ g/m³) (USEPA 2016) by over 50 times. In two salons (NS-10 and NS-15), MMA was never detected (Supplemental Figure S3).

EMA was identified as a safer substitute for MMA in 2002 (USFDA 2016). However, we detected EMA in only 15% (personal sampling) to 18% (area sampling) of salons. MMA and EMA results show that the use of nail products containing MMA monomer remains commonplace, which is consistent with previous findings in other U.S. states (Alaves et al. 2013; Garcia et al. 2015; Quach et al. 2011). Moreover, we obtained samples of pure MMA monomer from the salons. Thus, it is clear that MMA monomer has yet to be removed from the workplace, and that additional controls and ventilation could reduce exposures to workers and clients.

3.6 Source apportionment

The CMB approach provided acceptable model fits in most cases (61 of 68 with acceptable fractions, R² and p- values below 0.05). Contributions of the various products to indoor air concentrations are summarized in Figure 4. (Supplemental Table S9 provides detailed results.) Considering both area and personal samples, the base coat, polish, top coat and monomer products contributed 43, 31, 19 and 8% of VOC levels in the workplace, excluding MMA (see below) and "trace" VOCs like benzene. Personal samples had a lower share of the monomer and slightly higher shares of the other products compared to area samples, possibly reflecting drying rates and application practices, but overall, apportionments of area and personal samples were similar. Since MMA was not detected in the tested nail products, emission sources of MMA were not identified, and the apportionment excludes this compound. The apportionment reflects emissions and concentrations at the sampler; it may also reflect product use. While we could not determine product use, the analysis suggests that base and top coats are the predominant VOC sources, followed by top coat and the monomer.

The apportionment does not account for chemical reactions, e.g., between VOCs and ozone, that could alter concentrations and VOC composition (Zhong et al. 2017a), however, such reactions likely have only negligible effects given the relatively high VOC emission rates. Also, the source profiles may not fully reflect profiles of products used in each salon, which could alter results. Still, this first indoor application of the CMB method provided useful results and strong evidence regarding the sources that affect VOC levels in nail salons.

3.7 Limitations

We recognize a number of limitations in the laboratory and field elements of this work. First, no health or symptom information was collected; a much larger sample size is needed for an epidemiological investigation. Second, not all types of VOCs were measured due to constraints of the sampling and analysis method. Other VOCs of potential importance include ethanol and isopropanol in polishing products, acetone in polish removers, and others (Supplemental Table S3). Third, salons were visited randomly during open hours, and the number of clients, NSTs and activities present during the short-term observation periods may not be representative. While the collected data appear sufficient to characterize VOC levels, future studies might use long-term measurements, repeated measurements at different times and in each season, and shift samples that better characterize worker and client exposure. Similarly, additional measurements are needed to determine possible differences among salons serving different racial/ethnic communities. Fourth, analysis of possible effects due to the salon's ventilation system was limited; additional information on each building and HVAC system would be useful. Fifth, source apportionment results depend on the representativeness of source profiles, and while 35 nail products were tested, other products and products with different compositions might be used in nail salons. Nail product composition is not published, and the lack of a profile database highlights the need to obtain source profiles of both commercial and consumer products. Finally, our analysis was not intended to determine health risks or compliance with occupational and other standards and guidelines.

4 Conclusions

We sampled 17 Michigan nail salons in two seasons to characterize parameters relevant to VOC exposures of NSTs and salon clients. Elevated levels of VOCs associated with nail salon products were found and apportioned using chemical mass balance modeling and compositions of polishes, top coats, removers and other products measured in headspace tests. Important findings include: the use of MMA in nearly all salons, despite restriction on this product; estimates that worker exposure to VOCs determined using personal monitoring is 1.2 to 2.0 times higher than area measurements; the presence of low and possibly inadequate ventilation rates in a subset of salons; the identification of products responsible for emissions; and the demonstration that "informal" short-term sampling approaches can facilitate access to salons and provide useful measurements.

Understanding exposures in nail salons is important because VOCs are associated with a wide variety of symptoms and health effects, and NSTs represent a large and potentially vulnerable population. The VOC levels found, particularly for MMA and EMA, suggest the need for better controls. Chronic and acute exposures to toxic VOCs can be controlled by many means: appropriate licensing and certification requirements; setting and complying with standards and guidelines that recognize the potential sensitivity of the population; disclosing and translating product safety information for all products (e.g., adopted from material safety data sheets and translated into Korean, Vietnamese, and other languages common in the industry); improving point and area ventilation; and restricting product ingredients. Steps to ensure that salons are healthy and sustainable environments include:

coordination and information-sharing among stakeholders (NSTs, salon owners, building managers, engineers, architects, health scientists, policy makers, etc.); outreach, education and training for salon owners and NSTs regarding best practices; and restrictions on nail product formulations.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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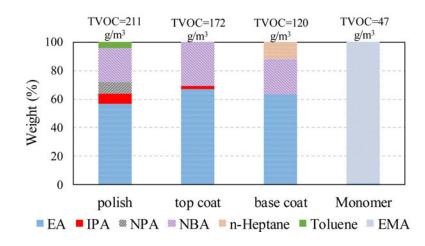


Figure 1.

Average chemical profile (by weight %) for VOCs in nail products. Headspace concentrations (sum of target compounds) shown for each product type.

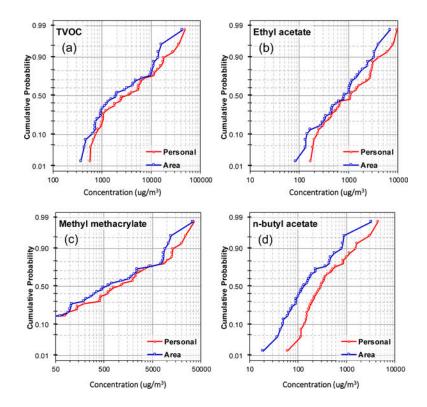


Figure 2.

Log probability plots of personal and area VOC concentrations in 17 nail salons and two seasons (n=34) for (a) TVOC, (b) ethyl acetate, (c) methyl methacrylate, and (d) n-butyl acetate.

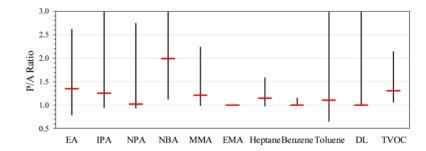


Figure 3.

Personal/area (P/A) concentration ratios at 10th, 50th (red line) and 90th percentiles. (EA is ethyl acetate; IPA is isopropyl acetate; NPA is n-propyl acetate; NBA is n-butyl acetate; MMA is methyl methacrylate; EMA is ethyl methacrylate; DL is d-limonene.)



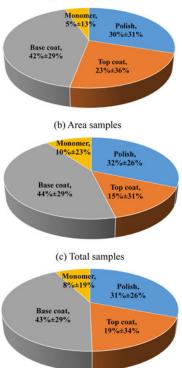


Figure 4.

Apportionment of VOCs in nail salons for (a) personal samples (n=17), (b) area samples (n=17), and (c) all samples (n=17). Pie charts show average and standard deviation of apportionments. Apportionments in each salon are averaged across two seasons.

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Table 1.

Summary statistics of VOC concentrations in personal and area air in 17 Michigan nail salons in the fall and winter seasons.

VOC	Person	Personal air (n=34)	4)		Area	Area air (n=34)			p-value	<i>I</i> *	ACGIH TLV ^{*2} (mg/m ³)	MATS ITSL*5 (µg/m ³)
	DF *4 %	Mean (μg/m ³)	Median (μg/m ³)	Range [*] 6 (μg/m ³)	%DF	Mean (μg/m ³)	Median (μg/m ³)	Range (µg/m ³)	Paired t-test	Signed rank		
Ethyl acetate	100	1900	1100	170–9650	100	1260	820	84-6900	0.001	0.010	1400	3200
Isopropyl acetate	71	29	18	<5-160	59	17	10	<5-96	0.007	0.007	420	4200
n-propyl acetate	<i>6L</i>	62	31	<5-290	71	43	18	<5-240	0.010	0.124	840	8350
n-butyl acetate	100	630	300	60-4500	100	320	130	19–3290	0.001	0.000	710	7100
Methyl methacrylate	85	4820	970	<2.5-36000	85	3500	550	<2.5-34200	0.015	0.000	210	700
Ethyl methacrylate	15	75	0.5	<0.5–1920	18	63	0.5	<0.5–1350	0.588	1.000	*3	*3
N-heptane	88	84	TT	<0.2–190	88	70	68	<0.2–170	0.000	0.000	1640	3500
Benzene	18	4	0.1	<0.1-30	12	3	0.1	<0.1-30	0.297	0.687	1.6	30
Toluene	94	110	70	<0.1-650	91	93	43	<0.1-380	0.339	0.112	75	5000
d-Limonene	41	28	0.2	<0.2-300	32	16	0.2	<0.2–200	0.135	0.013	*3	6250
Formaldehyde	N/A	N/A	N/A	N/A	24	10	9	<6-40	NA	NA	0.37	30
TVOC	100	7830	3050	570-48400	100	5450	1910	370-43100	0.003	0.000	*3	*3
* I : * I : P-value test for the difference between personal and area VOCs.	lifference	between pe	ersonal and	area VOCs.								
* 2; * 2: * 4: American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) are 8-hour time weighted averages (TWAs).	ce of Gov	ernmental I	Industrial H	ygienists (ACG	IH) Thr	eshold Lim	uit Values (T	LVs) are 8-hou	ır time we	ighted avei	rages (TWAs	÷
* . [*] J. Level was not established for ethyl methacrylate, d-limonene and TVOC.	lished for	ethyl meth	acrylate, d-l	imonene and T	VOC.							
*4. DF is detection frequency	uency											

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*5:

* 6: "<" indicates MDL. Author Manuscript

Evaluation of ventilation parameters in 17 Michigan nail salons in the fall and winter seasons.

Season	8	Women	Men	Manicure	Pedicure	Out-CO ₂ (ppm)	In-CO ₂ (ppm)	Air flow (m ³ /min)	AER (1/h)	L/s-person	L/s-person
Fall	NS-1	25	4	8	5	379	1206	14.5	2.2	6.9	8.4
	NS-2 *3	22	2	8	3	425	691	36.2	5.3	19.9	25.1
	NS-3	10	1	3	1	375	872	8.9	2.5	6.9	13.5
	NS-4	18	2	7	2	451	1674	6.6	1.0	3.2	5.5
	NS-6	8	7	3	1	421	850	9.6	1.8	7.2	16.0
	NS-8	5	0	1	0	414	608	9.7	1.2	4.4	32.4
	0-SN	3	2	2	0	419	624	10.2	2.7	8.4	34.0
	NS-10	5	0	1	1	404	914	3.9	1.0	3.8	13.1
	NS-12	3	1	1	1	410	740	5.1	2.0	5.5	21.2
	NS-14 *3	7	5	2	б	383	409	143.5	45.2	140.7	265.7
	NS-15	9	0	1	2	383	918	4.6	1.5	4.8	12.6
	NS-19	13	0	4	2	399	693	18.1	4.1	12.6	23.2
	NS-24	6	2	2	2	422	849	10.5	0.8	2.9	15.9
	NS-25	21	2	6	0	446	1654	7.7	2.6	8.1	5.6
	NS-27	8	4	3	0	444	684	20.1	3.4	10.5	27.9
	NS-28	10	4	5	1	451	1251	7.3	0.9	4.7	8.6
	NS-30	6	2	2	1	427	803	11.5	1.8	5.7	17.5
	Ave	11	2	4	1	415	806	6.6	2.0	6.4	17.0
	SD	٢	1	c,	1	24	340	4.4	0.9	2.5	8.5
Winter	NS-1	10	ю	2	2	401	60 <i>L</i>	17.6	2.7	8.3	22.5
	$NS-2^{*3}$	20	5	8	б	429	701	33.0	4.8	18.2	25.0
	NS-3	5	1	1	0	437	785	6.8	1.9	5.3	19.0
	NS-4	26	2	6	4	434	2905	4.6	0.7	2.2	2.7
	NS-6	8	2	2	2	418	790	11.0	2.1	8.2	18.3
	NS-8	5	0	1	0	396	578	10.6	1.3	4.8	35.2
	0-SN	3	7	1	1	398	560	13.1	3.4	10.8	43.5

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Season	Ð	Women		Men Manicure	Pedicure	Out-CO ₂ In-CO ₂ (ppm) (ppm)	In-CO ₂ (ppm)	Air flow (m ³ /min)	AER (1/h)	L/s-person	L/s-person
	NS-10	ю	0	1	0	425	682	4.6	1.2	4.4	25.6
	NS-12	ю	1	1	0	405	851	3.6	1.4	3.9	15.0
	NS-14	7	1	2	2	429	924	6.7	2.1	6.6	13.9
	NS-15	б	0	1	0	410	758	3.4	1.1	3.6	18.8
	NS-19	7	0	1	5	404	847	6.4	1.4	4.4	15.2
	NS-24	10	7	3	2	395	1464	4.6	0.4	1.3	6.4
	NS-25	15	1	7	0	399	1103	9.3	3.2	9.8	9.7
	NS-27	6	9	4	0	429	869	14.0	2.4	7.3	15.6
	NS-28	15	7	5	2	395	1313	7.6	1.0	4.9	7.4
	NS-30	8	4	2	2	400	854	11.0	1.7	5.4	15.2
	Ave	6	5	3	1	412	1000	8.4	1.7	5.7	17.8
	SD	9	2	3	1	15	542	3.9	0.8	2.5	9.8

^{7.7} Assumes occupant density of 25 people per 100 m². ASHRAE 62–2016 suggests the minimum ventilation rates in breathing zone in beauty and nail salons is 12.4 L/s-person. The activity level (Met) of technicians was set to 1.7, which leads to average CO2 emissions of 0.500 L/min for males and 0.442 L/min for female. Met of customers was set to 1.4, which leads to average CO2 emissions of 0.607 L/min for males and 0.442 L/min for female. L/min for males and 0.359 L/min for female.

*2. Calculation based on actual occupants there during visits. *3. NS-14 had open doors during fall visit, and NS-2 had open doors within a mall for both fall and winter visits, which were not included in mean and SD calculation.

Table 3.

Within- and between-nail salon variation in indoor VOC concentrations (n=34).

VOC	Percent of variation	n (%)	p-value*
	Within-nail salon	Between-nail salon	
Ethyl acetate	32	68	0.00
Isopropyl acetate	80	20	0.06
n-Propyl acetate	32	68	0.00
n-Butyl acetate	67	33	0.01
Methyl methacrylate	28	72	0.00
Ethyl methacrylate	58	42	0.00
N-heptane	8	92	0.00
Benzene	84	16	0.11
Toluene	58	42	0.00
d-Limonene	47	53	0.00
TVOC	27	73	0.00

Bold values are statistically significant (P<0.05).

* p-value test for the VOC differences between-nail salons.