Volatile Organic Compounds: Exposure and Mitigation in Colorado Nail Salons

by

Aaron David Lamplugh

B.S., Mechanical Engineering, University of Alabama Birmingham 2012

M.S., Mechanical Engineering, University of Colorado Boulder 2017

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Dr. Lupita D. Montoya

____
Prof. Shelly Miller

Date __________________________________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

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Lamplugh, Aaron David (Ph.D., Mechanical Engineering)

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Thesis directed by Dr. Lupita Montoya

ABSTRACT

Nail salon workers face chronic exposure to volatile organic compounds (VOCs) as a result of their employment, which can lead to adverse health outcomes including skin, eye, and respiratory irritation as well as headaches, neurological issues, reproductive complications, and cancer. The work presented in this dissertation includes an assessment of short-term health symptoms and VOC exposure in Colorado nail salons and estimations of long-term cancer risk based on measured concentrations of benzene and formaldehyde from 6 Colorado nail salons. It also includes a limited characterization of VOC content and VOC emission rates from common nail salon products, an evaluation of low-cost adsorbent materials for VOC removal, and an exploration of VOC mitigation in the nail salon environment using novel, low-cost sorbent sinks (air-cleaning art).

Results from the nail salon short-term health and VOC exposure assessment found that 70% of surveyed workers reported experiencing at least one health issue related to their employment, with 40% reporting multiple related symptoms. Indoor concentrations of formaldehyde ranged from 5.32 to 20.6 μg m^{-3}, across all 6 salons. Indoor concentrations of toluene ranged from 26.7 to 816 μg m^{-3}, followed by benzene (3.13 to 51.8 μg m^{-3}), xylenes (5.16 to 34.6 μg m^{-3}), and ethylbenzene (1.65 to 9.52 μg m^{-3}). Formaldehyde levels measured in one salon exceeded the Recommended Exposure Limit from the National Institute for Occupational Safety and Health (NIOSH) of 19.7 μg m^{-3}. Concentrations of aromatic compounds measured were comparable to those measured in previous studies of occupational VOC exposure among oil refinery and auto garage workers.

Cancer risk estimates for Colorado nail salon workers were calculated based on 20 years of exposure to measured concentrations to benzene and formaldehyde, as well as cancer slope factors from the United States Environmental Protection Agency (US EPA) and anthropometric data from the Centers for Disease Control and Prevention (CDC). Cancer risk from formaldehyde exposure exceeded the US EPA *de minimis* risk level ($1x10^{-6}$) for squamous cell carcinoma, nasopharyngeal cancer, Hodgkin's lymphoma, and leukemia; leukemia risk exceeded $1x10^{-4}$ in one salon. The average leukemia risk from benzene exposure also exceeded the US EPA *de minimis* risk level for all demographic categories modeled.

Results from nail product characterization showed that nail polishes were 56.3 to 61.5 % VOC content by mass, with an average estimated emission rate of 2.3-2.4 mg mL^{-1} min^{-1} over 250 min. Acetone-based nail polish remover contained 100 % VOC content by mass and an average estimated emission rate of 20 mg mL^{-1} min^{-1} over 40 minutes. Non-acetone-based nail polish remover contained 26.5 % VOC content by mass and an average estimated emission rate of 6.6 mg mL^{-1} min^{-1} over 40 minutes.

Removal of VOCs emitted by nail products was studied in a controlled environment using adsorbent materials including coco coir (CC), wood-based biochar (BC), and commercial activate carbon (AC). All 3 low-cost adsorbents were found to remove VOCs from acetone-based nail polish remover over the course of 22.5 hours under both passive and active flow conditions. Passive VOC adsorption rates for fine grain CC, BC, and AC at concentrations of acetone < 120 mg m^{-3} ranged from 0.0005 to 0.0030 mg g^{-1} min^{-1}, 0.0006 to 0.0052 mg g^{-1} min^{-1}, and 0.0009 to 0.0056 mg g^{-1} min^{-1}, respectively. Active flow conditions, generated using a synthetic jet actuator (SJA), were found to enhance VOC adsorption rates (up to a 100% increase in the first 2 h) in materials with smaller BET pore width (AC and BC) and decrease VOC adsorption rates for materials with larger BET pore width (CC). Adsorption rates were shown to be represented by a general n^{th}-order rate equation that used ambient VOC concentrations and the mass of VOCs adsorbed as fitting parameters.

Novel, low-cost sorbent sinks (air-cleaning art) were designed and constructed by embedding fine grain AC into common gypsum plaster; prototypes were then tested under controlled conditions in a closed chamber with acetone as the sorbate. Controlled testing showed that the air-cleaning art material can remove VOCs from nail salon products under both passive and active-flow conditions. *In situ* thermal regeneration of the sinks was also tested with an embedded resistance heating element. Testing showed that flow conditions and external surface area were the most important optimization parameters for increasing the VOC removal rate of the material. Regeneration experiments were inconclusive but suggest possible irreversibilities in the sorption process.

A mathematical model was developed to predict the effects of both raw adsorbent materials and air-cleaning art in a typical nail salon, using time-resolved total VOC (TVOC) concentration data from the pilot VOC exposure study as the input. Model results were positive, showing that raw adsorbents and air-cleaning art could have a significant beneficial impact on VOC concentrations in the nail salon environment. The use of SJAs to generate active flow across the surface of the adsorbents was shown to enhance removal for raw AC and BC, as well as all of the air-cleaning art samples tested. Effective ventilation rates for fine AC ranged from 29.3 m^3 h^{-1} (0.02 ACH), for 10 kg of fine AC under passive flow conditions, to 292 m^3 h^{-1} (0.21

ACH) for 250 kg under active flow conditions, while air-cleaning art provided 3.32-9.03 mg m^{-2} h^{-1}.

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TABLE OF CONTENTS

Chapter 1 Introduction 1

1.1. Project Introduction 1

1.2. VOCs in the Occupational Environment: Sources, Regulations, and the Nail Salon Industry 3

1.3. Indoor air quality control 6

1.4. Air Pollution and Health Disparities 8

1.5. Community-Based Participatory Research 11

1.6. Volatile Organic Compounds 12

US EPA Method TO-11A 14

US EPA Method TO-15 15

Passive Diffusive Sampling for Personal Exposure Measurement 17

Photo-Ionization Detection 19

Chapter 2 Occupational Exposure to Volatile Organic Compounds and Health Risks in Colorado Nail Salons 20

2.1. Introduction 22

2.2. Material and Methods 24

2.2.1. Recruitment of Salons and Technicians 24

2.2.2. Questionnaires 25

2.2.3. Air Sampling 25

2.2.4. Chemical Analyses....28

2.2.3. Data Analysis....30

2.2.4. Cancer Risk Estimation....31

2.3. Results....33

2.3.1. Questionnaires....33

2.3.2. Formaldehyde....34

2.3.3. BTEX....35

2.3.4. Personal Exposure VOCs....36

2.3.5. Health Symptoms versus Exposure Factors....37

2.3.6. Cancer Risk Estimates....38

2.4. Discussion....40

2.5. Conclusions....44

Chapter 3 VOC Emissions from Nail Salon Products and Effective Removal Using Affordable Adsorbents and Synthetic Jets....46

3.1. Introduction....47

3.2. Materials....50

3.2.1. Nail Care Products....50

3.2.2. Adsorbent Materials....51

3.2.3. Environmental Test Chamber....52

3.3. Methods....53

3.3.1. Material Preparation and Characterization 53
3.3.2. Experimental Setup 53
3.3.3. Headspace Analysis 54
3.3.4. Baseline VOC Emissions from Nail Products 55
3.3.5. Passive VOC Removal with Raw Adsorbent Materials 57
3.3.6. Active VOC Removal Using Synthetic Jet Actuators 57
3.3.7. Data Analysis 58
3.3.8. Model of VOC Removal for Nail Salons 59
3.4. Results 61
3.4.1. Materials Characterization 61
3.4.2. Headspace Analysis 62
3.4.3. Baseline VOC Emissions from Nail Products 63
3.4.4. Passive VOC Removal with Raw Adsorbent Materials 67
3.4.5. Active VOC Removal Using Synthetic Jet Actuators 71
3.4.6. VOC Removal Model for Nail Salon Application 74
3.5. Discussion 77
3.6. Conclusions 80
Chapter 4 VOC removal in nail salons using novel, low-cost sorbent sinks: Air-Cleaning Art. 81
4.1. Introduction 82

4.2. Materials.....85

4.2.1. Adsorbent Sink Samples.....85

4.2.3. Environmental Test Chamber.....87

4.3. Methods.....87

4.3.1. Experimental Setup.....87

4.3.2. Adsorbent-to-plaster mass ratio.....89

4.3.3. External surface area (at constant volume).....91

4.3.4. Flow conditions (passive vs. active flow).....92

4.3.5. Regeneration.....92

4.3.6. VOC Removal Model for Nail Salon Application.....94

4.4. Results.....96

4.4.1. Chamber Experiments.....96

4.4.2. Regeneration.....102

.....103

4.4.3. VOC Removal Model for Nail Salon Applications.....104

4.5. Discussion.....107

4.6. Conclusions.....108

Chapter 5 CONCLUSIONS, RECOMMENDATIONS, and future directions.....110

5.1. Summary Scientific Contributions.....110

5.2. Recommendations for Follow-Up Research.....113

5.3. Community-Based Methods, Community Interactions, and Engineering for Developing Communities 116
5.4. Cross-Disciplinary Art and Science Collaboration 118
5.5. Scientific Contributions 121
5.6. Funding, Support, and Acknowledgements 122
REFERENCES 124
Appendix I - Occupational Exposure to Volatile Organic Compounds and Health Risks in Colorado Nail Salons 144
Supplementary Tables and Figures 144
Supplementary Tables: 144
Supplementary Figures: 146
Appendix II – VOC Emissions from Nail Salon Products and Effective Removal Using Affordable Adsorbents and Synthetic Jets 150
Supplementary Tables and Figures 150
Supplementary Tables: 150
Supplementary Figures: 151
Appendix III – VOC REMOVAL IN THE NAIL SALONS USING NOVEL, LOW-COST SORBENT SINKS: AIR-CLEANING ART. 157
Supplementary Tables and Figures 157
Supplementary Tables: 157
Supplementary Figures: 158

LIST OF TABLES

Table 1.1 Classification of Inorganic and Organic Pollutants 13

Table 2.1 Published studies examining the nail salon environment. 24

Table 2.2. Worker health-related symptoms and PPE use 34

Table 2.3. Formaldehyde concentrations from nail salons...35

Table 2.4. Personal exposure VOC concentrations (ppm) 36

Table 2.5. Lifetime cancer risk increases due to measured benzene and formaldehyde levels 39

Table 4.1. List of nail care products used in this study. 51

Table 3.2. Results from BET and BJH analyses 62

Table 3.3. Results from headspace analyses 63

Table 3.4. Estimated density and VOC content based on gravimetric analyses. 64

Table 3.5. VOC mass removed and effective ventilation rates from adsorption models...........74

Table 4.1. Published studies on the use of adsorbents in indoor building materials..................84

Table 4.2. Sample compositions and characteristics...86

Table 4.3. VOC mass removed and effective ventilation rates from adsorption models.........105

LIST OF FIGURES

Fig. 1.1. Principle reaction between DNPH and carbonyl compounds used in US EPA TO-11A formaldehyde determination method (US EPA, 1999b). 15

Fig. 1.2. DNPH-Silica active sampling cartridges used for determination of formaldehyde (US EPA, 1999b). 16

Fig. 1.3. GC-MS/FID/ECD used to analyze VOC samples in this dissertation (Weber, 2018). 17

Fig. 1.4. Basic principle of a conventional PID (Zimmer et al., 2015). 19

Fig. 2.1. BTEX concentrations at each salon. Dash lines represent average BTEX concentrations (ppb) measured at the distribution terminal in an oil refinery (Singh et al. 2013) and at auto garages (Badjagbo et al. 2010). 36

Fig. 3.1. Experiments performed to evaluate adsorbent materials in a controlled environment. 54

Fig. 3.2. Theoretical equilibrium acetone concentrations at LC, MC, and HC compared to measured concentrations from baseline emission tests. 64

Fig. 3.3. Baseline TVOC emission profiles from 5 nail products over 22.5 h with standard error bars. 65

Fig. 3.4. (A) Nail polish emission rates over 300 min. (B) Nail polish remover emission rates over 100 min. 66

Fig. 3.5. Adsorption rates of (A) fine and (B) coarse CC, BC, and AC at LC across 22.5 h. 68

Fig. 3.6. Passive adsorption rates of fine (A) CC, (B) BC, and (C) AC at LC, MC, and HC across 22.5 h. 70

Fig. 3.7. Acetone removal using AC, BC, and CC at LC over 22.5 h with active flow provided by a SJA at 30 cm from the adsorbent material. 72

Fig. 3.8. Active adsorption rates of fine (A) CC, (B) BC, and (C) AC at LC, MC, and HC across 22.5 h. 73

Fig. 3.9. Salon models for (A) CC passive flow, (B) CC active flow, (C) BC passive flow, (D) BC active flow, (E) AC passive flow, and (F) AC active flow. 76

Fig. 4.1. A diagram of 3 controlled experiments performed with adsorbent sinks. (1) Dry mass ratio variation, (2) Surface area vs. volume, and (3) Passive vs. active flow. 89

Fig. 4.2. Diagram of regeneration test with embedded heating element. 93

Fig. 4.3. Schematic of thermal regeneration circuit..94

Fig. 4.4. Passive removal rates for Sm BL, AC20, and AC50 samples at (A) LC and (B) HC. 97

Fig. 4.5. (A) AC20 Sm, (B) AC20 Md, and (C) AC20 Lg samples at LC and HC. 98

Fig. 4.6. Acetone removal at LC over 20 h by all AC samples under passive flow. 99

Fig. 4.7. Acetone removal with AC20 Sm samples at LC, passive and active flow, with vectoring (Vec) and without vectoring (No Vec). 100

Fig. 4.8. SA-normalized active removal rates for acetone by Sm, Md, and Lg AC20 samples at LC..101

Fig. 4.9. Acetone removal at LC over 20 h by AC samples under passive and active flow. ...101

Fig. 4.10. (A) Results from regeneration (regen.) experiment with AC20 Sm sample, (B) Averaged concentration results, and (C) SA-normalized removal rates. 103

Fig. 4.11. Salon models for (A) AC20 passive flow (mass), (B) AC20 passive flow (SA), (C) AC50 passive flow (mass), (D) AC50 passive flow (SA), (E) AC20 active flow (mass), and (F) AC20 active flow (SA)..106

Fig. 5.1. Minimum recommended sampling plan for possible intervention study 114

Fig. 5.2. (A) Adsorbent sink material used in test samples and (B) Adsorbent sink materials used in art. 120

CHAPTER 1

INTRODUCTION

1.1. Project Introduction

Studies have documented that workers in nail salons are exposed to many volatile organic compounds (VOCs), including toluene, ethyl acetate, isopropyl acetate, methyl methacrylate (Quach et al., 2011; Alaves et al., 2013), and formaldehyde (Alaves et al., 2013; Lamplugh et al., 2019). These chemicals can cause skin and eye irritation, respiratory problems, allergies, neurological issues (Roelofs and Do, 2012), reproductive complications (John et al., 1994), and, in some cases, cancer (Swenberg et al., 1980; Swenberg et al., 2013).

The U.S. nail salon industry employs nearly 450,000 workers nationwide (NAILS Magazine, 2017), with as many as 7,500 workers employed in Colorado alone. Most of the workers employed in this industry are minority women (NAILS Magazine, 2017; BLS, 2018); as such, their exposure to VOCs likely contributes to existing, air pollution-related health disparities.

Due to lapses in regulation by both the Occupational Safety and Health Administration (OSHA) and the U.S. Food and Drug Administration (FDA), nail salon workers are especially vulnerable to occupational hazards involving VOCs (Lamplugh et al., 2019). Consequently, finding ways reduce VOC concentrations in nail salons, and mitigate VOC exposure among workers, is critical to addressing a major U.S. public health issue.

Additional challenges presented include the fact that many nail salon workers and owners come from tightly knit Asian communities and in many cases are immigrants with limited

English language comprehension. This can be problematic for researchers from outside communities, both in studying the problem and in translating findings into useful information and action that will benefit the nail salon community. Therefore, in addition to traditional engineering approaches, it is necessary to utilize community-based research methods that help engage the study community in the research process. Furthermore, any interventions considered should be selected with the help of the community, in order to reflect their priorities and values. This may include using alternatives to traditional, established technologies.

The research presented in this dissertation consists of two main parts: A pilot study of VOC exposure in 6 Colorado nail salons and a study of VOC emissions and removal using adsorbent materials. Six specific aims are addressed in this document: (1) quantifying VOC exposure in Colorado nail salons; (2) assessing acute health problems associated with occupational exposure in salons; (3) assessing cancer risk due to long-term, occupational exposure to VOCs; (4) evaluating VOC emissions from common nail salon products; (5) evaluating VOC removal using low-cost adsorbents; and (6) exploring the use of novel, low-cost adsorbent sinks (air-cleaning art) to remove VOCs found in nail salons.

Research team members include:

1. Dr. Lupita Montoya (PI), CU Boulder, Civil Environmental and Architectural Engineering
2. Aaron Lamplugh (Project Lead), CU Boulder, Mechanical Engineering
3. Dr. Arsineh Hecobian (Chemical Analysis), CSU, Atmospheric Sciences
4. Dr. Megan Harries (Chemical Analysis), NIST, Applied Chemicals and Materials Division
5. Adam Nguyen (Undergraduate Asst.), CU Boulder, Architectural Engineering
6. Feng Xiang (Undergraduate Asst.), CU Boulder, Environmental Engineering

7. Janice Trinh (Undergraduate Asst.), CU Boulder, Chemistry and Biochemistry
8. Camila Friedmann-Gerlicz (Artist), CU Boulder, Art and Art History

1.2. VOCs in the Occupational Environment: Sources, Regulations, and the Nail Salon Industry

Occupational exposure to air pollution has been studied for many years (Hoffman, 1922; Keatinge and Potter, 1945), and research on occupational VOC exposure gained momentum in the late 1960s and 1970s (Ricca, 1966). More recently, studies have focused on occupational VOC exposure to aromatic compounds from fuel and vehicle emissions at gasoline and diesel stations (Tunsaringkarn et al., 2012; Moolla et al., 2015), in auto garages and parking structures (Badjagbo et al., 2010; Taneepanichsku et al., 2017), and in the petroleum industry (Pandya et al., 2006; Singh et al., 2013). Similarly, studies have looked at exposure to benzene and carbon disulfide in slaughterhouses (Omidi et al., 2019), acetone and toluene in painting operations (Wang et al., 2017), and many organic solvents in nail and beauty salons (Quach et al., 2011; Alaves et al., 2013; Hadei et al., 2018; Zhong et al., 2019; Lamplugh et al., 2019).

Currently, the Occupational Safety and Health Administration (OSHA) publishes the only enforceable regulatory limits related to workplace VOC exposure outside of California. These limits, known as Permissible Exposure Limits (PELs), came into effect shortly after the passage of the Occupational Safety and Health Act in 1970. According to OSHA's website, most of these PELs have not been updated since that time and are, therefore, "outdated and inadequate for ensuring protection of worker health" (OSHA, 2017). Further, OSHA advises businesses to supplement PELs with internal corporate guidelines and to utilize other Occupational Exposure Limits (OELs) such as Recommended Exposure Limits (RELs) published by the National

Institute for Occupational Safety and Health (NIOSH) and Threshold Limit Values (TLVs) published by the American Conference of Government Industrial Hygienists (ACGIH). By failing to provide adequate exposure limits for workers, OSHA has, in effect, shifted the burden of safeguarding worker health to businesses. This is a substantial challenge for the U.S. small business sector, where owners and managers often lack the knowledge, personnel, and resources to develop safety strategies and guidelines to supplement OSHA regulations.

In addition to inadequate workplace protection policies, poor product safety regulations in some industries can lead to increased risk for workers. For example, the U.S. Food and Drug Administration (US FDA) is not required to approve cosmetic products or ingredients, with the exception of color additives, before they go to market; instead, it relies on manufacturers to ensure product safety. The US FDA also has limited power to recall hazardous cosmetic products (US FDA, 2013). Limited oversight of the cosmetics industry has led to product mislabeling and misbranding. California EPA investigated nail care products labeled “toluene-free” or “three-free” (i.e., free of toluene, formaldehyde, and dibutyl phthalate) and found that 10 out of the 12 products tested contained toluene in concentrations as high as 177,000 ppm (17.7%) (Guo et al., 2012). They also found products with the “three-free” label that contained dibutyl phthalate in higher concentrations than regular products.

Both aforementioned regulatory gaps affect workers in the U.S. nail salon industry - an $8.5 billion industry that employs nearly 450,000 workers nationwide (NAILS Magazine, 2017). Further, 64-76% of this workforce are from minority ethnic groups and 86-97% are female (NAILS Magazine, 2017; BLS, 2018). The state of Colorado alone has over 900 nail salons that employ close to 7,500 workers, according to industry statistics. The nail salon industry has existed in the U.S. since the late 1800’s, when the first nail salons opened in New York City, providing manicure services to high end clientele (Callahan, 2014). The industry underwent a dramatic change in the 1970's, when an influx of Vietnamese immigrants flooded the nail salon market, lowering the cost of nail services, and granting millions of Americans access to these services (Morris, 2015).

Interest in safety of nail products and services dates back several decades (Donsky, 1967); however, the initial focus was typically on consumer safety, and often failed to acknowledge occupational hazards related to chemical exposure (Cappelli et al., 1976). Limited research and attention related to occupational health in nail salons began to appear in the late 1980s and early 1990s (Brown, 1987; John et al., 1994), followed by a surge of interest in the late 1990s and 2000s (NIOSH, 1999; Baran, 2002; US EPA, 2007; Kwapniewski et al., 2008; Roelofs et al., 2008; Quach et al., 2008).

Previous publications related to nail salons can roughly be divided into three distinct categories: (1) guidance (Brown, 1987; NIOSH, 1999; US EPA, 2007; OSHA, 2012; CHNSC, 2014); (2) exposure and Compliance (Kwapniewski et al., 2008; Quach et al., 2011; Roelofs & Do, 2012; Alaves et al., 2013; Goldin et al., 2014; Pavilonis et al., 2018); and (3) health (John et al., 1994; Kreiss et al., 2006; Roelofs et al., 2008; Quach et al., 2008; Lamplugh et al., 2019). Few studies have explored intervention strategies to improve the air quality within nail salons (Quach et al., 2013).

Exposure and compliance studies frequently found exceedances of the NIOSH REL for formaldehyde (Alaves et al., 2013) and concentrations of ethyl acetate and toluene exceeding 500 ppb and 150 ppb, respectively (Quach et al., 2011). Investigations into nail salon ventilation found high prevalence of non-working (Roelofs & Do, 2012; Park et al., 2014) or inadequate (Goldin et al., 2014) ventilation systems.

Health related studies have uncovered correlations between nail salon work and numerous health symptoms including nose and throat irritation (Quach et al., 2011), respiratory irritation (Roelofs et al., 2008), headaches, and skin irritation (Park et al., 2014), as well as reproductive complications (John et al., 1994). Although many studies have explored cancer risk in various occupational environments (Lee et al., 2006; Tunsaringkarn et al., 2012; Moolla et al., 2015), only one other study to date, which was conducted in Iran, has considered the long-term carcinogenic risk of occupational exposure to VOCs in beauty salons (Hadei et al., 2018).

1.3. Indoor air quality control

Average Americans spend close to 90% of their time indoors, which means that the majority of their exposure to environmental pollutants also occurs indoors (Klepeis et al., 2001). Mitigating exposure to hazardous airborne pollutants indoors has traditionally been accomplished by increasing the ventilation rate of a building either by natural ventilation, through the opening of windows and doors, or using mechanical ventilation systems. However, there are limitations to the amount of ventilation that a building can naturally achieve, based on the building design and the number of operational openings, as well as seasonal temperature variability that may prevent adequate ventilation year-round. Conversely, mechanical ventilation systems function well under most conditions, but can be expensive to install and maintain and may consume a considerable amount of power. Buildings account for 40% of the U.S. primary energy consumption, and 52% of the energy in buildings is used for HVAC operations (DOE, 2011).

In the indoor environment, adsorbent materials have been shown to act as VOC sinks, reducing concentrations of indoor pollutants when ventilation rates are insufficient (Meininghaus et al., 2000). The rate and effectiveness of adsorption processes may be decreased or enhanced by various factors including surface roughness, porosity, and type of adsorbent material, as well as velocity and turbulence intensity near the surface. Similarly, environmental factors like air temperature and moisture can be important (Huang et al., 2006). Activated carbon (AC) is a common adsorbent material with a microporous structure; it is produced from coal and other carbon-rich materials that undergo carbonization and activation processes. AC has been utilized to remove heavy metals, dyes, toxins, and organic compounds from air and water supplies (Zhang et al., 2017a).

Biochar is any carbonaceous material that is created through pyrolysis in an inert atmosphere (Zhang et al., 2017b) and is an attractive, low-cost alternative to AC. It is also a byproduct of pyrolysis processes used to produce biofuels and biochemicals (Park et al., 2013). Kearns et al., (2015) found that biochars prepared at 900 °C were as effective as coal-generated AC at removing the compounds Warfarin and 2-methylisoborneol from water. Similarly, Park et al. (2013) found that some biochars outperformed coal-based AC at removing the polycyclic aromatic hydrocarbon phenanthrene. Several studies focused on air-quality applications of biochar have also been published (Hwang et al., 2018; Moreira et al., 2017; Zhang et al., 2017b).

Coco coir is a fibrous material made from the husks of coconuts, and often used in horticulture as a soil conditioner. In previous experiments performed at the University of Colorado Boulder, coco coir was found to remove formaldehyde in a series of column tests (Wrobetz, 2015); however, most previous research has been related to water quality applications (Franguelli et al., 2019; Malik et al., 2017; Gautam et al., 2016; Etim et al., 2012).

1.4. Air Pollution and Health Disparities

Air pollution causes as many as 7 million premature deaths every year - approximately 12.5% of all deaths worldwide (WHO, 2018). In 2016, 91% of the world's population were regularly exposed to unclean air and over 50% of people living in urban environments were exposed to ambient air pollution levels that were 2.5 times greater than World Health Organization (WHO) standards. Much of the world's population do not have access to clear air due in part to a number of economic and social factors.

Economic factors like income, occupation, and education level have long been associated with illness and exposure to environmental pollution (Sydenstricker, 1929; Stockwell, 1963). Individuals of low socio-economic status (SES) are disproportionately burdened with exposure to air pollution including PM2.5 emissions (Wang et al., 2016; Kioumourtzoglou et al., 2016; Huang et al., 2019), traffic-related air pollutants including NO_x (Molitor et al., 2011), and other criteria air pollutants (Hajat et al., 2015). For example, Ou et al., (2008) found statistically significant differences in risk of death from air pollution exposure when comparing home owners to renters, as well as blue collar to white-collar workers.

Social factors can also play an important role in an individual's exposure to air quality. It has been documented, for example, that members of minority ethnic groups in the U.S. and abroad experience elevated exposure to air pollution (Apelberg et al., 2005; Morello-Frosch and Jesdale, 2006; Hun et al., 2009; D'Souza et al., 2009). In some cases, this disparity exists even when controlling for income and other variables (D'Souza et al., 2009; Kravitz-Wirtz et al., 2016). This trend has been shown to affect the most vulnerable individuals in minority ethnic groups, including pregnant women (Benmarhnia et al., 2017) who experience disparities in air pollution exposure. Similarly, minority children have been shown to experience substantially higher rates of asthma compared to white children (Carr et al., 1992) and higher rates of neurotoxin exposure in school (Grineski and Collins, 2018).

Studies have shown that the use of folk remedies to combat health issues like asthma and cerebrovascular disease is fairly common among individuals from certain minority ethnic groups in the U.S. and Canada (Bearison et al., 2002; Golomb et al., 2003; Van Sickle et al., 2003; Mosnaim et al., 2006; Koinis-Mitchell et al., 2008; Palakiko, 2017). These remedies range from herbal remedies (Koinis-Mitchell et al., 2008), dietary supplements (Bearison et al., 2002), and physical manipulation (e.g., acupuncture and massage; Golomb et al., 2003) to religious healing ceremonies (Van Sickle et al., 2003) and medicinal prayer (Palakiko, 2017). Such practices can prevent timely treatment of these issues, leading to further exacerbation of illnesses. Studies also found that many people using folk remedies do not disclose them to their physicians (Pachter et al., 1995; Golomb et al., 2003), limiting effective care. This barrier may be due in part to language and cultural differences between patients and healthcare providers (Canino et al., 2006; Mosnaim et al, 2006; Canino et al., 2009), since African American, Latino, and American Indian physicians comprise less than 9% of all physicians in the United States (AAMC, 2013).

Access to geographical areas with good air quality can also be limited due to discriminatory housing practices and existing structural disparities. Communities with low socioeconomic status (SES) and high minority presence, for example, are often subject to undesirable environmental conditions like proximity to high traffic (Gunier et al., 2003; Houston et al., 2004) and stationary pollution sources (Morello-Frosch et al., 2001; Morello-Frosch et al., 2002; Morello-Frosch et al., 2011). Similarly, studies from around the world have documented racial, ethnic, and SES-based discrimination in the rental housing market (Bonnet et al., 2015; Gaddis and Ghoshal, 2015; Bosch et al., 2015; MacDonald et al., 2015; MacDonald et al., 2016;

Auspurg et al., 2017; Bunel et al., 2017; Murchie and Pang, 2018). Consequently, access to geographical areas with superior environmental conditions can be limited based on factors beyond an individual's control.

Access to air pollution control technology and environmental regulations are also important factors impacting air pollution exposure and health. Disproportionate levels of air pollution exposure occur in the developing world (WHO, 2018), where access to common control technologies can be limited and regulations are lax (Atash, 2007).

Adoption of air quality control technology and practices can present additional barriers to clean air access. Despite technological advances in clean cooking technologies (Mehetre et al., 2016; Verma et al., 2016; Suresh et al., 2016), alternative fuel vehicles (Agarwal et al., 2018; Cano et al., 2018), and passive indoor air cleaning devices (Krou et al., 2015; Darling and Corsi, 2016; Zuraimi et al., 2018; Huang et al., 2019), the problem of air pollution exposure remains pervasive throughout much of the world. As Webler and Tuler (2010) pointed out, developing technology capable of solving complex problems does not guarantee that the problem will be solved, or that the technology will be utilized. Many lessons about technology adoption have been learned from decades long, and largely unsuccessful efforts to improve and implement cookstove technology in the developing world. Although improved cookstove (ICS) technologies offered improved efficiency and reduced fuel use, their adoption has been largely unsuccessful (Urmee and Gyamfi, 2014), leading to the collapse of many ICS programs. It has been suggested that ICS designers often failed to account for social (Bielecki and Wingenbach, 2014), cultural (Hooper et al., 2018), and practical (Urmee and Gyamfi, 2014) aspects of cooking stoves when developing their interventions, and therefore, fell short of achieving acceptance and utilization of their technology. In order to facilitate adoption, researchers and engineers should consider community needs, incorporate user feedback (Donegan, 2018), and develop culturally appropriate technologies and interventions (Champion et al., 2017) for the target community.

1.5. Community-Based Participatory Research

Community Based Participatory Research (CBPR) is a method of conducting research that engages members of the affected community in the research process, alongside scientists and formally trained partners. The goal of CBPR is to make the research process more equitable by sharing resources, power, and credit, and by democratizing knowledge production. This means that researchers outside of the community do not exclusively determine the research questions, methods, interventions, and outcomes (Minkler and Wallerstein, 2008). CBPR also differs from traditional research by incorporating the concept of praxis, or "reflection and action directed at the structures to be transformed" (Freire, 1970).

CBPR has been employed extensively in fields like public health, where it has been shown to enhance the relevance and usefulness of research data, join together partners with diverse skills and expertise, improve the quality and validity of research, and create theory that is grounded in social experience (Israel et al. 1998). Research studies that employ CBPR often involve community members in planning, data collection, and analysis stages of the study, as well as for community outreach and engagement. Although the process of planning and executing community-based research can be extremely time-consuming and challenging, it can yield major benefits to research projects. Studies regarding the efficacy of CBPR methodology suggest that it has the potential to enhance the outcome of interventions (Salimi et al., 2012; Viswanathan et al., 2004), and increase study recruitment/retention (Viswanathan et al., 2004).

The key principles of CBPR, which are outlined in Israel et al. (1998), as well as LaVeaux and Christopher (2009) include:

1. Recognizing community as a unit of identity.
2. Building on strengths and resources of the community.
3. Facilitating collaborative partnerships in all phases of the research.
4. Integrating knowledge and action for mutual benefit of all partners.
5. Promoting a co-learning and empowering process that attends to social inequalities.
6. Employing a cyclical and iterative process.
7. Addressing health from both positive and ecological perspectives.
8. Disseminating findings and knowledge gained to all partners.

1.6. Volatile Organic Compounds

Volatile Organic Compounds (VOCs) are ubiquitous in the indoor environment. They are generally defined as “*organic chemical compounds whose composition makes it possible for them to evaporate under normal indoor atmospheric conditions of temperature and pressure*” (US EPA, 2017). This definition typically applies to compounds with low boiling points and high vapor pressures. VOCs are sometimes classified more specifically on the basis of volatility. Table 1.1 shows common VOC classifications, as provided by US EPA (US EPA, 2017).

Table 1.1 Classification of Inorganic and Organic Pollutants[1]

Description	Abbreviation	Boiling Point Range (°C)	Example Compounds
Very volatile (gaseous) organic compounds	VVOC	< 0 to 50-100	Propane, butane, methyl chloride
Volatile Organic Compounds	VOC	50-100 to 240-260	Formaldehyde, d-Limonene, toluene, acetone, ethanol (ethyl alcohol), 2-propanol (isopropyl alcohol), hexanal
Semi volatile organic compounds	SVOC	240-260 to 380-400	Pesticides (DDT, chlordane, etc.), plasticizers (phthalates), fire retardants (PCBs, PBB, etc.)

[1] US EPA (2017)

VOCs can be emitted by a wide range of sources including combustion, tobacco smoke, personal care products, industrial solvents and adhesives, and human biological functions (Cooper & Alley, 2011). The importance and consequences of VOCs in the indoor environment have been explored extensively over the past 50 years (Mølhave et al., 1986; Wallace et al., 1987; Weschler et al., 1992; Brown et al., 1994; Singer et al., 2006; Weschler and Nazaroff, 2008; Sarigiannis et al., 2011). VOC concentrations measured indoors have been shown to have negative human health effects including skin, eye, and respiratory irritation as well as headaches, asthma (Rumchev et al., 2002), allergies (Garrett et al., 2001), neurological issues (US EPA, 2007), reproductive complications (John et al., 1994), and cancer (Swenberg et al., 1980; Ireland et al., 1997; Glass et al., 2003; Swenberg et al., 2013). Exposure to indoor VOCs has also been linked to sick building syndrome (SBS) (Takigawa et al., 2010; Takigawa et al., 2012; Guo et al., 2013; Nakaoka et al., 2013) and other acute health symptoms (Carrer and Wolkoff, 2018). More recently, indoor VOCs have been investigated regarding their contribution to secondary organic aerosol (SOA) formation in the indoor environment (Fan et al., 2005; Chen et al., 2011;

Rossignol et al., 2013), as well as their contribution to tropospheric ozone formation (McDonald et al., 2018).

Determination of volatile compounds in the air has been researched for many decades. VOC measurement typically relies on the use of chromatography to separate compounds based on volatility. Standard sampling and analysis protocols for VOC detection and quantitation are published by US EPA in their Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, including pesticides (US EPA, 1999a), formaldehyde (US EPA, 1999b), and other common VOCs (US EPA, 1999c). Other documented techniques for VOC sampling and quantitation include passive diffusive sampling and low-cost, time-resolved techniques, using ultraviolet (UV) ionization-based, electrochemical, or metal-oxide sensors.

US EPA Method TO-11A

US EPA Method TO-11A establishes a protocol for determining time-averaged concentrations of formaldehyde in ambient air. The method relies on the use of active sampling cartridges loaded with silica coated with the compound 2,4-dinitrophenylhydrazine (DNPH). DNPH reacts with carbonyl compounds (aldehydes and ketones) to form a stable-color hydrazone derivative that can then be eluted with high-purity acetonitrile and analyzed using high-performance liquid chromatography (HPLC) with a UV diode array detector (DAD). Fig. 1.1 shows the general reaction between DNPH and carbonyls used in this analysis (US EPA, 1999b).

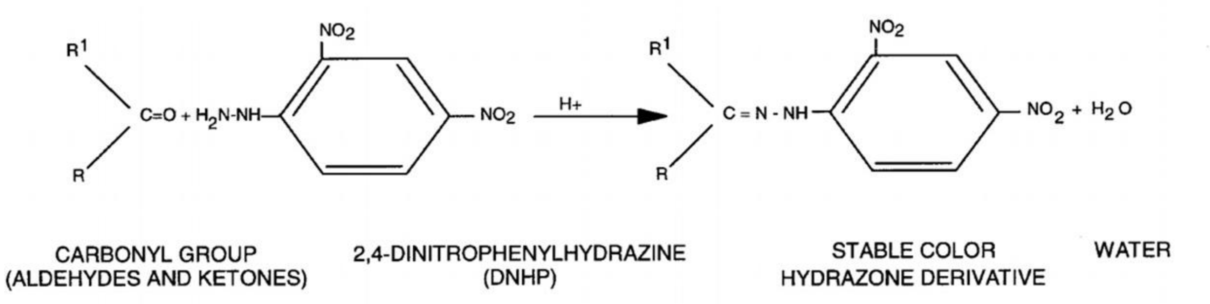

Fig. 1.1. Principle reaction between DNPH and carbonyl compounds used in US EPA TO-11A formaldehyde determination method (US EPA, 1999b).

Detection of formaldehyde concentrations on the order of ppbv is accomplished by drawing 1-2 LPM of air through a DNPH/Silica sampling cartridge for 1-24 h. These measurements are often performed over 8 h, in order to compare with relevant formaldehyde exposure limits. Two popular types of active sampling cartridges (Waters and Supelco) are shown in Fig. 1.2. Both types of DNPH-silica cartridges can be equipped with an ozone scrubber (not shown) to reduce chemical interference (as recommended by US EPA).

US EPA Method TO-15

US EPA Method TO-15 defines protocols for sampling and analyzing 97 VOCs in the ambient air using “specially-prepared canisters” and gas chromatography coupled with mass spectrometry (GC-MS). The method applies to VOCs with ambient concentrations above 0.5 ppbv, and vapor pressures greater than 10^{-1} Torr at 25°C and 760 mmHg (US EPA, 1999c).

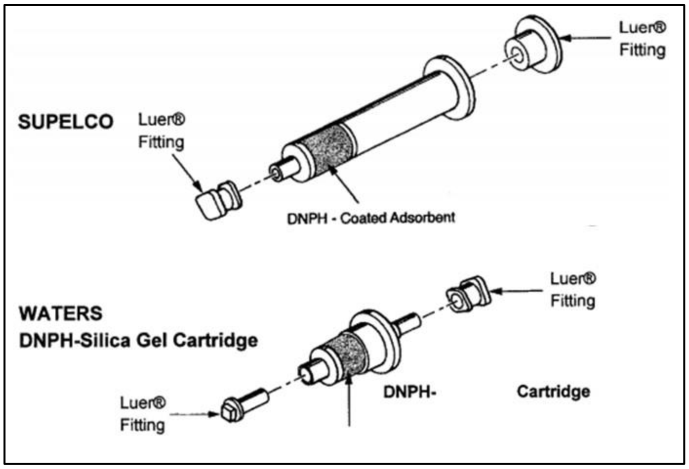

Fig. 1.2. DNPH-Silica active sampling cartridges used for determination of formaldehyde (US EPA, 1999b).

In this method, sampling is performed using an evacuated stainless-steel canister equipped with a critical orifice that controls the inlet flow rate across a range of differential pressures. Chemical analysis of the samples is performed by injecting a known volume of air from the canister into a pre-concentration system that captures VOCs from the sample onto the surface of an adsorbent. VOCs are then thermally desorbed from the surface of the adsorbent trap and injected into the gas chromatograph using a carrier gas (usually Helium). Previous studies Benedict et al. (2019) and Zhou et al. (2010) performed this analysis using a five-channel GC-MS/FID/ECD system with a cryogenic pre-concentration loop (cooled with liquid nitrogen) as shown in Fig. 1.3 (Weber, 2018). This system has five separate GC channels, each connecting to a different analytical device: 1 mass spectrometer (MS), 3 flame ionization detectors (FIDs), and 1 electron capture device (ECD). The MS channel is used to quantify C_6-C_{10} non-methane hydrocarbons (NMHCs) and the 3 FID channels are used to quantify C_2-C_7, C_6-C_{10}, and C_4-C_{10} NMHCs, respectively. The ECD channel is primarily used for the quantitation of halocarbons.

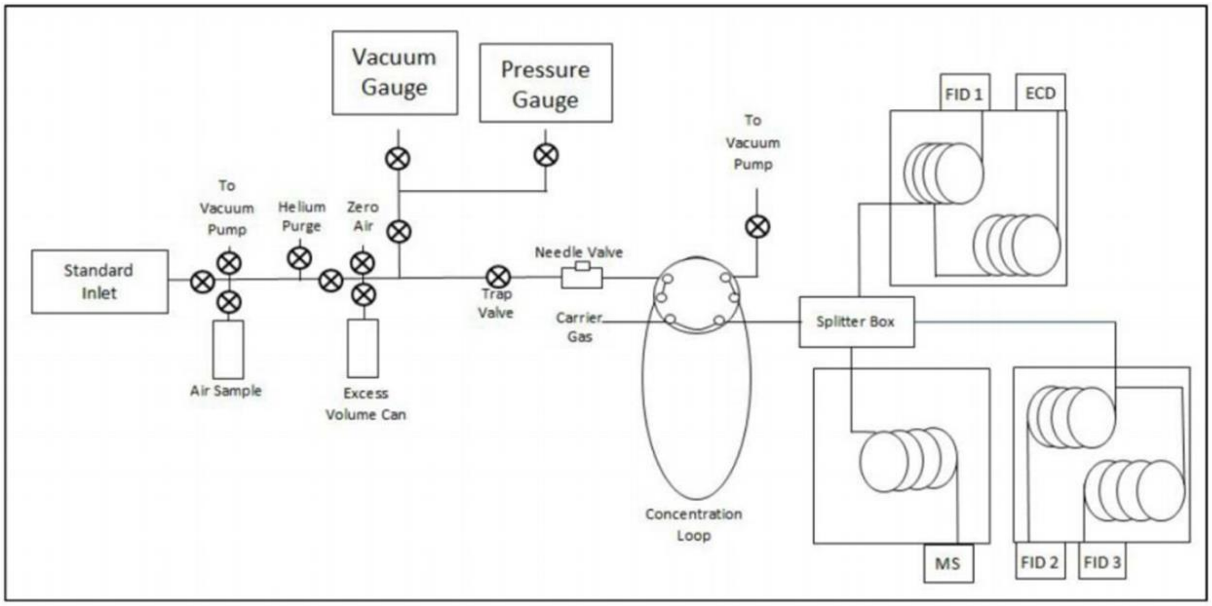

Fig. 1.3. GC-MS/FID/ECD used to analyze VOC samples in this dissertation (Weber, 2018).

Passive Diffusive Sampling for Personal Exposure Measurement

Passive sampling of VOCs using an adsorbent has been employed in a number of previous exposure studies (Quach et al., 2011; Raysoni et al., 2017; Colman Lerner et al., 2018). In this method, VOCs are removed from the air passively, through diffusion, and deposited onto the surface of an adsorbent. They are then removed from the adsorbent using a solvent or heat and analyzed via GC-MS. Passive samplers are typically worn by individuals on their collars during tasks or duties that may result in VOC exposure. Captured VOCs are eluted from the filters using carbon-disulfide, and the sample extractions are analyzed by GC-MS. VOC concentrations measured this way are used to determine individual or “personal” exposure to VOCs, since they are collected from a person’s breathing zone rather than from a fixed location nearby.

The use of passive air samplers is convenient for several reasons; however, most significant is that it does not require a sampling pump (i.e., without noise or electricity). There are several drawbacks with this type of sampling: poor retention of highly-volatile VOCs and competition between different VOC species for adsorption sites, which can lead to sampling bias. Although US EPA does not have a standard protocol for this sampling technique, it provides some guidance for it (Grosse and McKernan, 2015) due to its popularity in VOC exposure studies.

Since this sampling method relies on the principles of Fick's law of diffusion (Brown, 2000), determining the VOC concentration in the air requires knowledge about the VOC uptake rate of each species measured. 3M publishes a list of these rates, along with recovery coefficients that specify the fraction of each compound recovered from the adsorbent during the elution procedure (3M, 1993). Concentrations are calculated using the equation:

$$C[ppm] = (W \times B)/(r \times t) \qquad [1.1]$$

where W is the blank-corrected contaminant weight (μg) recovered from each filter, r is the recovery coefficient (published by 3M), t is the sampling time (min), and B is a constant determined by the equation:

$$B = (1000 \times 24.45)/(sampling\ rate \times molecular\ weight) \qquad [1.2]$$

where "sampling rate" is the uptake rate for each compound (published by 3M) and "molecular weight" is the molecular weight of each compound (g mol^{-1}).

Photo-Ionization Detection

Photo-ionization detectors (PIDs) can be used to make non-speciated measurements of total volatile organic compound (TVOC) concentrations. This measurement technique works by ionizing incoming gas flow using a UV lamp, typically with an ionization energy of 9.8. 10.6, or 11.7 eV, as shown in (Fig. 1.4). The ionization of gas molecules results in an electrical current that is used to determine TVOC concentration based on calibration with a reference gas (usually isobutylene). The energy of the UV lamp determines which compounds can be measured with this technique. For example, because oxygen ionizes at approximately 12 eV and nitrogen ionizes at 15.5eV (Linstrom and Mallard, 2018), air will not be detected by a PID with an 11.7 eV lamp. Similarly, formaldehyde (ionization energy = 10.9 eV) will not be detected by a PID with a 10.6 eV lamp.

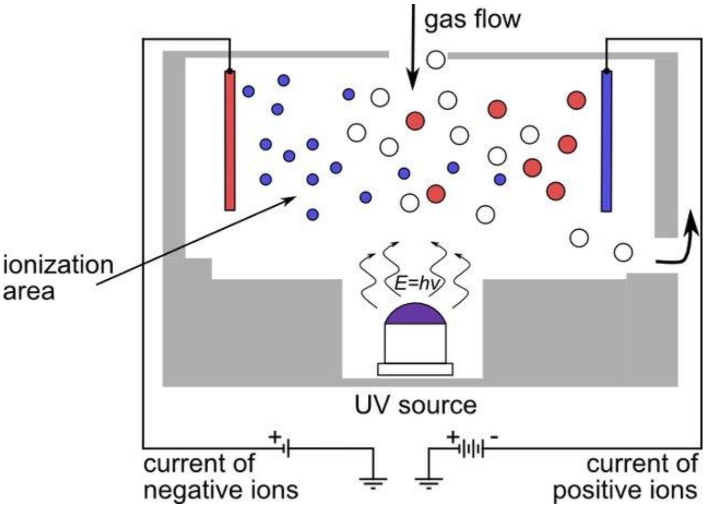

Fig. 1.4. Basic principle of a conventional PID (Zimmer et al., 2015).

PIDs can perform low-cost, time-resolved measurements of VOCs in the ambient air; however, PIDs cannot identify individual VOC species without the assistance of analytical techniques like gas chromatography. Time-resolved data from PIDs can be useful for resolving peaks in VOC concentration data and determining their source. Additionally, for known single or simple gas mixtures, PIDs can provide relatively accurate, pseudo-speciated time-resolved VOC concentration data.

CHAPTER 2

OCCUPATIONAL EXPOSURE TO VOLATILE ORGANIC COMPOUNDS AND HEALTH RISKS IN COLORADO NAIL SALONS[1]

Contributing Authors: Aaron Lamplugh, Megan Harries, Feng Xiang, Janice Trinh, Arsineh Hecobian, and Lupita D. Montoya

Abstract: Nail salon technicians face chronic exposure to volatile organic compounds (VOCs), which can lead to adverse health outcomes including cancer. In this study, indoor levels of formaldehyde, as well as benzene, toluene, ethylbenzene and xylene, were measured in 6 Colorado nail salons. Personal exposure VOC measurements and health questionnaires (n=20) were also performed; questionnaires included employee demographics, health symptoms experienced, and protective equipment used. Cancer slope factors from the United States Environmental Protection Agency (US EPA) and anthropometric data from the Centers for Disease Control and Prevention were then used to estimate cancer risk for workers, assuming 20-yr exposures to concentrations of benzene and formaldehyde reported here. Results show that 70% of surveyed workers experienced at least one health issue related to their employment, with many reporting multiple related symptoms. Indoor concentrations of formaldehyde ranged from 5.32 to 20.6 μg m^{-3}, across all 6 salons. Indoor concentrations of toluene ranged from 26.7 to 816 μg m^{-3}, followed by benzene (3.13 to 51.8 μg m^{-3}), xylenes (5.16 to 34.6 μg m^{-3}), and ethylbenzene (1.65 to 9.52 μg m^{-3}). Formaldehyde levels measured in one salon exceeded the Recommended Exposure Limit from the National Institute for Occupational Safety and Health.

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[1] This research is currently published in *Environmental Pollution*: Lamplugh, A., Harries, M., Xiang, F., Trinh, J., Hecobian, A., Montoya, L.D., 2019. Occupational exposure to volatile organic compounds and health risks in Colorado nail salons. Environ. Pollut. 249, 518–526.

Cancer risk estimates from formaldehyde exposure exceeded the US EPA *de minimis* risk level ($1x10^{-6}$) for squamous cell carcinoma, nasopharyngeal cancer, Hodgkin's lymphoma, and leukemia; leukemia risk exceeded $1x10^{-4}$ in one salon. The average leukemia risk from benzene exposure also exceeded the US EPA *de minimis* risk level for all demographic categories modeled. In general, concentrations of aromatic compounds measured here were comparable to those measured in studies of oil refinery and auto garage workers. Cancer risk models determined that 20-yr exposure to formaldehyde and benzene concentrations measured in this study will significantly increase worker's risk of developing cancer in their lifetime.

Keywords: personal care products; cancer risk estimation; electrochemical sensors; VOCs; BTEX

Capsule: VOCs measured in this study exceeded odor thresholds and NIOSH exposure limits, and 20-yr exposure to formaldehyde and benzene levels measured here will increase risk of cancer.

Highlights:

- VOCs in nail salons exceeded odor thresholds and inhalation reference concentrations
- BTEX levels in nail salons were similar to those in oil refineries and auto garages
- Most nail salon workers reported health issues related to their employment
- Nail technicians who work more than 20 years may experience increased cancer risk

2.1. Introduction

Studies have documented that workers in nail salons are regularly exposed to volatile organic compounds (VOCs), including acetone, toluene, ethyl acetate, methyl methacrylate, and formaldehyde (Quach et al., 2011; Alaves et al., 2013), which are ingredients in many nail salon products. These chemicals are known to cause skin, eye, and respiratory irritation as well as headaches, neurological issues (US EPA, 2007), reproductive complications (John et al., 1994), and cancer (Swenberg et al., 1980; Swenberg et al., 2013).

Despite the serious risks associated with exposure to these compounds, current regulations to protect U.S. workers from VOCs are often insufficient. The Occupational Safety and Health Administration (OSHA) issues a disclaimer along with its Permissible Exposure Limits (PELs) for workers, acknowledging that many of its PELs are “outdated and inadequate for ensuring protection of worker health” (OSHA, 2017). OSHA also advises businesses to supplement PELs with internal corporate guidelines and to utilize other Occupational Exposure Limits (OELs) such as Recommended Exposure Limits (RELs) published by the National Institute for Occupational Safety and Health (NIOSH) and Threshold Limit Values (TLVs) published by the American Conference of Government Industrial Hygienists (ACGIH). This poses a challenge for the U.S. salon industry, where 91% of all establishments are small businesses (Professional Beauty Association, 2014) that often lack the knowledge and resources to develop workplace guidelines capable of supplementing OSHA regulations. Consequently, salon technicians commonly report symptoms like eye irritation, skin irritation, respiratory irritation, headaches, reduced cognitive function, asthma, and work-related allergies (Kreiss et al., 2006; Roelofs et al., 2008; Quach et al., 2011).

Poor working conditions in nail salons may also contribute to health disparities since they disproportionately impact women and minority groups who constitute the majority of the industry's workforce. According to the Bureau of Labor Statistics, the "Miscellaneous Personal Appearance Workers" subgroup, which is comprised of manicurists, pedicurists, makeup artists, shampooers, and skin care specialists, is approximately 62% Asian, 9% Latino, 8% African American, and 82% female (BLS, 2018).

Previous research studies (Table 2.1) have examined various aspects of nail salon environments including VOC exposure (Quach et al., 2011), OEL compliance (Alaves et al., 2013), and ventilation (Roelofs & Do, 2012; Pavilonis et al., 2018). These studies provided characterizations of nail salon environments but did not attempt to estimate long-term health risks for nail salon workers based on VOC exposure.

In this study, an assessment of occupational VOC exposure was conducted in 6 Colorado nail salons between July 2017 and January 2019. The study included measurements of indoor levels of formaldehyde and the aromatic compounds benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as personal exposure concentrations for 9 VOCs (BTEX, acetone, ethyl acetate, n-butyl acetate, methyl methacrylate and 2-butanone). These compounds were selected because they are common ingredients in nail products, have been reported by other nail salon studies (Quach et al., 2011; Alaves et al., 2013), or are especially harmful to human health (IARC, 2012a; IARC, 2012b). Worker health questionnaires were also completed by 20 nail salon technicians, and self-reported health symptom data were correlated to exposure factors (e.g. age, years worked, VOC exposure concentrations). Formaldehyde and benzene concentration measured here were then used to estimate cancer risks along with modeling data published by the US EPA and Centers for Disease Control and Prevention (CDC).

Table 2.1 Published studies examining the nail salon environment.

Study	Location	n	Findings
Quach et al. (2011)	San Francisco, CA	20	VOC exposure among 80 workers in 20 nail salons was assessed. Average concentrations of ethyl acetate, toluene, and MMA were 530 ppb, 150 ppb, and 1.3 ppm, respectively.
Roelofs and Do (2012)	Boston, MA	22	Fourteen of 22 nail salons (64%) did not have functional mechanical ventilation systems, and 73% had CO_2 levels over 700 ppm.
Alaves et al. (2013)	Salt Lake County, UT	12	Fifty-eight percent of a randomly selected set of nail salons in Salt Lake County, UT exceeded NIOSH REL for formaldehyde (16 ppb)
Pavilonis et al. (2018)	New York City, NY	10	Mean and maximum Total VOC (TVOC) concentrations of 12 ppm and 67 ppm, respectively. Large increases in TVOC concentrations were observed when ASHRAE target CO_2 concentrations were exceeded.

2.2. Material and Methods

2.2.1. Recruitment of Salons and Technicians

Six nail salons located along the Colorado Front Range and within a radius of 100 km were recruited for this study through referrals from members of our research team and other collaborators. An initial contact was made to assess interest in participating in the study and a second visit was made to obtain informed consent. Five of the participating salons offered standard services, including acrylic nail services, and utilized popular product lines. Salon 6 was marketed as a “non-toxic” nail salon that used a custom product line and did not offer any acrylic nail services. Salons 3 and 4 also provided hair styling, although it represented a small percentage of services performed. All salons were equipped with mechanical ventilation systems, which were operational during the sampling period. The salons ranged in size from 90 to 260 m^2. All were located in attached storefronts near highways with 4 or more traffic lanes. Salons 1, 3, and 5 were located within 100 m of a gas station.

Three to 5 nail technicians from each salon participated in the study (n=20). All participants, aged 23 to 57, identified as non-smokers and were primarily of Vietnamese descent. Sixteen participants (80%) were female, and 4 (20%) were male. The study was approved by the University of Colorado Boulder Institutional Review Board. All participants were presented with information outlining the scope of the research and required to provide informed consent prior to participating in the study. Upon completion, participating businesses and subjects were provided a report that included a summary of study results as well as instructions for finding additional guidance on healthy workplace practices.

2.2.2. Questionnaires

Two brief questionnaires were utilized in this study. The manager questionnaire contained questions regarding the size and location of the salon, salon practices, products used, and services offered. Technician questionnaires included questions about demographics, employment history, business and safety practices, and work-related health symptoms. Neither questionnaire inquired about potential VOC exposure at home or other locations outside of the workplace. Both questionnaires were made available in English and Vietnamese and were administered by a research team member fluent in both languages.

2.2.3. Air Sampling

Air quality measurements were performed during regular business hours (between 9 am and 7 pm), over 4 business days (3 weekdays and 1 weekend day) for 8 continuous hours each day. Researchers were present in the salons during the entire 8 h measurement period and recorded the location, start time, end time, and type of every service performed.

2.2.3.1. Formaldehyde

Indoor formaldehyde levels were measured using DNPH-Silica cartridges analyzed with High-Performance Liquid Chromatography (HPLC), according to US EPA Method TO-11A (US EPA, 1999a). DNPH-silica cartridges were deployed on 1 day in each nail salon, and 1-2 LPM of air was drawn through the cartridges for 8 h using a GAST DOA P704-AA vacuum pump (Gast Manufacturing Inc., Benton Harbor, MI, Max flow: 3200 LPM, Max pressure: 4.2 bar). The flow rate at the inlet of each cartridge was measured 3 times over the course of each 8 h sampling period using a TSI 4100 flow meter (TSI Inc., Shoreview, MN, Range: 0-20 LPM, Accuracy: ±0.05 LPM). Following collection, samples were stored at 4° C for up to 4 weeks prior to analysis.

HalTech HFX-205 electrochemical formaldehyde monitors (Hal Technology, Fontana, CA, Range 0.00-10.00 ppm, Resolution 0.01 ppm) were also used to measure formaldehyde concentrations and to determine whether air inside salons was well-mixed. Two electrochemical monitors were deployed on 4 consecutive days in each salon and sampled at 1 min intervals. Both monitors were within 1 year of manufacturer calibration at the time of the study. They were positioned along interior walls, adjacent to electrical outlets and at heights ranging from 0.6 m to 1.2 m (the typical range of heights for pedicure and manicure stations). These monitors were deployed at 2 separate locations: one near manicure or pedicure stations (location A), and the other at the opposite end of the salon, 3.5 to 10 m away (location B). Appendix I Supplementary Fig. S1 shows a typical salon floor plan, including A and B locations. On days when DNPH-Silica cartridges were used, they were collocated with one of the electrochemical monitors.

2.2.3.2. BTEX

Indoor air samples were also collected to quantify concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX), according to methods similar to US EPA TO-15 (US EPA, 1999b). Samples were captured using 6 L Silonite-coated whole air sample canisters equipped with an Entech Toxic Organics Valve (TOV-2) and a CS1200ES flow controller (Entech Instruments, Simi Valley, CA). A single 8 h, time-integrated sample was collected at each salon. Prior to each deployment, the canisters were cleaned and evacuated using an Entech Instruments 3100D Canister Cleaning System following US EPA Compendium Method TO-15. Flow controllers were also cleaned using UHP nitrogen and calibrated for flow accuracy prior to deployment. Whole air sampling canisters were placed at location A along with a formaldehyde monitor. After sampling, the valve for each canister was closed, and the canister was stored at room temperature for up to 7 weeks prior to analysis.

2.2.3.3. Personal Exposure VOCs

Personal VOC exposure sampling was performed during regular business hours on 1 weekday and 1 weekend day using 3M OVM 3520 passive diffusive samplers (3M, Maplewood, MN) following manufacturer’s protocol. Three technicians at each salon wore a sampler on each measurement day. Sampling badges were attached to the workers’ collars, near the breathing zone, and worn throughout the worker’s shift (7-8 h). Field blanks were collected on every sampling day, and results were blank-corrected during data analysis. Following sample collections, samples were stored at 4°C until the time of analysis.

2.2.4. Chemical Analyses

2.2.4.1 HPLC

Formaldehyde was extracted from the DNPH-Silica cartridges with 3 mL of high-purity acetonitrile using a Waters extraction manifold operated at 457 mmHg. Extracted samples were then diluted to 5 mL with additional acetonitrile. Samples were analyzed using an Agilent 1260 Infinity HPLC system (Waters, Milford, MA) equipped with a Waters Nova-Pak C18 column (Waters, Milford, MA, Particle Size: 4 μm, ID: 3.9 mm, Length: 150 mm). The diode array detector was operated at 360 nm. Formaldehyde concentrations were determined using standard calibration curves and total volume of air sampled. A field blank, stored alongside the formaldehyde samples, was used for blank correction.

2.2.4.2 GC-FID-ECD-MS

Whole air samples were analyzed for BTEX using a 5-channel Gas Chromatography (GC) system coupled with 3 flame-ionization detectors (FID), an electron capture detector (ECD), and a mass spectrometer (MS). The system and its components are described in detail in Benedict et al. (2019). The 5-channel GC system was comprised of a 30 cm stainless steel cryogenic pre-concentration loop packed with 1 mm diameter glass beads, a splitter box, and an excess volume reservoir, which was connected to the combination of GCs and detectors. One of the GC-FIDs was used to quantify benzene and toluene, whereas the GC-MS was used to quantify ethylbenzene and xylenes. Throughout the analysis, US EPA’s TO-15 methods were followed, where applicable.

The 5-channel GC system was challenged using ultra high purity (UHP) nitrogen for baseline verification, and 8 dilutions of a high pressure 1 ppm BTEX standard (Airgas, Fort Collins, CO) were used for system calibration. During canister cleaning, a canister from each batch was selected as a batch blank and filled with UHP nitrogen and analyzed to ensure that the cleaning system was operating properly; blank correction was applied as needed.

BTEX concentrations (ppm) were determined using the calibration curve slopes for each compound and accounting for the difference in pressure between the sample and the calibration standard. Concentrations were calculated from the area under the peak obtained from the GC-FID or GC-MS system.

2.2.4.3. GC-MS

Personal exposure VOC samples were prepared following the procedures in the 3M Organic Vapor Monitor Sampling and Analysis Guide (3M, 1993), and analyzed using GC-MS. These samples were analyzed for 9 compounds: acetone, 2-butanone (MEK), ethyl acetate, methyl methacrylate (MMA), benzene, n-butyl acetate, toluene, ethylbenzene, and xylene (m-xylene used to quantify all isomers). Samples were eluted with 1.4 mL of carbon disulfide (CS_2), which was tested for purity before use. Samples were then placed on a Cole Parmer OR-100 orbital shaker (Cole Parmer, Vernon Hill, IL) for 30 min at 180 RPM. Samples were decanted into 2 mL glass autosampler vials, sealed with a Teflon® screw cap, and immediately analyzed with GC-MS. The instrument operated in single ion monitoring mode for the following ions: 51, 56, 58, 61, 69, 70, 72, 73, 91, 100, and 106. Reported results are the average of 3 injections per sample (n=3). Four standard solutions, prepared in CS_2, were used to calibrate for all 9 compounds. Samples were also analyzed once by GC-MS in scan mode to qualitatively screen for the presence of other compounds.

Personal exposure VOC concentrations were determined using the methods outlined in the 3M Organic Vapor Monitor Sampling and Analysis Guide (3M, 1993). The OVM 3520 model utilizes 2 adsorbent carbon pads, which are analyzed separately and then combined to obtain a total concentration for each sample. 3M guidelines state that the lower limit of quantitation (LLOQ) for a single compound measured using this method is 2-3 μg per sample. Any compound below the LLOQ (Appendix I Supplementary Table S1) was reported as 0 ppm.

2.2.3. Data Analysis

2.2.3.1. Questionnaires

Data from the questionnaires were analyzed according to data type; results for numerical values (e.g., age, years employed, length of shift) are reported as the median and range. Work-related health symptoms and use of personal protective equipment (PPE) were reported as binary answers (yes/no). Results are reported as percentages of technicians responding “yes” to each question. In addition, place of birth and language(s) spoken at home were reported.

2.2.3.2. Comparison to Air Quality Standards/Guidelines

Formaldehyde concentrations measured in salons using DNPH-Silica cartridges were compared to the 8-h NIOSH REL for workplace formaldehyde exposure (16 ppb).

BTEX concentrations were first converted from ppm to mass-based concentrations (μg m^{-3}) using the average salon temperature and theoretical surface pressure. The latter was calculated for each salon location using the compact barometric formula (Jacob, 1999):

$$P(z) = P(0)e^{-z/H} \qquad [2.1]$$

where *H* (atmospheric scale height) is 7400 m, and *z* is the altitude at each salon location (m). Where applicable, BTEX concentrations were compared to US EPA Reference Concentrations for Inhalation Exposure (RfCs) (US EPA, 2005). RfCs are recommended exposure limits to avoid specific non-carcinogenic health complications and are currently available for 104 compounds.

Personal exposure VOC concentrations were compared to both odor threshold values and US EPA RfCs. Odor threshold values for acetone (832 ppb), ethyl acetate (245 ppb), n-butyl acetate (4.3 ppb), MMA (210 ppb), and MEK (440 ppb) were obtained from previous studies (Nagata 2003; Cometto-Muniz et al., 2008; Cometto-Muniz et al., 2009).

2.2.3.3. Health Symptoms versus Exposure Factors

Health symptoms data from the questionnaires were compared with exposure factors, including VOC concentrations and demographic data. For each health symptom, exposure factors were compared between workers experiencing that symptom versus those who were not, and a t-test was used to determine if the population means differed significantly. Welch’s unequal variances t-test was used to account for the relatively small and unequal population sizes. VOC exposure concentration data was assumed to be log-normal and a log transformation was performed prior to testing.

2.2.4. Cancer Risk Estimation

Cancer risk estimates for benzene and formaldehyde exposure were calculated using cancer slope factors published by the US EPA in their Integrated Risk Information System (IRIS) (US EPA, 2005) as well as proposed cancer slope factors for formaldehyde exposure that were outlined in US EPA’s draft reassessment of formaldehyde-inhalation (US EPA, 2010). These 2 compounds were the only ones measured in this study for which cancer slope factors are presently available from US EPA. Estimates were based on a 20-yr occupational exposure duration and incorporate average body weight provided by the CDC as well as inhalation rates provided by US EPA. Worker chronic daily intake (CDI) for each compound was calculated according to the following equation (Tunsaringkarn et al., 2012):

$$CDI\ (\mu g\ kg^{-1} d^{-1}) = (CA \times IR \times ET \times EF \times ED)/(BW \times AT) \qquad [2.2]$$

where *CA* is the concentration of each compound in the salon air (μg m^{-3}), *IR* is the worker inhalation rate (m^3 h^{-1}), *ET* is the exposure time (h wk^{-1}), *EF* is the exposure frequency (wk yr^{-1}), *ED* is the exposure duration (20 yr), *BW* is the average body weight of the technician (kg), and *AT* is the averaged time (70 yr x 365 d yr^{-1}).

Lifetime cancer risks were calculated by multiplying *CDI* values by the cancer slope factors for formaldehyde and benzene (Tunsaringkarn et al., 2012):

$$Lifetime\ Risk = CDI \times CSF_i \qquad [2.3]$$

where CSF_i is the cancer slope factor for each compound calculated from US EPA's unit risk estimates. *CSF* values are calculated as (US EPA, 2005):

$$CSF_i = URE_i/CDE \qquad [2.4]$$

where URE_i is the unit risk estimate for pollutant exposure published in IRIS, and *CDE* is the continuous daily exposure (given as 0.143 μg kg^{-1} d^{-1}). A 90% absorption factor for inhalation exposure was applied to each CDI for both benzene (Colman Lerner et al., 2012; Gong et al., 2017; Zhang et al., 2018) and formaldehyde (US EPA, 2010).

Cancer risks were calculated for the 3 demographics represented in this study population: Asian Females, Asian Males, and White Females, who all differ in terms of average body weight

(BW) and inhalation rate (IR). Cancer risk values were compared to the US EPA threshold for *de minimis* cancer risk (1×10^{-6}); a cancer risk $>10^{-6}$ was considered a carcinogenic effect of concern. Values for BW and IR were obtained from Tables 3 and 5 of the CDC Anthropometric Reference Data Handbook (CDC, 2016) and Table 6-28 of The US EPA Exposure Factors Handbook (US EPA, 2011), respectively. IR for Asian males was 0.8 m^3 h^{-1}, while IR for both Asian and White females was 0.5 m^3 h^{-1}. BW values used for Asian Males (73.20 kg) and White Females (76.20 kg) are for individuals aged 40-59 and 20-39, respectively. The BW value selected for the Asian Females (60.75 kg) is a weighted average that assumes 30% between ages 20-39 and 70% between ages 40-59. These values were determined using the demographic data captured in the worker questionnaires. The ET used was the median number of hours worked per week, as reported by nail technicians in this study. EF was set at 50 weeks.

2.3. Results

2.3.1. Questionnaires

Results indicated that the median age of the technicians was 42 yr old (range: 23-57). Similarly, the median values for the time they had been employed in the nail salon industry, the number of hours they worked per week, and the number of hours per shift were 7.5 yr (range: 0.17-19), 52.5 h wk^{-1} (range: 33-80), and 9 h d^{-1} (range: 7-11), respectively. Seventy percent of participants were born in Vietnam and speak primarily Vietnamese at home, while 25% reported being U.S. born and speaking English at home.

Table 2.2 lists the health-related symptoms reported by the participants as well as their PPE use. Seventy percent of all workers reported wearing either nitrile or latex gloves, with 65% wearing latex gloves. Sixty-five percent reported wearing some type of facemask when performing nail services, with 55% wearing surgical style facemasks. No workers reported wearing N95 dust masks.

Table 2.2. Worker health-related symptoms and PPE use

Symptom Experienced	*Number of Respondents n (%)*
Nose irritation	4 (20%)
Throat irritation	2 (10%)
Lung irritation	1 (5%)
Skin irritation	6 (30%)
Eye irritation	5 (25%)
Headaches	8 (40%)
Nausea	0 (0%)
Coughing	2 (10%)
Increased pulse rate	1 (5%)
Confusion	2 (10%)
Shortness of breath	3 (15%)
Chest tightness	3 (15%)
Type of PPE Used	Number of Respondents n (%)
Latex Gloves	13 (65%)
Nitrile Gloves	3 (15%)
Surgical Mask	11 (55%)
N95 Dust Mask	0 (0%)
N95 w/ Odor ctrl.	2 (10%)
Air purifying respirator	1 (5%)

Workers across all 6 salons reported headaches as the most common symptom (40%), followed by skin irritation (30%), eye irritation (25%), and nose irritation (20%). Seventy percent of technicians reported experiencing at least one of the health symptoms listed (Appendix I Supplementary Fig. S2). Of those respondents reporting symptoms, 57% experienced multiple health-related symptoms, and nearly 30% reported 4 or more of them.

2.3.2. Formaldehyde

A comparison of formaldehyde concentrations measured with both electrochemical monitors and DNPH-Silica cartridges analyzed with HPLC (US EPA Method TO-11A) showed that there was low correlation between the 2 sampling methodologies (Appendix I Supplementary Table S2 and Fig. S3). Consequently, data from the electrochemical monitors were only used to verify well-mixed conditions for the indoor air in the salons. Results showed that air was well-mixed inside each nail salon (Appendix I Supplementary Fig. S4).

Table 2.3 shows the 8 h average formaldehyde concentration for each salon measured with the DNPH-Silica cartridges as well as the 8 h formaldehyde REL published by NIOSH. Only Salon 5 exceeded the NIOSH 8 h REL (16 ppb) for formaldehyde with a concentration of 20.6 μg m^{-3} (21.5 ppb).

Table 2.3. Formaldehyde concentrations from nail salons

Salon ID	Concentration (μg/m^3)
Salon 1	10.6
Salon 2	7.85
Salon 3	5.32
Salon 4	13.1
Salon 5	20.6*
Salon 6	7.29

*Exceeded NIOSH 8-h REL for formaldehyde exposure (16 ppb, 19.6 μg m^{-3})

2.3.3. BTEX

The LLOQ for benzene and xylenes was determined to be approximately 0.03 μg m^{-3}; the LLOQ for toluene and ethylbenzene was approximately 0.07 μg m^{-3}. Fig. 2.1 shows 8 h average BTEX concentrations measured inside each nail salon. Toluene was detected in the highest concentrations, ranging from 26.7 μg m^{-3} to 816 μg m^{-3}, followed by benzene (3.13 μg m^{-3} - 51.8 μg m^{-3}), xylenes (5.16 μg m^{-3} - 34.6 μg m^{-3}), and ethylbenzene (1.65 μg m^{-3} - 9.52 μg m^{-3}). Average BTEX levels from 2 published studies that measured occupational BTEX exposure are also shown. Singh et al. (2013) investigated BTEX exposure inside the distribution terminal of an oil refinery, while Badjagbo et al. (2010) documented BTEX exposure among mechanics and painters in auto garages. In most cases, the BTEX levels measured in this study fell between those reported by Badjagbo et al. (2010) and Singh et al. (2013). Salon 1 also exceeded the RfC for benzene (30 μg m^{-3}).

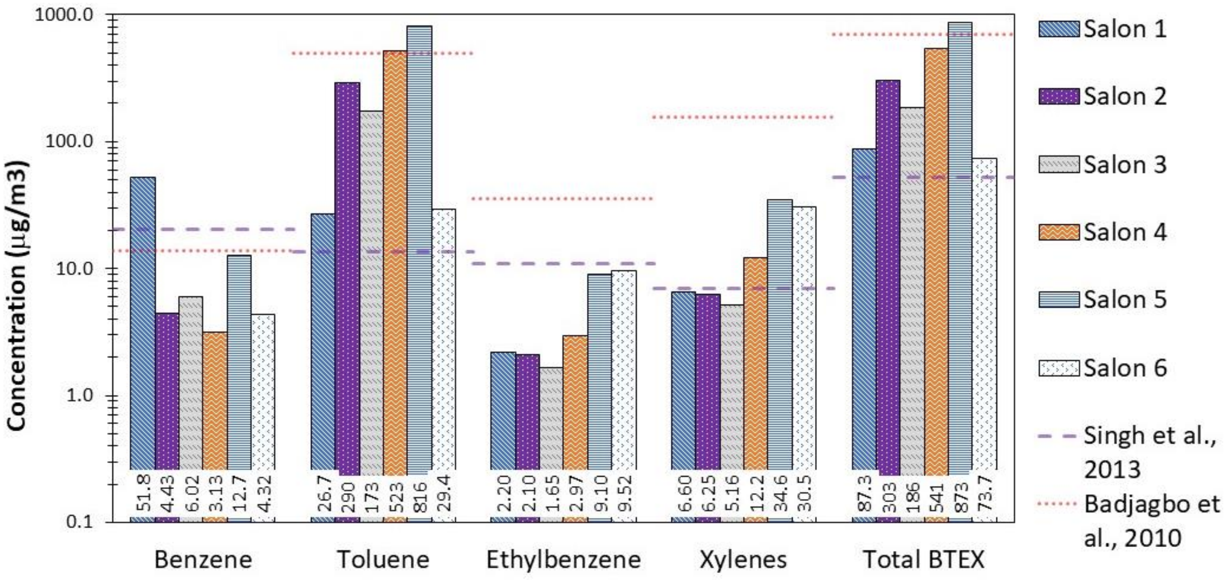

Fig. 2.1. BTEX concentrations at each salon. Dash lines represent average BTEX concentrations (ppb) measured at the distribution terminal in an oil refinery (Singh et al. 2013) and at auto garages (Badjagbo et al. 2010).

2.3.4. Personal Exposure VOCs

Of the 9 analytes quantified by GC-MS, only acetone, ethyl acetate, and n-butyl acetate were detected at all 6 salons. The other 6 analytes were detected infrequently or not at all. Table 2.4 summarizes the blank corrected personal exposure results for each salon. The median of 6 personal exposure measurements for each analyte is reported along with the minimum and maximum personal exposure concentrations measured in each salon.

Table 2.4. Personal exposure VOC concentrations (ppm)

Salon	Acetone	MEK	Ethyl Acetate	MMA	n-Butyl Acetate
Salon 1	8.0 (6.0 - 14)	0.00 (0.00 - 0.00)	0.34 (0.19 - 0.59)	0.19 (0.070 - 0.33)	0.14 (0.080 - 0.21)
Salon 2	17 (12 - 32)	0.00 (0.00 - 0.00)	0.42 (0.23 - 0.68)	0.00 (0.00 - 0.00)	0.10 (0.060 - 0.28)
Salon 3	14 (10 - 27)	0.00 (0.00 - 0.080)	0.23 (0.090 - 0.51)	0.00 (0.00 - 0.00)	0.040 (0.00 - 0.12)
Salon 4	14 (3.6 - 24)	0.00 (0.00 - 0.00)	0.21 (0.14 - 0.33)	0.00 (0.00 - 0.00)	0.080 (0.00 - 0.16)
Salon 5	19 (13 - 31)	0.00 (0.00 - 0.13)	0.31 (0.19 - 0.95)	0.52 (0.16 - 1.1)	0.10 (0.060 - 0.16)
Salon 6	30 (25 - 45)	0.00 (0.00 - 0.00)	0.55 (0.39 - 1.4)	0.00 (0.00 - 0.00)	0.28 (0.18 - 0.67)

The VOC with the highest concentration measured at every salon was acetone, ranging from 3.6 to 45 ppm. Ethyl acetate ranged from 0.090 to 1.4 ppm, and n-butyl acetate ranged from 0 to 0.67 ppm. MEK and MMA were also detected in some salons. MMA concentrations in Salon 5 were exceptionally high, exceeding 1 ppm on one occasion. Benzene, toluene, ethylbenzene, and xylene concentrations were below limits of quantitation (53, 39, 55, and 54 ppb, respectively) for this method.

Average acetone and n-butyl acetate concentrations exceeded odor threshold values by more than an order of magnitude in all 6 salons. Average concentrations of ethyl acetate exceeded the odor threshold value in 5 out of 6 salons and the average MMA concentrations exceeded the odor threshold value in one salon. MEK concentrations were relatively low and never exceeded the odor threshold concentration. Salons 1 and 5 exceeded the RfC for MMA (~171 ppb) on several occasions.

A qualitative analysis of personal exposure samples was also performed from GC-MS scans of each sample. This analysis found ethyl methacrylate in salons 1 through 5, styrene in Salons 1 and 2, and Butane in Salons 4, 5, and 6. Samples from Salons 1 and 6 also showed significant levels of ethanol, which is known to interfere with the type of electrochemical formaldehyde sensor used in this study (Hal Technology, 2015). These ethanol levels likely caused the discrepancies observed between the two formaldehyde sampling methods at salons 1 and 6.

2.3.5. Health Symptoms versus Exposure Factors

Results from Welch’s unpaired t-test are shown in Appendix I Supplementary Table S3 and Fig. S5. Due to the small sample size (n=20), few correlations were found to be significant. Of the 252 comparisons performed, only 16 had p-values below 0.05. The full list of p-values for each comparison is shown in Appendix I Supplementary Table S3. Appendix I Supplementary Fig. S5 shows boxplots from all comparisons that were statistically significant. A comparison of PPE used vs total number of symptoms experienced was also performed; however, there were no statistically significant results.

2.3.6. Cancer Risk Estimates

Table 2.5 shows the estimated increase in lifetime cancer risk for workers in each of the participant salons based on 20 years of exposure to the benzene and formaldehyde levels observed in this study. These estimates are based on cancer risk slope factors proposed by US EPA for Squamous Cell Carcinoma (SCC), nasopharyngeal cancer (NPC), and Hodgkin's lymphoma from formaldehyde exposure as well as leukemia from both benzene and formaldehyde exposure. All cancer risk values (or range of values) estimated in this study exceeded the US EPA *de minimis* risk level of 1×10^{-6}. Elevated lifetime risk for SCC from formaldehyde exposure ranged from approximately 6 in 1,000,000 (5.88×10^{-6}) to almost 4 in 100,000 (3.78×10^{-5}). Average lifetime risk of SCC for Asian females, Asian males, and White females across all salons were 1.65×10^{-5}, 2.18×10^{-5}, and 1.31×10^{-5}, respectively. Elevated lifetime risk for NPC ranged from 4.05×10^{-6} to 2.61×10^{-5}, with average risk increases of 1.13×10^{-5}, 1.51×10^{-5}, and 9.04×10^{-6} for Asian females, Asian males, and White females, respectively. Elevated lifetime risk for Hodgkin's lymphoma ranged from 6.24×10^{-6} to 3.02×10^{-5}, with average risk increases of 1.75×10^{-5}, 2.32×10^{-5}, and 1.39×10^{-5} for Asian females, Asian males, and White females, respectively.

Table 2.5. Lifetime cancer risk increases due to measured benzene and formaldehyde levels[1]

Demographic	SCC[2]	NPC[3]	Hodgkin Lymphoma[3]	Leukemia (Formaldehyde)[3]	Leukemia (Benzene)[2]
Asian Female					
Salon 1	1.47×10^{-5}	1.01×10^{-5}	1.56×10^{-5}	5.23×10^{-5}	$1.21 \times 10^{-5} - 4.30 \times 10^{-5}$
Salon 2	1.09×10^{-5}	7.49×10^{-6}	1.15×10^{-5}	3.88×10^{-5}	$1.05 \times 10^{-6} - 3.72 \times 10^{-6}$
Salon 3	7.37×10^{-6}	5.08×10^{-6}	7.83×10^{-6}	2.63×10^{-5}	$1.39 \times 10^{-6} - 4.94 \times 10^{-6}$
Salon 4	1.81×10^{-5}	1.25×10^{-5}	1.93×10^{-5}	6.48×10^{-5}	$7.33 \times 10^{-7} - 2.60 \times 10^{-6}$
Salon 5	2.85×10^{-5}	1.96×10^{-5}	3.02×10^{-5}	1.02×10^{-4}	$2.97 \times 10^{-6} - 1.05 \times 10^{-5}$
Salon 6	1.01×10^{-5}	6.96×10^{-6}	1.07×10^{-5}	3.60×10^{-5}	$1.03 \times 10^{-6} - 3.65 \times 10^{-6}$
Average	1.65×10^{-5}	1.13×10^{-5}	1.75×10^{-5}	5.87×10^{-5}	$3.22 \times 10^{-6} - 1.14 \times 10^{-5}$
Asian Male					
Salon 1	1.95×10^{-5}	1.34×10^{-5}	2.07×10^{-5}	6.95×10^{-5}	$1.61 \times 10^{-5} - 5.71 \times 10^{-5}$
Salon 2	1.44×10^{-5}	9.95×10^{-6}	1.53×10^{-5}	5.15×10^{-5}	$1.39 \times 10^{-6} - 4.94 \times 10^{-6}$
Salon 3	9.79×10^{-6}	6.75×10^{-6}	1.04×10^{-5}	3.49×10^{-5}	$1.85 \times 10^{-6} - 6.56 \times 10^{-6}$
Salon 4	2.41×10^{-5}	1.66×10^{-5}	2.56×10^{-5}	8.60×10^{-5}	$9.73 \times 10^{-7} - 3.45 \times 10^{-6}$
Salon 5	3.78×10^{-5}	2.61×10^{-5}	4.02×10^{-5}	1.35×10^{-4}	$3.95 \times 10^{-6} - 1.40 \times 10^{-5}$
Salon 6	1.34×10^{-5}	9.24×10^{-6}	1.42×10^{-5}	4.79×10^{-5}	$1.37 \times 10^{-6} - 4.85 \times 10^{-6}$
Average	2.18×10^{-5}	1.51×10^{-5}	2.32×10^{-5}	7.80×10^{-5}	$4.27 \times 10^{-6} - 1.52 \times 10^{-5}$
White Female					
Salon 1	1.17×10^{-5}	8.05×10^{-6}	1.24×10^{-5}	4.17×10^{-5}	$9.67 \times 10^{-6} - 3.43 \times 10^{-5}$
Salon 2	8.67×10^{-6}	5.97×10^{-6}	9.20×10^{-6}	3.09×10^{-5}	$8.37 \times 10^{-7} - 2.97 \times 10^{-6}$
Salon 3	5.88×10^{-6}	4.05×10^{-6}	6.24×10^{-6}	2.10×10^{-5}	$1.11 \times 10^{-6} - 3.94 \times 10^{-6}$
Salon 4	1.45×10^{-5}	9.97×10^{-6}	1.54×10^{-5}	5.16×10^{-5}	$5.84 \times 10^{-7} - 2.07 \times 10^{-6}$
Salon 5	2.27×10^{-5}	1.57×10^{-5}	2.41×10^{-5}	8.11×10^{-5}	$2.37 \times 10^{-6} - 8.41 \times 10^{-6}$
Salon 6	8.05×10^{-6}	5.55×10^{-6}	8.55×10^{-6}	2.87×10^{-5}	$8.21 \times 10^{-7} - 2.91 \times 10^{-6}$
Average	1.31×10^{-5}	9.04×10^{-6}	1.39×10^{-5}	4.68×10^{-5}	$2.57 \times 10^{-6} - 9.10 \times 10^{-6}$

[1] Based on 20-year exposure to measured concentrations at 52.5 h/wk

[2] Cancer slope factor derived from current US EPA IRIS inhalation risk values (US EPA 2005)

[3] Cancer slope factor derived from proposed US EPA inhalation risk values (US EPA 2010)

Leukemia risk from formaldehyde exposure ranged from 2.10×10^{-5} to 1.35×10^{-4}, with average risk increases of 5.87×10^{-5}, 7.80×10^{-5} and 4.68×10^{-5} for Asian females, Asian males, and White females, respectively. Increased cancer risk from benzene exposure is presented as a range of values based on US EPA's published unit risk. The lowest range observed in this study was $5.84 \times 10^{-7} - 2.07 \times 10^{-6}$, and the highest was $1.61 \times 10^{-5} - 5.71 \times 10^{-5}$. The average range of lifetime cancer risk for Asian Females, Asian Males, and White Females was $3.22 \times 10^{-6} - 1.14 \times 10^{-5}$, $4.27 \times 10^{-6} - 1.52 \times 10^{-5}$, and $2.57 \times 10^{-6} - 9.10 \times 10^{-6}$, respectively.

2.4. Discussion

Seventy percent of workers in this study reported experiencing health symptoms, similar to the 62% reported by Quach et al. (2008). Their study (n=201) also found that 47% of participants experienced health symptoms potentially related to solvents. Occupational exposure to odors has previously been linked to several symptoms commonly reported in our health questionnaire (Carrer & Wolkoff, 2018). Of the 252 health-related correlations that were tested (Appendix I Supplementary Table S3), 16 were found to be significant ($p < 0.05$). Of these, 13 were related to VOC exposure concentrations. The majority of these findings (8 of 13) were negative associations between symptoms and exposure concentrations (Appendix I Supplementary Fig. S5). This result may have been due to the small sample size (n=20). It is also likely that workers who were frequently exposed to higher concentrations of VOCs were desensitized based on their exposure. For example, based on the exceedance of RfC values for MMA, workers in Salons 1 and 5 were at risk of olfactory epithelium degeneration, which affects sensitivity to smell (US EPA, 2005).

Workers in Salon 1 were at risk of decreased lymphocyte count due to benzene exposure (based on RfC exceedance). Chronic exposure to low-level concentrations of BTEX has also been reported to alter central nervous system sensory and motor function (de Oliveira et al., 2017) and cause oxidative stress and genotoxicity in humans (Xiong et al., 2016).

Measurable levels of MMA in 2 nail salons were unexpected because MMA is banned by the Colorado Office of Barber and Cosmetology Licensure (CDORA, 2018). Several nail salon owners in this study reported that despite this ban, MMA can still be purchased from Colorado nail supply stores. It is also frequently requested by technicians in their shops, who prefer it to safer ethyl methacrylate alternatives because they find it easier to apply. Similar findings were published by Quach et al. (2011), Alaves et al. (2013), and Zhong et al., (2019). Discouraging technicians from requesting these products will likely require additional education regarding statutes and safety.

Salon 6 had the highest personal exposure concentrations of acetone, ethyl acetate, and n-butyl acetate, but the BTEX and formaldehyde levels were similar to those measured in other salons in this study. Since this salon was marketed as “non-toxic”, these results may have implications regarding product labeling regulations and practices in the cosmetics industry. The U.S. Food and Drug Administration (US FDA) is not required to approve cosmetic products or ingredients, with the exception of color additives, before marketing; instead, it defers to manufacturers to ensure product safety. The US FDA has limited power to recall hazardous cosmetic products (US FDA, 2013). Limited oversight of the cosmetics industry has led to product mislabeling and misbranding. California EPA investigated nail products labeled “toluene-free” or “three-free” (i.e., free of toluene, formaldehyde, and dibutyl phthalate) and found that 10 out of the 12 products tested contained toluene in concentrations as high as

177,000 ppm (17.7%) (Guo et al., 2012). Additionally, products containing the “three-free” label were found to contain dibutyl phthalate in higher concentrations than regular products. Such misrepresentation effectively negates the ability of nail professionals to mitigate exposure to harmful ingredients and creates a false sense of safety in their working environment. The safety of nail products should be independently assessed before any recommendations can be made regarding their use.

Formaldehyde is designated by both US EPA and the International Agency for Research on Cancer (IARC) as a known human carcinogen (US EPA, 2010; IARC, 2012a; IARC, 2012b). Estimated lifetime risk of SCC, NPC, Hodgkin’s lymphoma, and leukemia from formaldehyde exposure in this study exceeded the US EPA *de minimis* risk level of one-in-a-million (1×10^{-6}) for all categories of worker at every salon; leukemia risk in one salon exceeded 1×10^{-4}. Although risk levels were considered significant, formaldehyde concentrations measured in this study were similar to those previously measured in homes (Francisco et al., 2016), early childhood education environments (Bradman et al., 2016), and other nail salons (Alaves et al., 2013; Zhong et al., 2019). Additional research is needed to determine whether formaldehyde levels measured in salons are impacted by emissions from building materials and other indoor sources. Similarly, exposure to formaldehyde and VOCs in other locations, like home, should be assessed but was not included in this study. Additional exposure to these compounds in these other locations would effectively increase the cancer risk for these participants. Determination of formaldehyde exposure should adhere to established methodology, and the use of electrochemical formaldehyde monitors should be discouraged in environments where interfering VOCs, like ethanol, may also be present.

The National Academy of Sciences (NAS) stated in their review of US EPA's draft Reassessment of Formaldehyde Inhalation Exposure that proposed cancer slope factors for SCC, NPC, and Hodgkin's lymphoma were reasonable (NAS, 2011). However, the NAS also stressed the need to: (1) determine the mode of action by which formaldehyde exposure causes Leukemia and Hodgkin's lymphoma and (2) validate the dose-response models used in US EPA's unit risk estimate calculations. Starr and Swenberg (2016) suggested that top-down approaches to modeling formaldehyde cancer risk with linear dose-response models can lead to over-estimation, and that bottom-up models may provide improved accuracy. Also, since CDI depends on body weight, cancer risk estimates were higher for all Asian workers due to their low average body weight compared to other ethnic groups. Additionally, higher inhalation rates for Asian males result in consistently higher estimated cancer risk versus Asian females. These factors must be considered when setting exposure limits, in order to avoid one-size-fits-all approaches that fail to account for diverse populations.

The upper estimate of increased leukemia risk from benzene exposure exceeded 1×10^{-6} for all demographics and salons in this study. Similarly, for each demographic, the average leukemia risk across all salons also exceeded 1×10^{-6} . This finding is noteworthy since no previous study of nail salon VOC exposure reported significant benzene concentrations. The source of this pollutant in the nail salon environment was not identified; however, it was observed in all 6 salons and is likely linked to activities performed inside these businesses.

In this study, 65 to 70% of workers reported using basic PPE, reflecting a culture of safety in these salons; this fact provides a foundation for improvements. It should be noted, however, that 10% of respondents reported using an in-table ventilation system, 10% reported using N95 face masks with odor control, and 5% reported using air purifying respirators; however, none of them were observed by researchers during the study or were reported by the salon managers in their questionnaire responses. This suggests that approximately 10% of respondents were either confused by the questionnaire or unfamiliar with the technologies described therein. When questioned about their knowledge of best practice guidelines for healthier nail salons, most salon managers indicated that they were unaware of educational materials published by US EPA (US EPA, 2007), OSHA (OSHA, 2012), NIOSH (NIOSH, 1999), and the California Healthy Nail Salon Collaborative (CHNSC, 2014). Therefore, in addition to improving the regulatory structure surrounding the nail salon industry, nail technicians and managers should be trained in established best practices and safety technologies.

Results from this study provide new evidence of environmental health disparities among minority populations. It is well-documented that individuals from some ethnic minority groups experience higher air pollution exposure compared to majority groups (Apelberg et al., 2005; Hun et al., 2009; D’Souza et al., 2009). Asian and Pacific Islander populations experience some of the largest cancer risks from air toxics of any racial or ethnic group in the U.S. (Morello-Frosch and Jesdale, 2006). This study also found that BTEX exposure among nail salon workers closely resembles that of workers in oil refineries (Singh et al., 2013) and auto garages (Badjagbo et al., 2010). Similar BTEX exposure in beauty salons was also reported in Baghani et al. (2018). These findings conflict with the public perception that cosmetology is safer than other industrial occupations.

2.5. Conclusions

This study contributes to growing evidence suggesting nail salons are hazardous working environments, where chronic exposure to VOCs can lead to negative health effects and increases in lifetime cancer risk. This exposure may contribute to minority health disparities, affect employee performance (Collins et al., 2005), and lead to higher employee turnover rates (Huang et al., 2016). The current regulatory structure meant to protect workers and consumers does not address these issues and creates a need for interventions that reduce occupational VOC exposure in the nail salon industry. Results from this study are comparable to previous studies that investigated individual aspects of the larger nail salon issue. Further research, including longitudinal and cross-sectional studies of nail salon worker health, is needed to better understand and evaluate the health risks associated with employment in this industry.

CHAPTER 3

VOC EMISSIONS FROM NAIL SALON PRODUCTS AND EFFECTIVE REMOVAL USING AFFORDABLE ADSORBENTS AND SYNTHETIC JETS[2]

Contributing Authors: Aaron Lamplugh, Megan Harries, Adam Nguyen, and Lupita D. Montoya

Abstract: Volatile organic compounds (VOCs) like acetone, ethyl and n-butyl acetate, toluene, and formaldehyde have been measured inside nail salons, where they are emitted from nail care products. Exposure to these compounds can have negative health impacts on both workers and costumers, and their release into the atmosphere can lead to ozone and secondary aerosol formation. This research characterized VOC emissions from 5 common nail products (3 nail polishes and 2 nail polish removers). It also investigated VOC removal by 3 low-cost adsorbent materials (coco coir, biochar, and activated carbon) in chamber studies. These removal experiments were conducted under both passive and active flow conditions using synthetic jet actuators. Mass-normalized adsorption rates were determined for these products using n^{th}-order rate equations. Adsorption rate models were then developed for all materials under both flow conditions and used to estimate the effect of low-cost adsorbents in an actual nail salon.

Nail polishes were found to contain 56.3-61.5% VOC by mass and emit VOCs at a rate of 2.3-2.4 mg mL^{-1} min^{-1}. The use of active flow with synthetic jets was shown to enhance adsorption processes for both biochar and activated carbon, but not for coco coir. Model results predicted

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activated carbon with active flow enhancement could achieve an effective ventilation rate of nearly 300 m^3 h^{-1} if 250 kg were placed in a 1400 m^3 salon.

Keywords: Adsorption, Coco Coir, Biochar, Passive Removal, Active Flow, Cosmetics

Highlights:

- Over half the mass of nail polish was composed of VOCs
- Activated carbon, coco coir, and biochar removed acetone from air
- Synthetic jet flow enhanced VOC removal for microporous adsorbents
- Models predicted that adsorbent materials can enhance VOC removal by HVAC

3.1. Introduction

Americans work an average of 34.5 hours per week (BLS, 2018) and spend close to 90% of their time indoors (Klepeis et al., 2001). Consequently, much of their exposure to airborne pollutants occurs indoors, including occupational environments. Volatile organic compounds (VOCs) are air pollutants that are ubiquitous in the indoor environment, with hundreds of different chemical species present inside of typical non-industrial buildings (Ayoko and Wang, 2018). VOCs have also been found in workplaces, where industrial operations and solvent use can release them into the air (Badjagbo et al., 2010; Lee et al., 2006; Pandya et al., 2006). Previous studies in nail salons identified VOCs like acetone, toluene, ethyl acetate, methyl methacrylate, and formaldehyde (Lamplugh et al., 2019; Alaves et al., 2013; Quach et al., 2011), which are emitted from nail care products (Kelly et al., 1999; Kwon et al., 2007; Huzar et al., 2011; Zhong et al., 2019; Heaton et al., 2019). Exposure to these compounds can cause skin, eye, and respiratory irritation, and in some cases may lead to headaches, neurological issues (US EPA, 2007), reproductive complications (John et al., 1994), and cancer (Swenberg et al., 1980; Swenberg et al., 2013). Mitigating occupational exposures to indoor air pollution has traditionally been accomplished by increasing the ventilation rate of a building, either naturally or mechanically by ventilation systems. However, there are limits to the amount of ventilation and thermal comfort achievable year-round using natural means. Alternatively, mechanical ventilation systems function well under most conditions, but they can be expensive to install and maintain and may consume a considerable amount of power. Buildings, for example, accounted for 41% of primary U.S. energy consumption in 2010, with 50% of the energy in buildings going toward heating, ventilation, and air-conditioning (HVAC) operations (DOE, 2011).

Ventilation problems in nail salons have been documented, including non-functioning (Roelofs & Do, 2012; Park et al., 2014) and undersized (Goldin et al., 2014; Roelofs & Do 2012) ventilation systems. Some states and municipalities have adopted ventilation standards that apply to nail salons, including the International Mechanical Code (ICC, 2015); however, many of these rules only apply to new salons and can include vague language that provides limited guidance (ELI, 2017). Pavilonis et al. (2018) investigated VOC levels at salons in the State of New York, which has specific ventilation requirements for new and existing nail salons, and found that CO_2 levels correlated strongly with VOC concentrations. Furthermore, when CO_2 levels exceeded target concentrations set by the American National Standards Institute/American Society of Heating, Refrigerating and Air-Conditioning Engineers (ANSI/ASHRAE), a nearly tenfold increase in VOC levels was observed.

Many VOCs commonly found in the indoor environment could be removed from the air through adsorption. The adsorption process involves gas-phase molecules (adsorbates) bonding to the solid surface of a material (adsorbent) through physical or chemical processes (Zhang et al., 2017a). In contrast to chemical adsorption, physical adsorption processes are reversible, and adsorbents can be regenerated thermally (Shah et al., 2014). In the indoor environment, adsorbent materials have been shown to act as VOC sinks, reducing concentrations of indoor pollutants when ventilation rates are insufficient (Meininghaus et al., 2000). In some cases, natural and engineered sorbent materials have even been used to create passive, diffusion-based VOC removal systems for the built environment, which can improve indoor air quality (Zuraimi et al., 2018; Huang et al., 2018; Darling and Corsi, 2016).

Alternative, sustainable adsorbents like biochar (Hwang et al., 2018; Moreira et al., 2017; Zhang et al., 2017b) and char-based activated carbon from agricultural feedstocks (Li et al., 2016) have received some attention in recent years as potential VOC adsorbents. Raw, natural adsorbent materials like coconut husk (coco coir) (Franguelli et al., 2019; Malik et al., 2017; Gautam et al., 2016; Etim et al., 2012) and rice husk (Alexander et al., 2017) have also been investigated, primarily for water-quality applications. Despite the popularity of these adsorbent materials, and claims that they may be more environmentally friendly than traditional adsorbents (Moreira et al., 2017), relatively little is known about their adsorption potential, especially with regards to VOC removal.

Among factors that influence adsorption processes are near-surface fluid conditions (Hoang et al., 2009), which can be controlled and optimized. Synthetic jet actuators (SJAs) are low-cost, energy efficient devices used to generate jet flows and have been shown to affect the direction of air flows in a room (McQuillan et at., 2014) and to enhance the removal of pollutants from indoor air (Montoya et al., 2017; Montoya et al., 2010). One recent study (Li et al., 2019) also found that vortex rings from synthetic jets can penetrate through porous surfaces, and even form downstream transmitted vortex rings.

This study quantified seven compounds present in 5 nail care products (3 nail polishes and 2 nail polish removers) using headspace analysis. The total VOC content from these nail products were evaluated through gravimetric analysis, while emission rates were determined in a closed environmental chamber. VOC removal using coco coir, biochar, and activated carbon as adsorbent materials was also investigated in this closed chamber. VOC removal was studied under both passive and active flow conditions using SJAs. VOC removal rate models were then developed for these 3 materials under both flow conditions. The resulting models were applied to time-resolved VOC concentration data from a previous field study to estimate the impact these materials could have on air quality inside an actual nail salon.

3.2. Materials

3.2.1. Nail Care Products

Five nail care products (3 nail polishes and 2 nail polish removers) were used in this study and are listed in Table 3.1, along with product information provided in the manufacturer safety data sheet (SDS). All products were obtained from retail stores or nail salons in the Denver-Boulder, CO area. SDSs for each product were obtained from the manufacturers and information from each is included in Table 3.1. Volatile content listed is the sum of all volatile ingredients listed for each product in the SDS. Since each individual value is provided as a range, the sum total is also presented as a range with a maximum that could exceed 100%, based on the information supplied by the manufacturer.

Table 3.1. List of nail care products used in this study.

Identifier	Product Name	Manufacturer	Product Class	Volatile Ingredients (SDS)	Volatile Content (SDS)
NP-1	Exceptionally Gifted	China Glaze	Nail Polish	n-butyl acetate, ethyl acetate, isopropyl alcohol, propyl acetate, camphor	50.2 – 110%
NP-2	Pompeii Purple	OPI	Nail Polish	n-butyl acetate, ethyl acetate, isopropyl alcohol, propyl acetate, n-butyl alcohol, ethanol, heptane, camphor	55 – 133%
NP-3	Fluffy White Puppy	Diamond Cosmetics	Nail Polish	n-butyl acetate, ethyl acetate, isopropyl alcohol, n-butyl alcohol	50 – 62%
PR-1	Non-Acetone	Up&Up	Nail Polish Remover	methyl acetate, SD Alcohol 40, methyl alcohol	15 – 40%
PR-2	100% Acetone	Up&Up	Nail Polish Remover	Acetone	Not Provided

All products were obtained new, in sealed containers, and were stored in a temperature-controlled environment throughout the duration of the study. Nail products from the same bottle were used in multiple experiments, and in some cases more than one bottle of a single product was used. No efforts were made to control for potential variability among bottles of the same product or along the lifetime of each bottle used (i.e., from opening to depletion).

3.2.2. Adsorbent Materials

A total of 3 different absorbent materials were tested in this study: coco coir (CC), biochar (BC), and activated carbon (AC). Each material was tested in two sizes: fine (<355 μm) and coarse (355-841 μm) grains. CC was purchased from Sunleaves Garden Products

(Mooresville, IN), BC was obtained from Biochar Solutions (Carbondale, CO), and MICROBE-LIFT® AC pellets were purchased from Ecological Laboratories, Inc. (Malverne, NY).

3.2.3. Environmental Test Chamber

All non-gravimetric experiments in this study were performed inside of a sealed environmental chamber made of high-finish 304 stainless-steel with dimensions 75 cm (W) x 75 cm (H) x 121 cm (L) (0.68 m^3 total volume). A leak test was performed on the chamber using carbon dioxide (CO_2) as the tracer gas. CO_2 concentrations in the chamber were measured with an Extech SD800 CO_2 datalogger (Extech, Nashua, NH, Range: 0-4000 ppm, Accuracy: ±5%, Resolution: 1 ppm). CO_2 concentrations outside of the chamber were measured with a Telaire T7001 CO_2 monitor (Onset Computer Corporation, Bourne, MA, Range: 0-2500 ppm, Accuracy: ± 50 ppm) connected to an Onset Hobo U12-013 Temp/RH/2 external channel logger (Onset, Bourne, MA, Temp Range: -20°C – 70°C, Temp Accuracy: ±0.35°C, RH Range: 5% – 95%, RH Accuracy: ±2.5%).

Ultra-pure 99.999% CO_2 (Airgas, Cinnaminson, NJ) was introduced into the chamber until the concentration was approximately 3900 ppm. The instrument was then allowed to equilibrate for 8 hours. CO_2 concentrations were then recorded for 66.5 additional hours in 5 second intervals. The average external CO_2 concentration was 448 ppm (±25 ppm). The average leakage (exchange) rate for the chamber was determined to be 1.7×10^{-5} m^3 h^{-1}, or 2.5×10^{-5} air changes per hour. Temperature and relative humidity (RH) in the chamber were fairly constant for all experiments performed; temperature ranged from 20.4 °C to 22.6 °C with a mean of 21.1 ± 0.002 °C, and RH ranged from 21.0% to 39.1% with a mean of 27.9 ± 0.02 %. Appendix II Supplementary Fig. S1 shows a boxplot of all temperature and relative humidity data recorded during all of the experiments included here (n=55,452).

3.3. Methods

3.3.1. Material Preparation and Characterization

The adsorbent materials were first ground using a Nasco-Asplin soil grinder (Patent #2,903,198, NASCO, Fort Atkinson, WI) and then sized using U.S.A standard test sieves #20 and #45. Surface area (SA), pore size, and volume, were determined for all materials using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analyses. Prior to analysis, samples were degassed overnight at 100°C and < 50 mTorr. Analyses were performed on a Micromeritics Gemini V 2380 surface area analyzer (Micromeritics Instrument Corp., Norcross, GA). Each sample underwent a 5-point BET analysis, as well as a 40-point BJH desorption analysis. The BET surface area (BET SA), Langmuir SA, BET pore width, BJH pore width, and pore volume of each material were measured.

3.3.2. Experimental Setup

Fig. 3.1 shows the 3 sets of experiments performed in the chamber. First, a series of experiments were used to determine the baseline VOC emissions from 5 different nail salon products (Fig. 3.1A). Next, the experiment was repeated in the presence of adsorbent materials contained in a cylindrical sample holder (Fig. 3.1B) to determine the passive VOC removal by each adsorbent material. Finally, the VOC removal experiment was repeated with active flow provided by a SJA, which was directed at the adsorbent material (Fig. 3.1C).

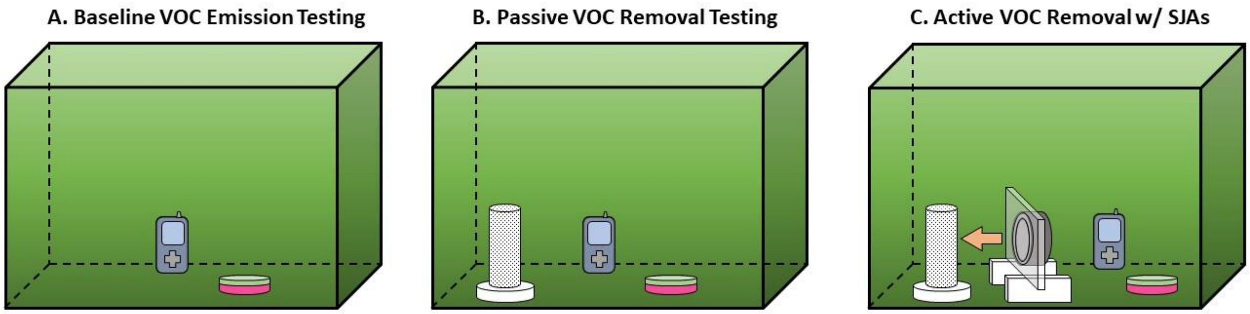

Fig. 3.1. Experiments performed to evaluate adsorbent materials in a controlled environment.

In all 3 experiments, the concentrations of Total Volatile Organic Compounds (TVOCs) were measured using a HalTech HVX-501 Photoionization Detector (PID) (Hal Technology, Fontana, CA, Range 0-200 ppm, Resolution 0.03 ppm) with a 3-min sampling frequency. The PID was calibrated for acetone at two points (0 ppm and 175 ppm) using a zero-air standard (Scott Specialty Gases, Plumsteadville, PA, O_2: 20-21%, Total Hydrocarbon: < 1 ppm) and an acetone gas standard (GASCO, Oldsmar, FL, Acetone: 175 ppm), respectively. The line between these points was used to determine the PID correction factor for acetone (1.56). Temperature and relative humidity (RH) in the chamber were measured with an Onset Hobo U12-013 Temp/RH/2 External Channel Logger (Onset, Bourne, MA, Temp Range: -20°C – 70°C, Temp Accuracy: ±0.35°C, RH Range: 5% – 95%, RH Accuracy: ±2.5%).

3.3.3. Headspace Analysis

Headspace analyses were conducted on the 5 nail products, using gas chromatography coupled with mass spectrometry (GC-MS), to determine the composition of gas-phase emissions from each product. Seven compounds in total were measured for each nail product: ethyl acetate, n-butyl acetate, propyl acetate (n-propyl and isopropyl isomers quantified together), ethanol, isopropanol (2-propyl alcohol), acetone, and methyl acetate.

Samples were prepared by placing approximately 0.5 mL of each product in a 4 mL septum-capped vial, which was allowed to equilibrate at room temperature for at least 1 h. The initial mass of nail product used in each sample were measured using an Ohaus Analytical Plus AP250D balance (Ohaus, Florham Park, NJ). Using a 10 uL gas-tight syringe primed 3 times with headspace vapor, a sample consisting of 5 uL headspace and a 1 uL plug of air was manually introduced to the GC-MS. The syringe was cleaned between injections and tested with regular blanks. Reported results are the average of 3 injections per sample (n=3). The reproducibility of manual injections was tested with replicate injections of pure acetone. Two standard solutions were prepared in cyclohexanone to quantify all 7 compounds. One stock solution contained the 5 compounds specific to the nail polishes, while the other contained acetone and methyl acetate, the 2 volatile components in the nail polish removers. Separate standards were prepared due to the co-elution of acetone and isopropanol. Serial dilutions of the standards were used to create a calibration curve for each compound across the range of concentrations expected in the samples. Triplicate injections were averaged to generate each curve.

3.3.4. Baseline VOC Emissions from Nail Products

The density and total VOC content of each of the 5 nail products listed in Table 3.1 were determined using a simple gravimetric analysis. Briefly, 3 samples of each nail product (1 mL of NP-1, NP-2, NP-3, or PR-1 and 0.1 mL of PR-2) were placed into pre-weighed Petri dishes (for nail polishes) or auto-sampling vials (for polish removers). Their mass was then measured using a TR-64 balance (Denver Instrument, Bohemia, NY, Max: 61 g, Precision: 0.1 mg). Samples were placed in a fume hood, uncovered, and allowed to evaporate. Nail polish samples were allowed to evaporate for a full 24 h, while polish removers evaporated over 10 h. The mass of the remaining materials was then measured again. The VOC contents for products (mg g^{-1}) were reported as the average mass difference between pre and post-emission measurements (n=3), divided by the average mass of product used. Additional gravimetric analyses were performed for PR-2 at volumes of 0.2 and 0.3 mL. Theoretical equilibrium concentrations ($C_{eq,theo}$) of PR-2, were calculated using the VOC content from the gravimetric analysis (mg) and dividing it by the volume of the chamber (m^3). These values were then compared with the equilibrium concentrations measured with the PID ($C_{eq,PID}$) to determine experimental deviation from predicted values.

Baseline emission testing was performed inside the closed chamber as shown in Fig. 3.1A. In each experiment, a standard volume of each product (1 mL of NP-1, NP-2, NP-3, PR-1 and 0.1 mL of PR-2), referred to as low concentration (LC) volumes, were used. The products were measured using a 1 mL syringe (for nail polishes) or 2 mL glass pipette (for nail polish removers) and then placed on a Petri dish inside of the environmental chamber, which was promptly sealed. The nail product was then allowed to evaporate for 22.5 h. Before the chamber was sealed for each experiment, the internal pressure was equilibrated with the external pressure of the laboratory Each baseline VOC emission test was performed a minimum of 3 times (n=3).

Average TVOC concentration curves (in ppm) for each product were generated along with standard error values. Concentration data was averaged in 9-min intervals, and emission rates (ppm min^{-1}) were plotted and compared. Average emission rates ($\dot{S}_{avg}$) for each nail product were estimated using the gravimetric equilibrium concentration ($C_{eq,theo}$) and the time required to reach equilibrium in the baseline emission experiments:

$$\dot{S}_{avg}[mg\ min^{-1}] = \frac{C_{eq,theo}}{t_{eq}} \qquad [3.1]$$

where t_{eq} is the length of time required to reach equilibrium (min). This rate assumed constant emissions of VOCs between t=0 and t=t_{eq}.

3.3.5. Passive VOC Removal with Raw Adsorbent Materials

Since acetone is the primary VOC found in most nail salons (Alaves et al., 2013; Lamplugh et al., 2019), acetone-based nail polish remover (PR-2) was used in all VOC removal testing. In these experiments, 20 g of CC, BC, or AC were used as the adsorbent. The individual materials were loaded into a custom-made, 3D printed sample holder (Fig. 3.1B), made of polylactic acid (PLA) with dimensions: height 12.5 cm, diameter 3 cm, wall thickness 0.25 cm. The sample holder was covered on the outside with two layers of 100% nylon mesh material. The mesh prevented the adsorbent material from escaping during the experiment but was permeable to gases in the chamber. The loaded sample holder was placed near the center of the chamber, the nail polish remover was added, and then the chamber was sealed.

Each VOC removal experiment was performed 3 times (n=3) with the LC volume (0.1 mL) of acetone-based remover. This experiment was also performed once (n=1) with both medium concentration (MC, 0.2 mL) and high concentration (HC, 0.3 mL) volumes.

3.3.6. Active VOC Removal Using Synthetic Jet Actuators

In the active flow experiments (Fig. 3.1C), VOC removal was achieved using raw adsorbent materials and enhanced using active flow provided by a ZFlow 87 Synthetic Jet Actuator (SJA) (Aavid Thermalloy, Laconia, NH, 5VDC, 95mA, 475mW). A similar model of SJA from the same manufacturer was previously characterized (Abarr et al., 2017) and used in a proof of concept experiment (Montoya et al., 2017). In the active flow experiments, the SJA was directed at the sample holder from a distance of 30 cm and operated throughout the duration of the experiment. Active VOC removal experiments were performed once at LC, MC, and HC using fine grain CC, BC, and AC.

3.3.7. Data Analysis

Concentrations of PR-2 from baseline and (passive and active flow) removal experiments were first converted from ppm to mass-based concentrations, using the equation:

$$C_{mass}[mg\ m^{-3}] = C_{ppm} \times CF \times MW/(RT/P) \qquad [3.2]$$

where P is the surface pressure in Boulder, CO (0.803 atm), R is the universal gas constant (0.08206 L atm mol^{-1} K^{-1}), T is the mean chamber temperature (K) during the experiment, MW is the molecular weight of acetone, and CF is the acetone correction factor for the PID (1.56).

To reduce noise in the VOC removal time series, concentration data were binned in intervals of approximately 15 min and presented as the geometric mean of that range. The normalized mass of acetone removed at each point in time, q(t) (mg g^{-1}), was calculated as:

$$q(t) = \frac{V_{chamber}}{m_{sorb}}[C_o(t) - C(t)] \qquad [3.3]$$

where $V_{chamber}$ is the volume of the environmental chamber (0.68 m^3), $C_o(t)$ is the baseline concentration at t (mg m^{-3}), C(t) is the concentration at t during the removal test (mg m^{-3}), and m_{sorb} is the mass of adsorbent material in the chamber (g).

The adsorption rate of each material was then calculated over 22.5 hours using the equation:

$$k_{ads,exp}(t) = \frac{q(t+0.5\Delta t)-q(t-0.5\Delta t)}{\Delta t} \qquad [3.4]$$

where $k_{ads,exp}$ is the experimental VOC adsorption rate at time (t), which is the midpoint between two data points, and Δt is the time between the two data points (approximately 15 min).

Adsorption rate data for all 3 materials at the 3 VOC concentration levels, and 2 flow conditions, were fitted using R non-linear least squares regression analysis. Results were used to develop VOC adsorption rate models for each material of the form:

$$k_{ads} \sim f\{C(t), q(t)\} \qquad [3.5]$$

3.3.8. Model of VOC Removal for Nail Salons

A simple box (mass balance) model was developed to predict the impact of using adsorbent materials to reduce VOC concentrations inside a nail salon. This model was then applied under both active and passive flow conditions. Time-resolved TVOC data from a previous nail salon field study (Lamplugh et al., 2019) were used as model inputs, and new VOC concentrations (C_{new}) were calculated using the adsorption rate models determined for each material, from Eq. 3.5.

For purposes of this exercise, the field TVOC concentrations (measured with a PID) were assumed to be acetone. The correction factor for acetone (1.56) was applied to convert ppm to mass concentrations. Eq. 3.6 shows the mass balance performed at each time-step:

$$C_{new,i} = C_{field,i} + \frac{[\dot{m}_{i-1}\times(t_i - t_{i-1}) + k_{ads,i-1}\times m_{sorb}\times(t_i - t_{i-1})]}{V_{salon}} \quad [3.6]$$

where i is the time-step, t is time (min), V_{salon} is the volume of the salon (m^3), $C_{field,i}$ is the VOC concentration (mg m^{-3}) measured during the field study at i, m_{sorb} is the mass of the adsorbent used (g), and ṁ is the derivative of VOC mass with respect to time (mg min^{-1}) calculated from field study concentration data:

$$\dot{m}_i = \frac{V_{salon}[C_{field,i+1} - C_{field,i-1}]}{t_{i+1} - t_{i-1}} \quad [3.7]$$

This term accounted for changes in the mass of acetone in the salon air due to all processes (e.g., ventilation, chemical reactions, and emission) except adsorption onto the test materials. This step was necessary since the impact of each of these other processes could not be determined independently.

The total predicted mass of VOCs adsorbed over the 8 h period was reported along with an average effective ventilation rate (Q_{eff}), which was calculated as:

$$Q_{eff}\left(\frac{m^3}{hr}\right) = \frac{q_{total}\times m_{sorb}}{8\ h \times C_{med}} \quad [3.8]$$

where q_{total} is the predicted total mass of VOCs adsorbed per gram of adsorbent (mg g^{-1}), over the 8 h removal period and C_{med} is the median concentration (mg m^{-3}) of VOCs during the same time period.

Q_{eff} was used to estimate the contribution of the adsorbents toward indoor air-cleaning operations and allowed comparisons with traditional ventilation rates. A similar metric was previously employed by Ataka et al. (2004), Seo et al. (2009), and Huang et al. (2019). The effective ventilation rate estimated in this study does not account for other non-VOC air pollutants that may be present indoors, including particulate matter and CO_2, and approximates a constant ventilation rate across all 8 h from a clean source of air (i.e., with no acetone). A volume-normalized metric was also considered, which is referred to here as the effective air exchange rate (ACH_{eff}), and was calculated as:

$$ACH_{eff} = \frac{Q_{eff}}{V_{salon}} \tag{3.9}$$

where V_{salon} is the volume of the nail salon (m^3) and ACH_{eff} is in hr^{-1}.

3.4. Results

3.4.1. Materials Characterization

Results from the materials characterization, using BET and BJH analyses, are shown in Table 3.2. The analyses determined that AC had the greatest surface area and pore volume of all three materials characterized, followed by BC and CC. The particle size of the material (i.e. fine or coarse) had relatively little impact on the SA, except in the case of CC, where fine particles had a 43-79% greater SA than the coarse material. The pore volume of BC and CC were affected by particle size: fine BC had 356% more pore volume than coarse BC and fine CC had 52% more pore volume than coarse CC. The average pore width (BET) and average pore diameter (BJH) of both fine and coarse AC were substantially smaller (2-3 nm) than those of all BC or CC types. This pore size range fell at the intersection of what the International Union of Pure and Applied Chemistry (IUPAC) defines as microporous (< 2 nm) and mesoporous (2 - 50 nm) (Rouquerol et al., 1994). Both BC and CC fell well within the range of mesoporous materials. Distributions of pore surface area and pore volume showed that a significant portion of BC and CC pore volume is located in macroporous structures (> 50 nm).

Table 3.2. Results from BET and BJH analyses

Sorbent	**Size**[a]	**BET SA (m^2 g^{-1})**	**Langmuir SA (m^2 g^{-1})**	**BET Pore Width (Å)**	**BJH Pore Diameter (Å)**	**BJH Pore Volume**[b] **(cm^3 g^{-1})**
AC	Fine	916.7	1231	---	30.50	0.2059
	Coarse	957.4	1297	20.70	28.74	0.2158
BC	Fine	5.893	8.001	37.71	131.0	0.0041
	Coarse	5.030	6.791	27.78	114.6	0.0009
CC	Fine	5.759	7.963	83.66	171.2	0.0173
	Coarse	4.035	4.458	99.63	166.7	0.0114

[a] Fine (< 355 μm); Coarse (355 - 841 μm)

[b] Desorption cumulative volume of pores between 17 and 3,000 Å

3.4.2. Headspace Analysis

Results from the headspace analyses are shown in Table 3.3. NP-2 and NP-3 emitted ethyl acetate, propyl acetate, n-butyl acetate, isopropanol and ethanol at measurable levels. NP-1 emitted only the first 4 of these compounds. For all polishes, ethyl acetate was the primary VOC emitted with a mole fraction ranging from 52.8% to 71.5%. Ethanol was the second most emitted VOC for both NP-2 and NP-3. Each nail polish remover contained a single volatile compound: PR-1 only emitted methyl acetate, while PR-2 only emitted acetone. Chromatograms for each product are shown in Appendix II Supplementary Fig. S2.

Table 3.3. Results from headspace analyses

Compound		NP-1	NP-2	NP-3	PR-1	PR-2
Ethyl Acetate	Concentration[b]	305	344	274	---	---
	Molar Fraction[c]	71.5	56.0	52.8	---	---
Propyl Acetate[a]	Concentration	34.0	65.9	44.4	---	---
	Molar Fraction	6.87	9.25	7.39	---	---
n-Butyl Acetate	Concentration	29.1	29.7	54.4	---	---
	Molar Fraction	5.18	3.67	7.96	---	---
Isopropanol	Concentration	47.8	39.4	28.3	---	---
	Molar Fraction	16.5	9.39	8.01	---	---
Ethanol	Concentration	0.00	69.9	64.6	---	---
	Molar Fraction	0.00	21.7	23.9	---	---
Acetone	Concentration	---	---	---	0.00	335
	Molar Fraction	---	---	---	0.00	100
Methyl Acetate	Concentration	---	---	---	204	0.00
	Molar Fraction	---	---	---	100	0.00

[a] n-propyl and isopropyl acetate quantified together

[b] Reported as (g m^{-3})

[c] Reported as percent of total moles of VOC in headspace sample

3.4.3. Baseline VOC Emissions from Nail Products

Table 3.4 shows the densities and VOC content, determined from the gravimetric analyses, for the nail products studied. Results are reported as the mean of 3 samples ± the standard error on the mean (SE). VOC content ranged from 56.3-61.5% for nail polishes and was 26.5% and 100% for PR-1 and PR-2, respectively. All values determined here were within ranges specified in the SDS for each product. NP-1 had the highest VOC content of all 3 nail polishes measured, followed by NP-3 and NP-2; however, the VOCs content did not vary markedly overall. Conversely, the VOC content difference between PR-1 and PR-2 was substantial, with PR-1 having 73.5% less VOC content by mass than PR-2.

Table 3.4. Estimated density and VOC content based on gravimetric analyses.

ID	ρ (g mL^{-1})	VOC Content (mg g^{-1})
NP-1	0.983 ± 0.002	615 ± 2
NP-2	1.016 ± 0.002	563 ± 2
NP-3	0.976 ± 0.006	593 ± 20
PR-1	0.990 ± 0.003	265 ± 2
PR-2	0.799 ± 0.013	1000 ± 41

The results of the gravimetric analysis were then compared to $C_{eq,PID}$ for acetone to determine if predicted values matched experimental PID measurements. Fig. 3.2 shows $C_{eq,theo}$ versus $C_{eq,PID}$ for PR-2 at LC, MC, and HC. The resulting 1:1 line has a slope of 1.0811 and an R^2 of 0.9915, indicating that measured concentrations of acetone closely matched theoretical predictions (within 9%), based on gravimetric results. This demonstrates that VOC loss from leakage, surface deposition, and emission prior to chamber sealing was minimal for even the most volatile compound tested.

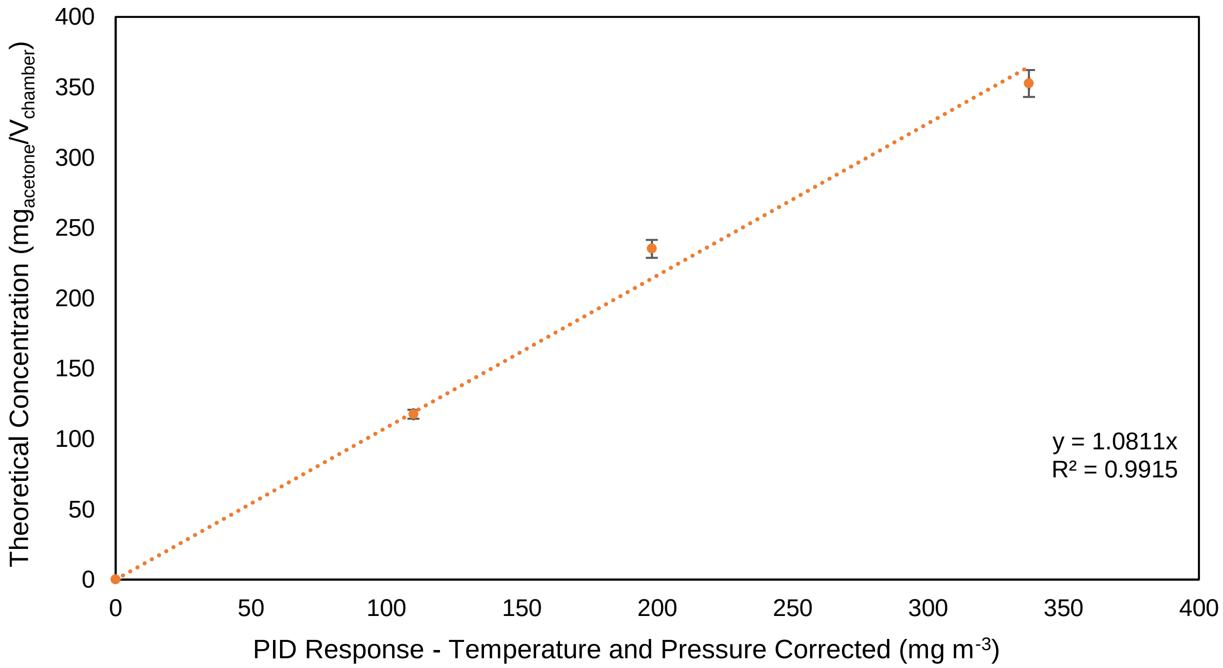

Fig. 3.2. Theoretical equilibrium acetone concentrations at LC, MC, and HC compared to measured concentrations from baseline emission tests.

Fig. 3.3 shows baseline TVOC emission profiles for all 5 nail products in this study. Results show that emissions from the 3 nail polishes were fairly similar but were considerably different from the nail polish removers. Nail polish removers were very different from each other; however, they both reached equilibrium in < 1 h. Nail polishes reached equilibrium in about 5 h. This difference likely reflects the fact that nail polish removers were composed of the more volatile compounds methyl acetate (boiling point 56.9°C) and acetone (boiling point 56.1°C). In contrast, the primary ingredient in all nail polishes was ethyl acetate (boiling point 77.1°C).

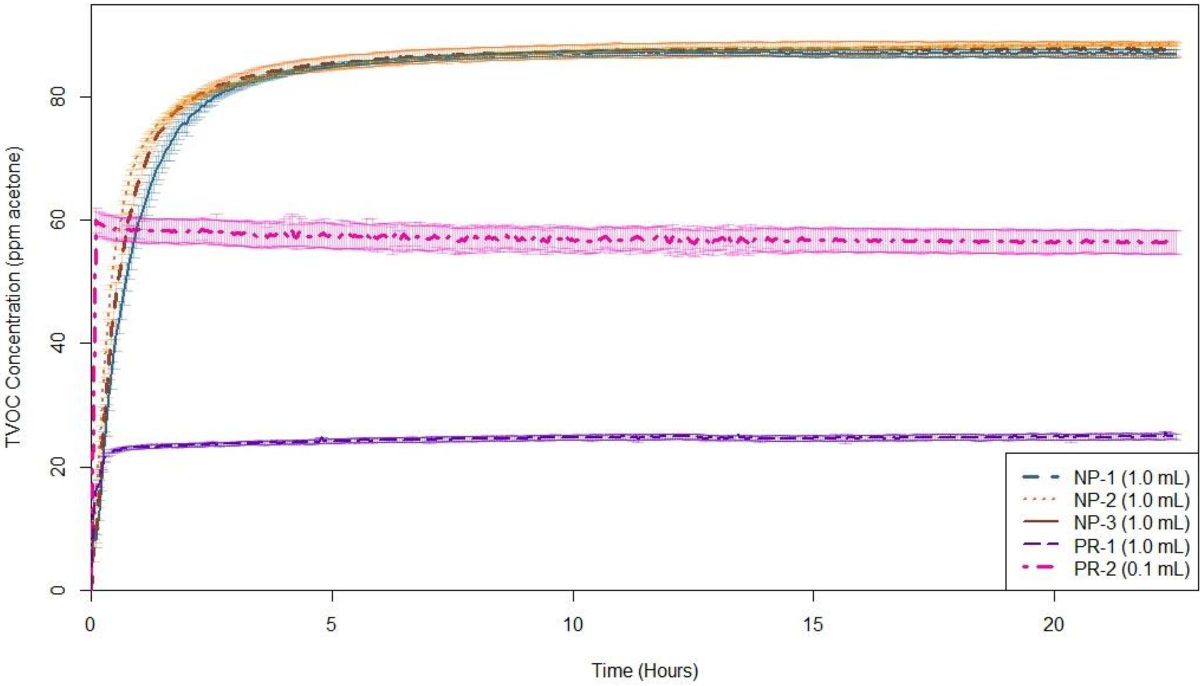

Fig. 3.3. Baseline TVOC emission profiles from 5 nail products over 22.5 h with standard error bars.

Emission rates (ppm min^{-1}), for nail polishes and nail polish removers, are shown in Fig. 3.4A and 3.4B, respectively. The nail polish emission rates decreased to zero within 250-300 min (Fig. 3.4A). Nail polish removers (PR-1 and PR-2) reached equilibrium more quickly (Fig. 3.4B), and stopped emitting VOCs after approximately 40 min. All 3 nail polishes showed very similar emission profiles, both in terms of the emission rate and the equilibrium concentration, supporting the results of the gravimetric analysis. Average estimated emission rates, $\dot{S}_{avg}$, for nail polishes (t_{eq}=250 min) were 2.4 mg mL^{-1} min^{-1}, 2.3 mg mL^{-1} min^{-1}, and 2.3 mg min^{-1} for NP-1, NP-2, and NP-3, respectively. The average estimated emission rate for PR-1 and PR-2 (t_{eq}=40 min) was 6.6 mg mL^{-1} min^{-1} and 20 mg mL^{-1} min^{-1}, respectively.

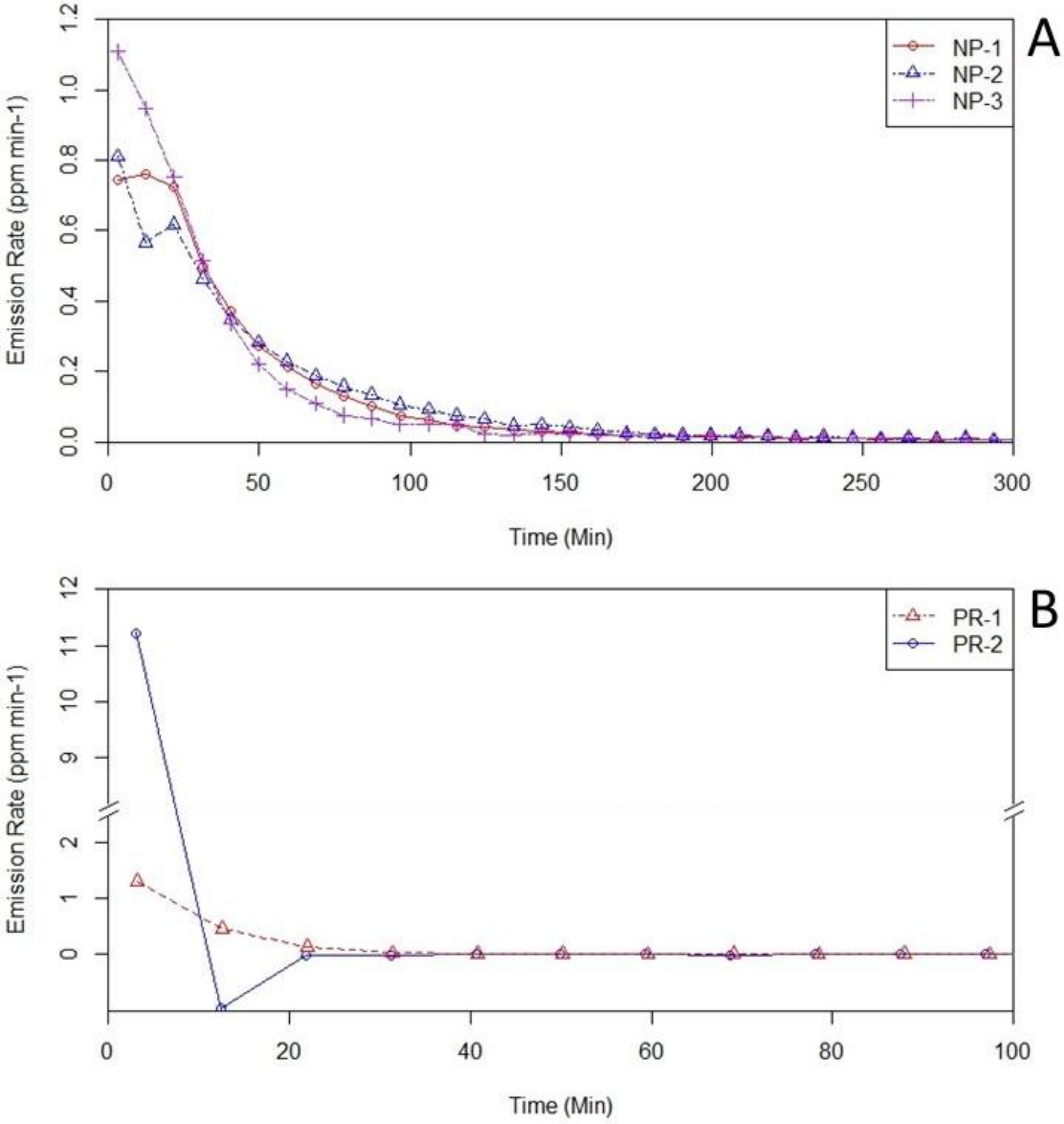

Fig. 3.4. (A) Nail polish emission rates over 300 min. (B) Nail polish remover emission rates over 100 min.

3.4.4. Passive VOC Removal with Raw Adsorbent Materials

Removal rates from passive adsorption experiments with fine and coarse CC, BC, and AC at LC from PR-2 are shown in Fig. 3.5A and 3.5B, respectively. Of all 3 fine grain materials, AC showed the highest adsorption rates of during most of the 22.5 h test period (0.0056 – 0.0009 mg g^{-1} min^{-1}), followed closely by BC (0.0052 - 0.0006 mg g^{-1} min^{-1}) and CC (0.0027 – 0.0005 mg g^{-1} min^{-1}). Coarse grain materials followed a very similar trend, with AC performing the best (0.0053 – 0.0007 mg g^{-1} min^{-1}), followed by BC (0.0044 – 0.0008 mg g^{-1} min^{-1}) and CC (0.0030 – 0.0005 mg g^{-1} min^{-1}). This suggests that the size distribution of adsorbent particles has little impact in passive adsorption rates. This result agrees with the BET and BJH analyses, which show that fine and coarse particles of each material had very similar properties overall.

Passive removal rates for all materials decreased by 50% or more during the initial 5 h. After 20 h, all materials showed removal rates near zero (< 0.001 mg g^{-1} min^{-1}), although none of the materials reached equilibrium. Coarse AC removal data showed significant variability between 10 and 14 h (Fig. 3.5B). A review of the data suggests that this was likely due to a temporary sensor malfunction during one of the 3 removal experiments used in calculating the average rate values.

Fig. 3.6A, 3.6B, and 3.6C show adsorption rates of fine CC, BC, and AC at different concentrations of VOCs (LC, MC, and HC, respectively) emitted from PR-2. The rate of adsorption was found to increase significantly with increased VOC concentration, and scaled approximately linearly with respect to the initial concentration of acetone. It was also observed that higher concentrations lead to greater total mass of VOCs adsorbed by each material, as previously reported in the literature (Cheung et al., 2000; Huang et al., 2006). The passive adsorption rates for all fine grain materials (CC, BC, AC) at MC and HC concentrations are included in Appendix II Supplementary Fig. S3.

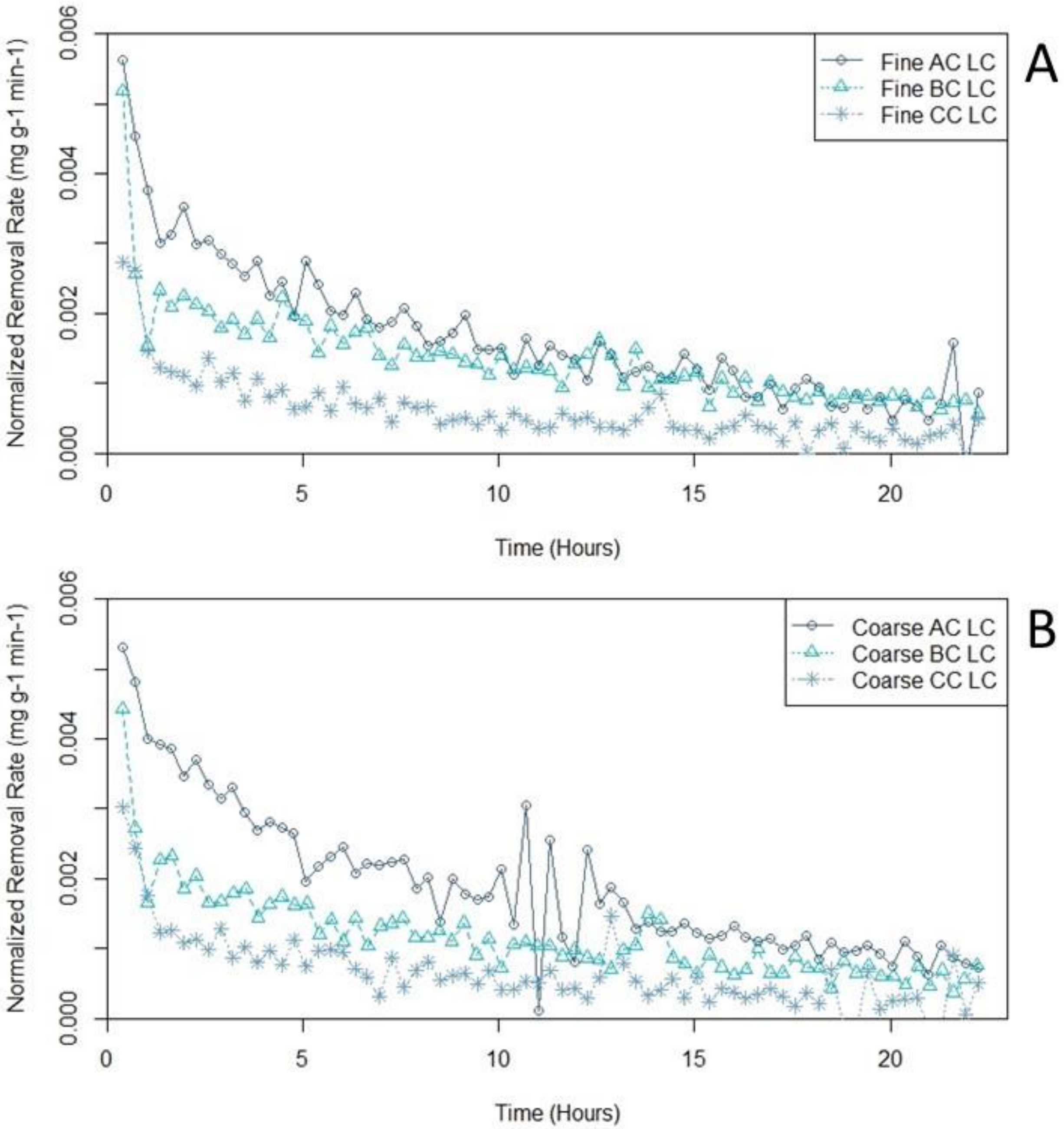

Fig. 3.5. Adsorption rates of (A) fine and (B) coarse CC, BC, and AC at LC across 22.5 h.

The best-fit model for adsorption rates measured in this study was a nth-order equation similar to the one proposed by Ritchie (1977):

$$k_{ads} = a * C(t)\left(1 - \frac{q(t)}{1.05 * q_{max}}\right)^{n} \qquad [3.9]$$

where C(t) is the concentration of VOCs at a given time, q(t) is the normalized mass of VOCs adsorbed (mg g^{-1}) at the same time, a is a rate constant for each material, n is an exponent related to the order of the reaction (number of gas molecules adsorbed per adsorption site), and q_{max} (mg g^{-1}) is a quasi-equilibrium value of the maximum mass adsorbed onto 1 g of the material observed at HC and t = 22.5 h. Since q_{max} is only a quasi-equilibrium value, a factor of 1.05 was applied to approximate the actual equilibrium value. Similar nth-order models have previously been proposed for bio-adsorbents (Liu and Shen, 2008), and can account for unknown adsorption mechanisms as well as materials with heterogenous surfaces. Appendix II Supplementary Table S1 includes rate constant values and correlations for each material under passive flow conditions. Fitted removal rate graphs for all cases considered are shown in Appendix II Supplementary Fig. S4.

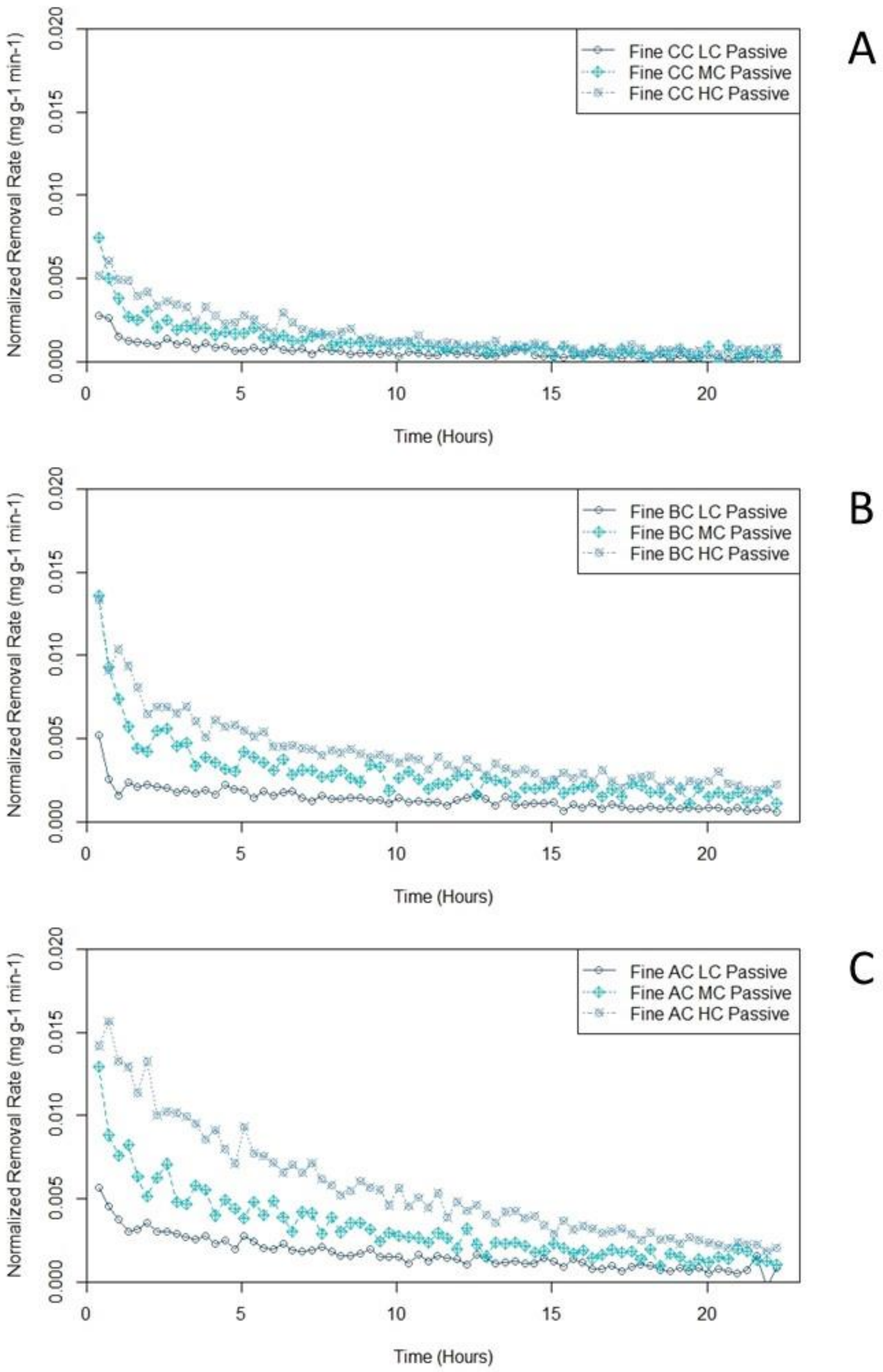

Fig. 3.6. Passive adsorption rates of fine (A) CC, (B) BC, and (C) AC at LC, MC, and HC across 22.5 h.

3.4.5. Active VOC Removal Using Synthetic Jet Actuators

Results from the VOC removal experiments using fine CC, BC, and AC at LC are shown in Fig. 3.7. Concentrations (C) from these removal experiments were normalized by their corresponding baseline VOC concentrations (C_0) and plotted as C/C_o. Fig. 3.7A shows the case for passive flow; Fig. 3.7B shows the case for active flow case, which was provided by a SJAs at a distance of 30 cm from the adsorbent material. Results show that AC was the most effective adsorbent; CC was the least effective. None of the adsorbents reached equilibrium within the 22.5 h testing period; an initial fast removal was also observed for CC and BC. The effect of the SJAs is noticeable when compared to the passive adsorption case especially for BC and AC adsorbents. Appendix II Supplementary Fig. S5 and Fig. S6 show the results at MC and HC for the passive and active flow cases, respectively. Higher initial concentrations led to increased total mass of acetone removed, q_{total}, by factors of 1.4, 2.3, and 2.5, for CC, BC and AC, respectively.

The normalized removal rates for the active-flow experiments are shown in Fig. 3.8. Adsorption rates for fine CC (Fig. 3.8A) decreased slightly under the active flow conditions tested and did not change with increasing concentrations of acetone. This may be due to the flow velocity preventing the buildup of acetone on the CC surface. This hypothesis agrees with changes in the order of the rate model (n) between passive and active flow experiments, which decreased from ~1.2 to 0.9 after the addition of active flow.

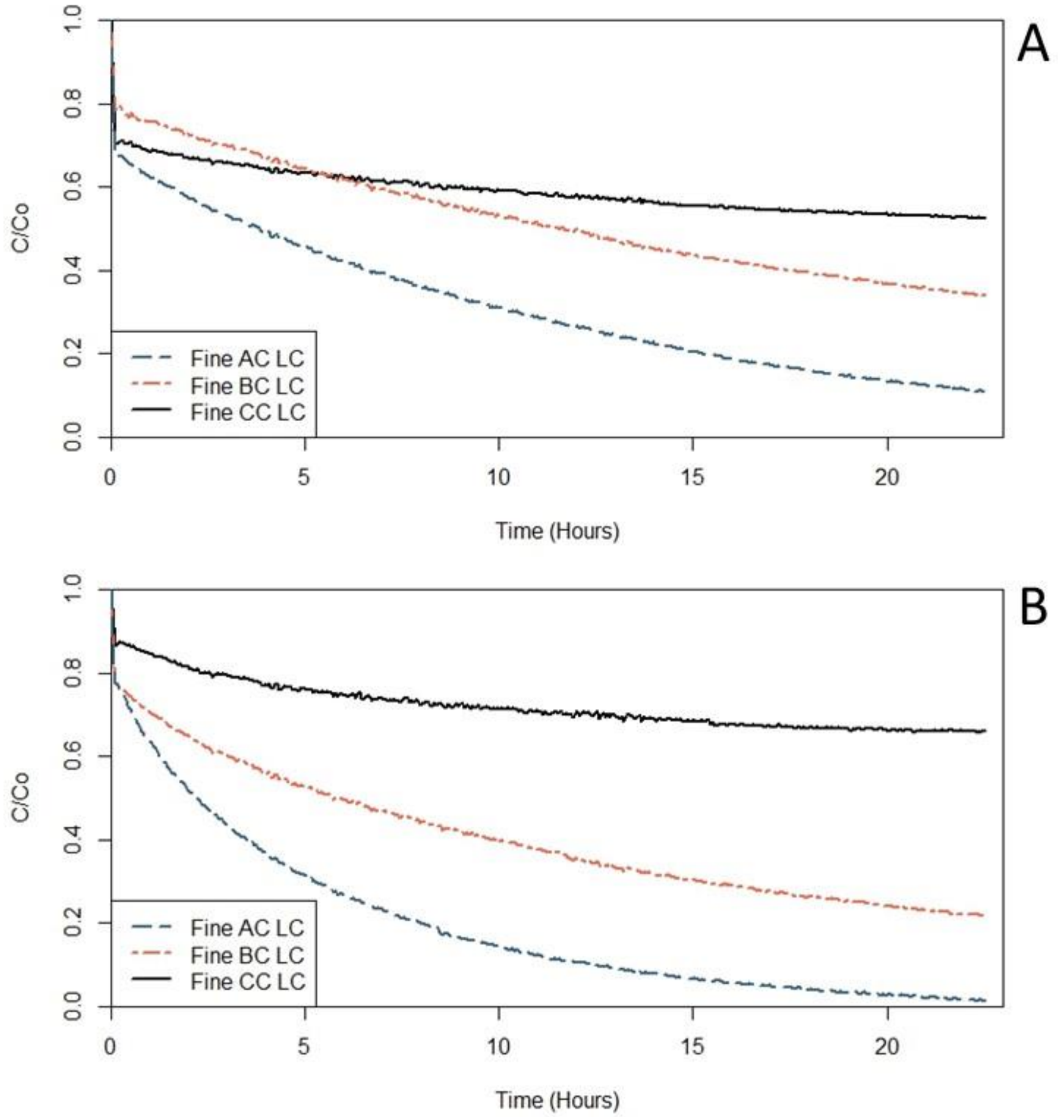

Fig. 3.7. Acetone removal using AC, BC, and CC at LC over 22.5 h under (A) passive flow, and (B) active flow provided by a SJA at 30 cm from the adsorbent material.

Conversely, normalized adsorption rates for fine BC (Fig. 3.8B) and AC (Fig. 3.8C) increased significantly, with fine AC under active flow conditions achieving adsorption rates 50-100% greater in the first 2 h compared with passive flow experiments. Under active flow conditions, the order of the adsorption rate models for BC and AC increased by factors of 1.85 and 3.02, respectively.

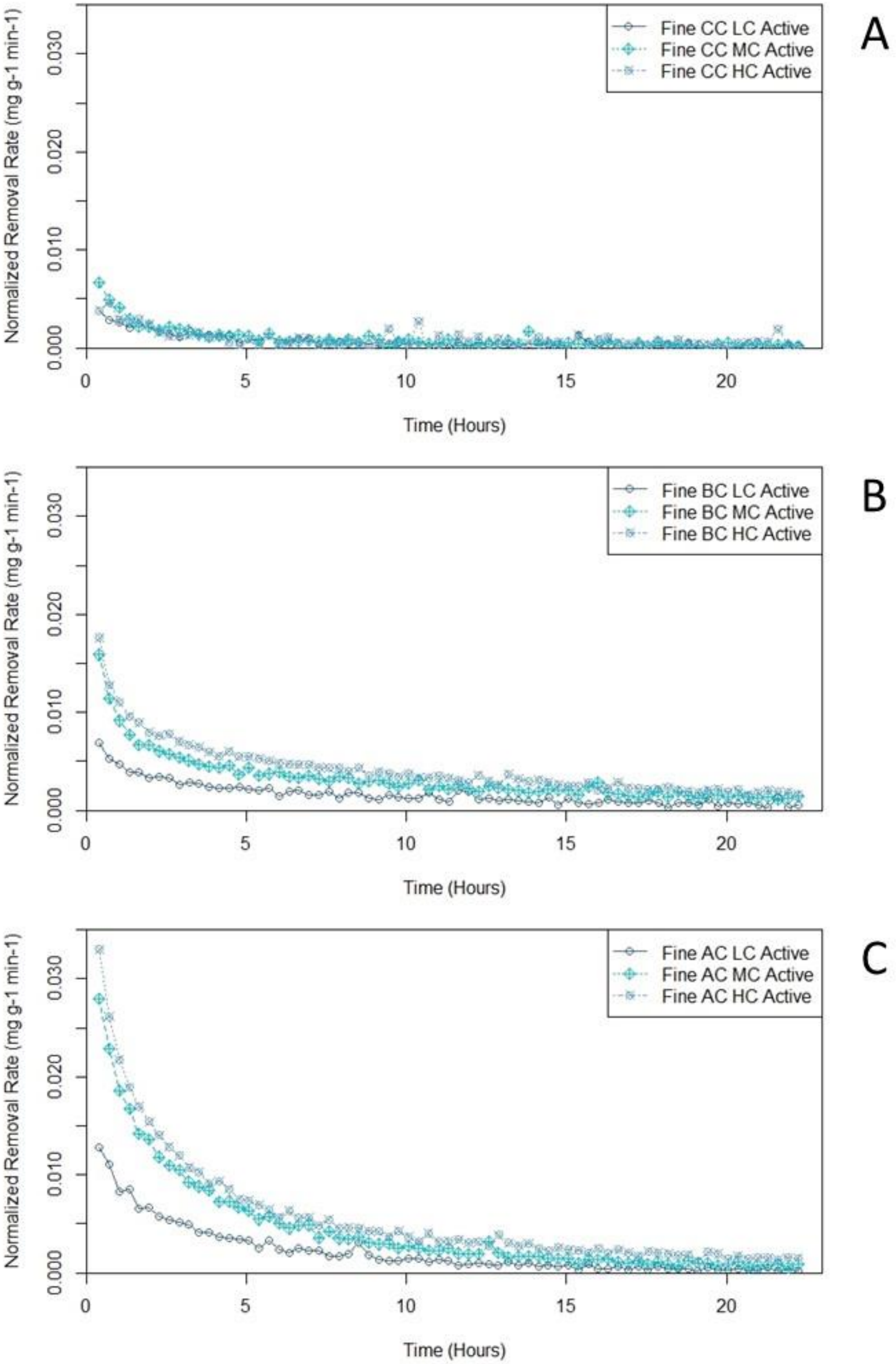

Fig. 3.8. Active adsorption rates of fine (A) CC, (B) BC, and (C) AC at LC, MC, and HC across 22.5 h.

3.4.6. VOC Removal Model for Nail Salon Application

Mathematical models for VOC removal were constructed for the fine version of the 3 materials (CC, BC, and AC). Calculations were performed using different amounts of adsorbent material (10 kg, 50 kg, and 250 kg), under both passive and active flow conditions. Time-resolved VOC concentration data measured in a real nail salon during a single day were used as the input (Lamplugh et al., 2019). The volume of the salon used in the model was 1400 m^3. The total predicted VOC mass removal and effective ventilation rates (Q_{eff} and ACH_{eff}) for each case are shown in Table 3.5. Effective ventilation rates for fine AC under passive removal conditions ranged from 29.3 m^3 h^{-1} (0.02 ACH) to 222 m^3 h^{-1} (0.16 ACH) for 10 kg and 250 kg of AC, respectively. This was followed by fine BC and fine CC, which ranged from 18.2 m^3 h^{-1} to 182 m^3 h^{-1} and 16.7 m^3 h^{-1} to 179 m^3 h^{-1}, respectively.

Table 3.5. VOC mass removed and effective ventilation rates from adsorption models

Passive Flow		**Total VOC Removed (g)**	**Q_{eff} (m3 h^{-1})**	**ACH_{eff} (h^{-1})**
Fine CC	10 kg	7.09	16.7	0.01
	50 kg	29.9	70.5	0.05
	250 kg	76.4	179	0.13
Fine BC	10 kg	7.75	18.2	0.01
	50 kg	31.8	74.9	0.05
	250 kg	77.4	182	0.13
Fine AC	10 kg	12.4	29.3	0.02
	50 kg	45.1	106	0.08
	250 kg	94.4	222	0.16
Active Flow		**Total VOC Removed (g)**	**Q_{eff} (m3 h^{-1})**	**ACH_{eff} (h^{-1})**
Fine CC	10 kg	2.46	5.79	0.00
	50 kg	11.6	27.2	0.02
	250 kg	43.2	101	0.07
Fine BC	10 kg	10.8	25.6	0.02
	50 kg	41.3	97.3	0.07
	250 kg	90.3	213	0.15
Fine AC	10 kg	24.1	56.8	0.04
	50 kg	68.1	160	0.11
	250 kg	124	292	0.21

The use of jets was shown to remove significantly more VOCs for both fine AC and fine BC, where total mass removal values across cases increased by 31-94% and 17-39%, respectively. In the case of fine CC, VOC removal quantities decreased with the addition of jet flow by 43-65%.

Fig. 3.9 shows the results of the various simulations performed. Fig. 3.9A, 3.9C, and 3.9E show the predicted impact of CC, BC, and AC in the salon environment under passive flow conditions, respectively. Figs. 3.9B, 3.9D, and 3.9F show the impact of CC, BC, and AC under active flow conditions, respectively. Significant reductions in VOC concentrations are shown for all adsorbents at the 250 kg level; less significant reductions were produced with 50 kg and 10 kg of adsorbent. The largest removal was achieved with 250 kg of fine AC and active flow (Fig. 3.9F), decreasing VOC concentrations to 0 mg m^{-3} in approximately 3 h and remaining there for the 8-h simulation period.

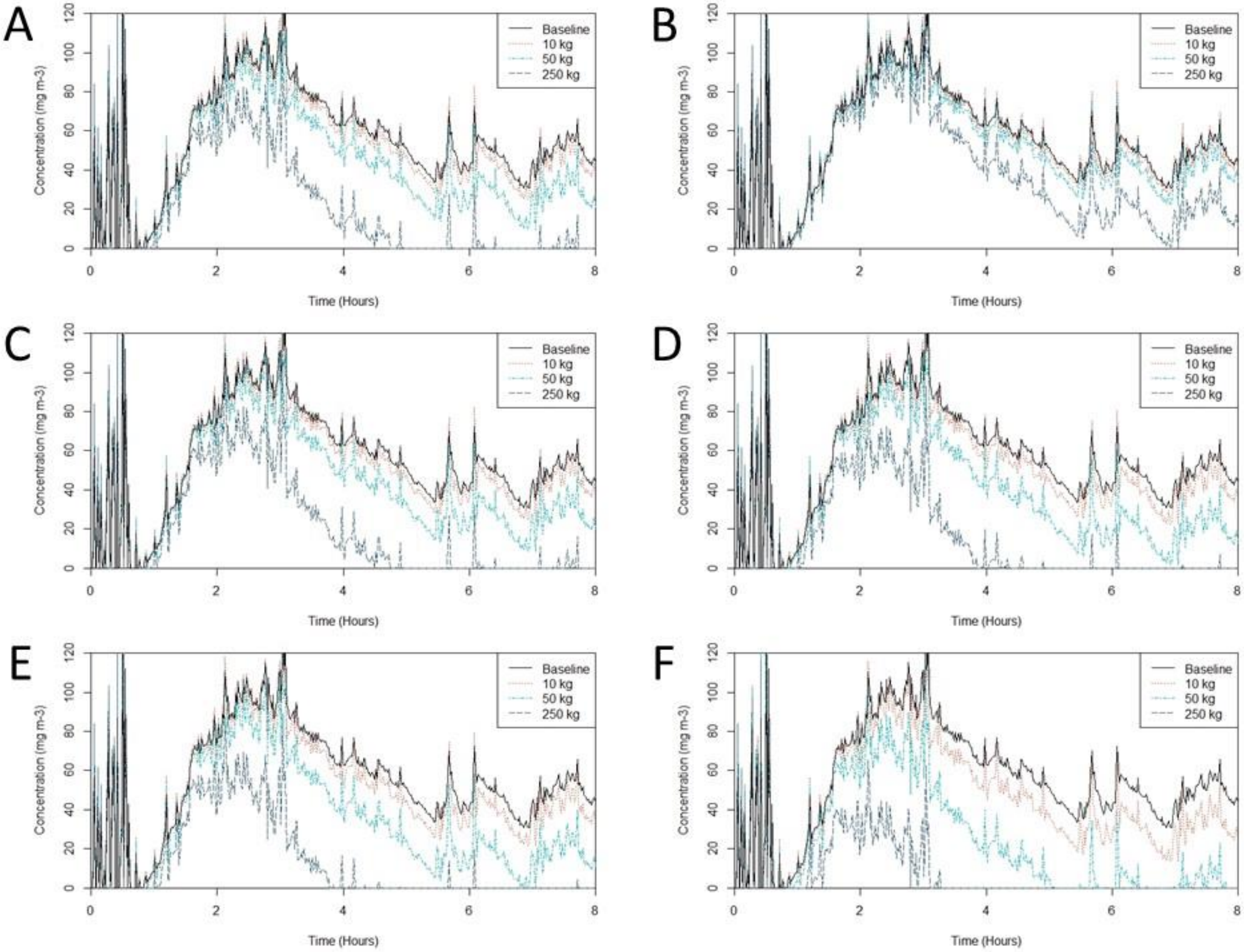

Fig. 3.9. Salon models for (A) CC passive flow, (B) CC active flow, (C) BC passive flow, (D) BC active flow, (E) AC passive flow, and (F) AC active flow.

3.5. Discussion

The ingredient information contained in the SDSs for the nail products used in this study was often imprecise (Table 3.1). For example, the total reported VOC content sometimes exceeded 100% and the reported total VOC content differed as much as a 78% between the upper and lower values. This poor information is problematic for consumers and nail professionals who are unable to make informed purchasing decisions. Similarly, this information is insufficient for researchers trying to accurately determine emissions from these products. The headspace analyses performed in this study, however, found that product ingredients generally matched what was reported by manufacturers in the product SDSs, and those reported by others (Zhong et al., 2019). Gravimetric estimates of nail polish total VOC content were within the range provided by manufacturers in their SDSs, and near the lower limit of VOC emissions from "other cosmetics" (0.80 ± 0.20) estimated by McDonald et al. (2018) (0.80 ± 0.20). These SDSs listed more volatile compounds than were determined through GC-MS analysis in this study and presented wider ranges of VOC content than observed here. This is likely because SDSs are typically written for more than one product formulation and are general in nature. To provide consumers and nail professionals with the most detailed product and safety information available, SDSs should include only compounds found in that specific product. This information is especially important for consumers that have asthma or allergies to specific chemicals (Sainio et al., 1997; Moulin et al., 2008; Roelofs and Do, 2012; Kwok et al., 2014; Mattos Simoes Mendonca et al., 2015; Arora and Tosti, 2017).

VOC removal experiments with CC, BC, and AC showed that all 3 materials can adsorb VOCs under both passive and active flow conditions. Removal was also strongly linked to both ambient VOC concentrations and available adsorption sites, represented here as $(1 - q(t)/q_{max})$.

Adsorbent particle size (e.g. fine or coarse) was shown to have relatively little effect on removal rates at LC. Results showed that material surface area and average pore size impacted the performance of the adsorbent material as VOC remover.

The use of SJA to provide local ventilation was shown to enhance the adsorption process for BC and AC in this study. Their use in actual indoor environments could be convenient and economical. For example, the minimum International Mechanical Code (IMC) ventilation rate for a 93 m^2 (1,000 ft^2) salon is approximately 4.25 m^3 min^{-1} (150 CFM), which would require a 115 V blower operating at approximately 1 A (115 W). Comparatively, 115 W could power over 240 SJAs (consuming 475 mW each). As demonstrated by McQuillan et al. (2014), SJAs can impact flows from HVAC systems. In this study, SJAs were also shown to increase the removal of VOCs for BC and AC during the test period. Using synthetic jets to alter local flow conditions was especially advantageous for adsorbents with smaller average pore sizes as determined by BET and BJH analyses.

The VOC removal models showed that as little as 10 kg of AC could achieve a measurable reduction of VOCs in the nail salon environment, especially when active flow conditions are in effect. Additionally, effective ventilation rates calculated for all VOC removal models using 250 kg of adsorbent in passive flow conditions approached the minimum ventilation requirements set by the IMC for a 1400 m^3 nail salon (approximately 250 m^3 h^{-1}). When used in active flow conditions, 250 kg of fine AC was shown to achieve 0.21 ACH_{eff}, which is nearly 17% greater than the minimum ventilation rate published in the IMC for a nail salon of this volume (ICC, 2015). Poor curve fits were obtained in some cases for CC and BC materials due to extreme non-linearity at the beginning of the experiments. This fast initial VOC removal may be due to preferential adsorbing onto fully available sites, a phenomenon previously documented by Ritchie (1977). Identifying the mechanism and obtaining better fits for this portion of the data would require more precise instrumentation and faster sampling rates than could be achieved in this study. This issue primarily affected data at the upper end of adsorption rates, leading to lower predicted adsorption values. The model presented here also did not account for the effect of concentration changes on $\dot{m}$ (Eq. 3.7); which may be significant.

This study presents results that support the utilization of adsorbents in indoor environments with high VOC levels; however, further optimization of such systems is needed. For example, factors such as regeneration of the adsorbents and the location of these materials were not addressed here. Typically, adsorbents of this type are regenerated thermally at temperatures of less than 100°C, which can be achieved using consumer-grade heating technology. The release of volatile compounds during regeneration processes presents a potential timing issue; however, regeneration cycles could be scheduled overnight, when building occupants are not present. Release of adsorbed VOCs during the night may have an added environmental benefit as well, since photolytic reactions that contribute to ozone and secondary organic aerosol (SOA) formation are unlikely to occur; however, other conditions must also be optimal (e.g., crosswinds and no atmospheric inversions).

Although BC and CC were shown to remove VOCs from the air under both passive and active flow conditions, their removal capacities were noticeably lower than commercial AC under all conditions tested in this study. When used under active flow conditions, BC achieved VOC removal comparable to commercial AC under passive flow conditions. This suggests that flow conditions should be considered during the optimization of adsorbent-based VOC removal systems for the indoor environment.

Although this study showed biochar to be an effective adsorbent for VOCs, it is also known to include residual pollutants as a result of the pyrolysis process under which it is generated. VOCs and polycyclic aromatic hydrocarbons (PAHs) have been found in biochars from a number of different feedstocks (Dutta et al., 2017; Buss and Mašek, 2016; Buss et al., 2015; Spokas et al., 2011). These compounds could potentially be released from the adsorbent materials into the indoor environment where they may affect the health of occupants (Buss and Mašek, 2016). Consequently, their use in air quality control applications will require additional research.

3.6. Conclusions

While biochar and coco coir used in this study were shown to remove VOCs from the ambient air, their removal capacities were both substantially lower than the commercially available activated carbon. This suggests that these alternative adsorbent materials may not be optimal for indoor VOC removal applications without some additional treatment to increase their adsorption capacity. The cost of such treatment should be considered when determining the advantages and disadvantages of these less common materials. Reducing and capturing VOCs emitted in the indoor occupational environment is necessary to safeguard worker health and may also help to address urban ozone pollution and SOA formation. Results from this study are promising and suggest that indoor adsorbent sinks could play a role in future VOC mitigation efforts. Further exploration of this technology should be conducted to address issues of material regeneration and implementation strategies, which were not covered in this study.

CHAPTER 4

VOC REMOVAL IN NAIL SALONS USING NOVEL, LOW-COST SORBENT SINKS: AIR-CLEANING ART.

Contributing Authors: Aaron Lamplugh, Adam Nguyen, and Lupita D. Montoya

Abstract: This study investigated the VOC removal capability of a novel, low-cost technology that utilizes activated carbon (AC) embedded in common gypsum plaster. VOC removal experiments were conducted in a closed chamber under passive and active flow conditions with acetone used as the sorbate. Normalized mass removal rates were calculated from concentration data. Optimization parameters including mass of AC in the sink mixture and external surface area (SA) of the sink were studied. Two different mass removal rate equations (mass-normalized and surface area-normalized) were determined from experimental data, using an n^{th}-order general rate model with VOC concentration in air and VOC mass adsorbed as fitting parameters. These equations were used in a mathematical model to predict the impact of sorbent sinks in a typical nail salon. *In-situ* regeneration of the sink via resistance heating was also tested.

Results showed that the performance of sorbent sinks was dependent on both external surface area and sample thickness, and active flow conditions were demonstrated to enhance acetone removal from the air. Model results indicated that sorbent sinks could provide beneficial VOC removal in nail salons but required a SA of approximately 25 m^2. Surface-area-normalized effective ventilation rates from the model ranged from 3.32-9.03 $m^3\ h^{-1}\ m^{-2}$, similar to values reported in a previous study. Regeneration tests were inconclusive but indicated that substantial portions of the removal observed here may not be easily reversible.

Keywords: VOC removal, Passive removal, Sorption, Synthetic jets, Nail Salons, Occupational Exposure

Highlights:

- Novel sorbent sinks of activated carbon and plaster removed acetone from air
- Synthetic jet flow enhanced VOC removal for sorbent sinks
- Models predicted an effective ventilation rate of 9.03-143 m^3 h^{-1} for 1-25 m^2 sinks

4.1. Introduction

The indoor environment is unique with respect to the types and concentrations of pollutants generated and observed (Ayoko and Wang, 2018). Additionally, because average Americans spend close to 90% of their time indoors (Klepeis et al., 2001), they typically experience more exposure to airborne pollutants indoors than anywhere else. Volatile organic compounds (VOCs) are among the most common indoor air pollutants and can cause a wide range of issues for occupants including acute and chronic health issues like headaches, neurological issues (US EPA, 2007), reproductive complications (John et al., 1994), and even cancer (Swenberg et al., 1980; Swenberg et al., 2013).

Among the most polluted indoor environments are workplaces, especially those in which air pollutants are emitted from occupational activities like painting (Can et al., 2015; Colman Lerner et al., 2012), solvent and adhesive use (Martins et al., 2016; Mølgaard et al., 2015), cooking (Sofuoglu et al., 2015), and other industrial operations (Badjagbo et al., 2010; Lee et al., 2006; Pandya et al., 2006). Nail salons fall into this group as well, since VOCs like acetone, toluene, ethyl acetate, methyl methacrylate, and formaldehyde (Lamplugh et al., 2019; Alaves et al., 2013; Quach et al., 2011) are emitted from nail products (Kelly et al., 1999; Kwon et al., 2007; Huzar et al., 2011; Zhong et al., 2019; Heaton et al., 2019).

Controlling indoor air quality is typically accomplished by increasing ventilation, either by natural or mechanical means. Building configuration and seasonal variations directly affect thermal comfort and limit the amount of ventilation that can be achieved naturally. Likewise, mechanical ventilation systems function well under most conditions but can be expensive to install and maintain and may consume a considerable amount of power. In 2010, buildings accounted for 41% of all U.S. primary energy consumption, with 50% of the energy in buildings used for heating, ventilation, and air-conditioning (HVAC) operations (DOE, 2011).

VOCs can also be removed from the indoor air through adsorption processes, whereby gas-phase molecules (adsorbates) bond to the solid surface of an adsorbent, like activated carbon (AC), through physical or chemical processes (Zhang et al., 2017a). These processes can take place passively through the diffusion of VOCs onto the surface of a material, or actively by directing VOCs at the adsorbent surface using some ventilation source (e.g., from a fan, synthetic jet, or HVAC system).

Several recent studies (Table 4.1) have looked at the use of adsorbents in indoor building materials for improving indoor air quality (IAQ) including cement pastes with embedded AC (Krou et al., 2015), clay wall coatings (Darling and Corsi, 2016), micro-carbonized plywood (Huang et al., 2019), and commercially available indoor passive panel technologies (IPPT) that range from wall paper to hardwood flooring (Zuraimi et al., 2018). In many of these cases, use of the adsorbent product or technology would require substantial retrofits or renovations to an existing structure, and in some cases may even require new construction. They often have no clear means of being regenerated once installed, which may lead to substantial decreases in efficiency over time. Additionally, reactive adsorbent surfaces, such as photocatalytic oxidation (PCO)-based IPPT, have been shown to generate harmful gas species like ozone and formaldehyde (Zuraimi et al, 2018).

Table 4.1. Published studies on the use of adsorbents in indoor building materials

Study	Adsorbent(s)	Adsorbate(s)	Findings
Ataka et al. (2004)	Formaldehyde-decomposing gypsum board	Formaldehyde	Adsorption rate of material was proportional to the concentration of adsorbate in the air but was not greatly affected by temperature or relative-humidity. Adsorption rate of 0.0018 mg m^{-2} min^{-1}. Effective ventilation rate of 5.5 to 6.1 m^3 h^{-1} m^{-2}.
Seo et al. (2009)	Seven including: AC and Gypsum board with AC	Toluene, ethylbenzene, styrene, and p-xylene	Effective reduction of VOCs by sorptive building materials. Effective ventilation rates of 1.0-1.1 m^3 h^{-1} m^{-2} for AC and 0.2 m^3 h^{-1} m^{-2} for gypsum board with AC.
Krou et al. (2015)	Two types of cement paste: one reference and one with AC	Acetaldehyde and toluene	Hydrated cement paste with AC was able to capture toluene from the air. Cement and AC composite was far less effective of an adsorbent at 200 min. compared to raw, powdered AC.
Darling and Corsi (2016)	One clay-based interior paint and one clay-based plaster	Ozone	Passive clay-based adsorbents were generally effective at reducing ozone, however there was also measurable emission of C_5-C_{10} n-alkanes from the materials.
Zuraimi et al. (2018)	Eight sorptive and 3 (PCO)-based materials	Formaldehyde and toluene	Despite a wide range of removal rates, all passive adsorbent building materials performed better than their conventional counterparts. PCO materials were shown to emit ozone and carbonyls at rates of 1.0 and 3.2 mg h^{-1}, respectively.
Huang et al. (2019)	Latex paint, micro-carbonized wood, and moisture-buffering siding	Formaldehyde	Use of formaldehyde removing sorptive materials significantly improved effective ventilation efficiency. Equivalent ventilation rates between 0.21 and 1.26 m^3 h^{-1} m^{-2}. Projected reduction in cancer risk of 4.84-5.73 x 10^{-4}.

This study explores the use of novel, low-cost adsorbent sinks for reducing concentrations of VOCs in the indoor environment. The sinks are modular, easy to install and remove without retrofitting, and decorative. The sinks were tested in a controlled environment under both passive and active flow conditions. Design parameters, including AC composition and external surface area were studied. *In-situ* regeneration of the sinks was also investigated using a common resistance heating unit.

4.2. Materials

4.2.1. Adsorbent Sink Samples

Gypsum plaster (Rocky Mountain Clay, Denver, CO) and AC (MICROBE-LIFT, Ecological Laboratories, Inc., Malverne, NY) were used to construct the adsorbent sinks. The AC was previously used and characterized in Chapter 3, and results from BET and BJH analyses are included in Table 3.2.

AC was first ground using a Nasco-Asplin soil grinder (Patent #2,903,198, NASCO, Fort Atkinson, WI), and sieved to < 355 μm using a U.S.A #45 standard test sieve. It was then mixed dry with powdered gypsum plaster in various dry mass ratios (Table 4.2). The volume of MiliQ water used in each mixture was previously established, experimentally. Since AC is highly porous, the amount of water used had to be varied depending on the amount of AC in the mixture. Values shown in Table 4.2 are for standard sized samples with length (L)=127 mm, width (W)=152 mm, and thickness (TH)=17.4 mm; larger samples (used in SA tests) had the same mass composition as standard AC20 samples (AC20 Sm) but different dimensions. Medium samples (AC20 Md) had dimensions of 214 mm (L) x 152 mm (W) x 10.4 mm (TH) and large samples (AC20 Lg) had dimensions of 298 mm (L) x 152 mm (W) x 7.4 mm (TH), with average masses of 331 g and 326 g, respectively.

Table 4.2. Sample compositions and characteristics

ID	AC	Gypsum Plaster	Total Dry Mass	MiliQ Water	Avg. Sample Mass
AC00	0 g	410 g	410 g	200 mL	368 ± 7 g
AC20	70 g	280 g	350 g	225 mL	327 ± 4 g
AC50	136 g	136 g	272 g	250 mL	242 ± 3 g

Plaster and AC were mixed dry and water was slowly added to the dry mixture. The mixture was stirred until homogenous and then poured into a cottle-board mold. Samples dried in the mold for approximately 1 h under pressure from a 37 mm thick solid wood board. Samples dried and hardened at room temperature for approximately 24 h before being placed in an oven at 75°C, for over 48 h (until the day of testing). Prior to testing, samples were removed from the oven and placed in a fume hood until they reached room temperature (~21°C).

The length, width, and thickness of all samples were measured after drying using digital calipers (Pittsburgh Tools, Accuracy: ± 0.02 mm). Target external surface area for samples:

$$SA = 2 \times (L \times W) + 2 \times (L \times TH) + 2 \times (TH \times W) \qquad [4.1]$$

were set to be within 2% of 483.2, 726.7, or 972.5 cm^2 for Sm, Md, and Lg samples, respectively.

4.2.3. Environmental Test Chamber

A 304 stainless-steel environmental chamber was used, with dimensions 75 cm (W) x 75 cm (H) x 121 cm (H) (0.68 m^3 total volume). Additional details are provided in Chapter 3.

4.3. Methods

4.3.1. Experimental Setup

Three sets of VOC removal experiments (Fig. 4.1) were conducted in the environmental test chamber to assess the impact of three optimization parameters on VOC removal by sorbent sinks: (1) Composition of dry mixture (AC% by mass), (2) External surface area (at constant volume), and (3) Flow conditions (passive or active). One additional experiment tested our ability to regenerate the adsorbent sink *in situ* using an embedded heating element.

In this study, acetone was used as the model VOC and was emitted from a nail polish remover purchased from a retail store in Boulder, CO. All experiments were conducted at either low concentration (LC, 0.1 mL) or high concentration (HC, 0.3 mL) volumes. In each case, a standard LC or HC volume of acetone was pipetted into a Petri dish and placed in the environmental chamber. The chamber was then sealed, and measurements were collected for 22.5 h. The concentration of acetone inside of the chamber was measured using a HalTech HVX501 photo-ionization detector (PID) (Hal Technology, Fontana, CA, Range 0-200 ppm, Resolution 0.03 ppm), with a 3-min sampling rate.

Temperature and relative humidity (RH) in the chamber were not controlled but were monitored during experiments with an Onset Hobo U12-013 Temp/RH/2 external channel logger (Onset, Bourne, MA, Temp Range: -20°C – 70°C, Temp Accuracy: ±0.35°C, RH Range: 5% – 95%, RH Accuracy: ±2.5%). The conditions were shown to be fairly constant; temperature ranged from 20.4 to 22.7 °C with a mean of 21.1 ± 0.003 °C and RH ranged from 19.0 to 32.9% with a mean of 25.8 ± 0.02%. Boxplots of all temperature and RH data (n=23,931) are shown in Appendix III Supplementary Fig. S1.

A two-point calibration (0 ppm and 175 ppm) was performed for the PID using a zero-air standard (Scott Specialty Gases, Plumsteadville, PA, O_2: 20-21%, Total Hydrocarbon: < 1 ppm) and an acetone gas standard (GASCO, Oldsmar, FL, Acetone: 175 ppm), respectively. The line between these points was used to determine the PID correction factor for acetone (1.5608). PID responses (ppm) were then converted to mass-based acetone concentrations, using the equation:

$$C_{mass}[mg\ m^{-3}] = C_{ppm} \times CF \times MW/(RT/P) \qquad [4.2]$$

where CF is the correction factor for acetone, MW is the molecular weight of acetone (g mol^{-1}), P is the surface pressure in Boulder, CO (0.803 atm), R is the universal gas constant (0.08206 L atm mol^{-1} K^{-1}), and T is the mean chamber temperature (K) during the experiment.

Three baseline experiments were also performed with the LC volume and one with HC, in the absence of any adsorbents, to establish a baseline concentration of acetone.

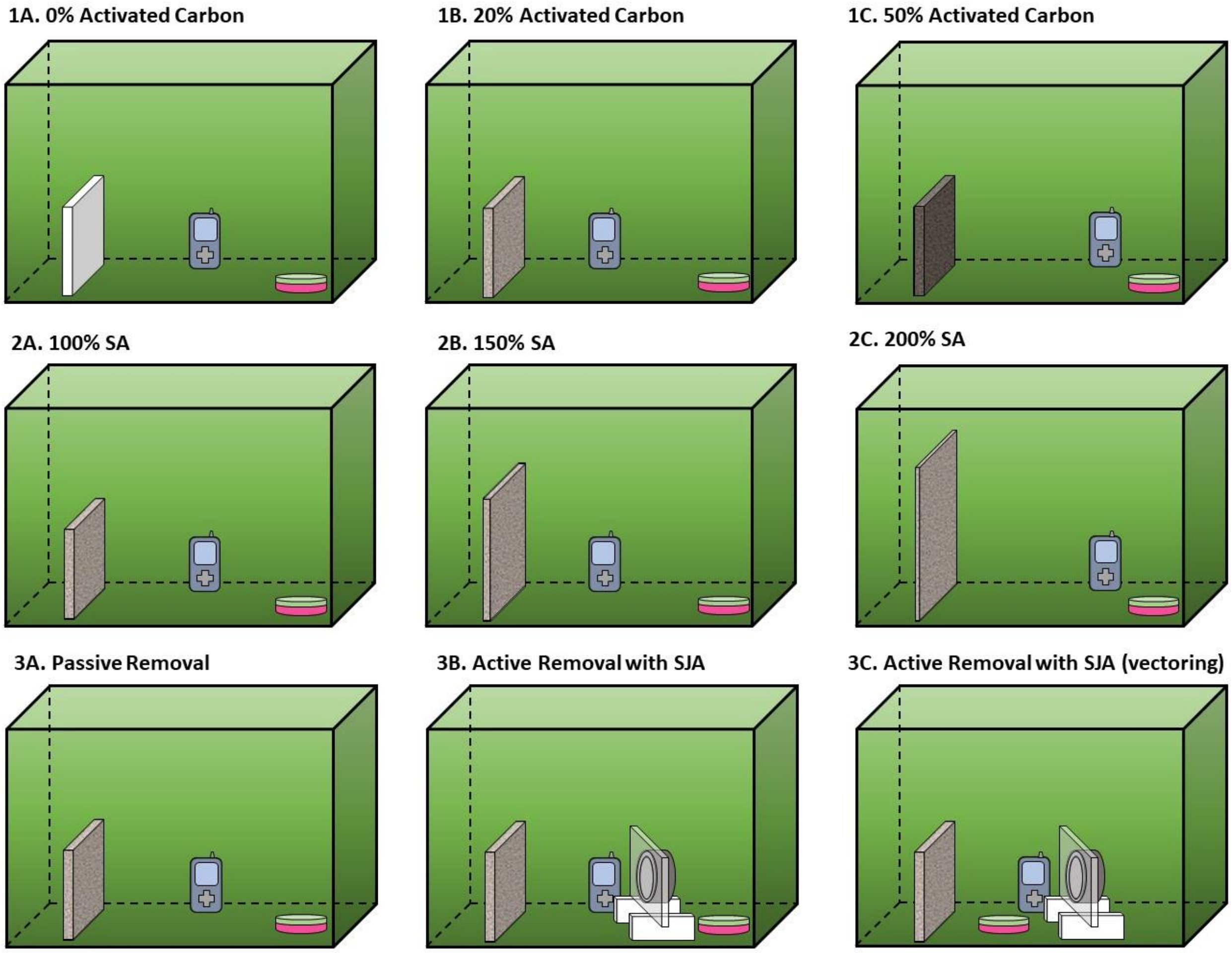

Fig. 4.1. Sets of controlled experiments performed to study: (1) Adsorbent-to-plaster mass ratio, (2) External surface area vs. volume, and (3) Passive vs. active flow conditions.

4.3.2. Adsorbent-to-plaster mass ratio

The experiments shown in the top row of Fig. 4.1 focused on the optimization of the mass-of-adsorbent-to-mass-of-plaster ratio in the sample (sink). This set of experiments were conducted only under passive flow conditions. The test samples contained 0% (Fig. 4.1-1A), 20% (Fig. 4.1-1B), or 50% (Fig. 4.1-1C) AC (adsorbent) on a dry mass basis. All samples had the same length (L=127 mm), width (W=152 mm), and thickness (TH=17.4 mm). They all possessed the same external surface area (483.2 cm^2). Samples were placed in the center of the chamber in an upright position for the duration of the experiment (22.5 h). Concentrations of acetone measured during this experiment were averaged over 15-min intervals and subtracted from the baseline concentrations. That value was then multiplied by the chamber volume and divided by the mass of the sample to calculate, q_m, the mass of acetone removed, normalized by the mass of the sink (mg g^{-1}):

$$q_m(t) = \frac{V_{chamber}}{m_{sink}}[C_o(t) - C(t)] \tag{4.3}$$

where $V_{chamber}$ is the volume of the environmental chamber (0.68 m^3), $C_o(t)$ is the baseline concentration at t (mg m^{-3}), C(t) is the concentration at t during the removal test (mg m^{-3}), and m_{sink} is the mass of the sink (g). The mass-normalized removal rate ($k_{rem,expm}$, mg min^{-1} g^{-1}) for each experiment was then calculated as the change in q_m over time:

$$k_{rem,\text{exp}m}(t) = \frac{q_m(t+0.5\Delta t) - q_m(t-0.5\Delta t)}{\Delta t} \tag{4.4}$$

where Δt is approximately 15 min.

Mass-normalized removal rate data were also fitted in R, using non-linear least squares regression analysis of the form previously used in Chapter 3:

$$k_{rem,m} = a * C(t)\left(1 - \frac{q_m(t)}{1.05 * q_{m,max}}\right)^n \tag{4.5}$$

where $k_{rem,m}$ is the mass normalized removal rate of the sink material (mg g^{-1} min^{-1}), a is a rate constant for the material, n is a constant exponent related to the order of the removal, and $q_{m.max}$ is a mass-normalized, quasi-equilibrium value of removed VOC mass (mg g^{-1}), taken at HC and t=22.5 h. A factor of 1.05 was applied to $q_{m.max}$ to estimate the actual equilibrium mass removed.

4.3.3. External surface area (at constant volume)

The experiments shown in the middle row of Fig. 4.1 focused on the optimization of the external surface area (SA) to volume ratio of the sink. This set of experiments were conducted under both passive and active flow conditions. The first experiment (Fig. 4.1-2A) was the same setup in Fig. 4.1-1B. Figs. 4.1-2B and 4.1-3B, show cases where the SA of the sample was increased by 50% and 100%, respectively. A 20% AC content was used for all samples in this set of experiments. Acetone concentrations measured during this experiment were averaged over 15 min and subtracted from baseline concentrations; however, in this case, concentrations were multiplied by the chamber volume and divided by the SA of the sink:

$$q_{SA}(t) = \frac{V_{chamber}}{SA}\left[C_o(t) - C(t)\right] \qquad [4.6]$$

where SA is the external surface area of the adsorbent sink (cm^2) and q_{SA} is in units (mg cm^{-2}). A SA-normalized removal rate ($k_{rem,SA}$, mg cm^{-2} min^{-1}) was then calculated as:

$$k_{rem,expSA}(t) = \frac{q_{SA}(t+0.5\Delta t) - q_{SA}(t-0.5\Delta t)}{\Delta t} \qquad [4.7]$$

Removal rates evaluated for samples of 100%, 150%, and 200% SA were compared to determine how adsorption changed with SA scaling. SA-normalized removal rate data were also fitted in R, using a SA-normalized version of equation 4.5:

$$k_{rem,SA} = a * C(t)\left(1 - \frac{q_{SA}(t)}{1.05 * q_{SA,max}}\right)^{n} \qquad [4.8]$$

where $k_{rem,SA}$ is in units mg cm^{-2} min^{-1}, and $q_{SA.max}$ is in units mg cm^{-2}.

4.3.4. Flow conditions (passive vs. active flow)

The last set of experiments, shown in the bottom row of Fig. 4.1 explored the effect that local flow conditions have on removal rates. Again, the experiment in Fig. 4.1-3A was the same as the one in Fig. 4.1-3B (i.e., under passive flow conditions). Figs. 4.1-3B and 4.1-3C show experiments under active flow conditions, provided by a synthetic jet actuator (SJA) (Aavid Thermalloy, Laconia, NH, 5VDC, 95mA, 475mW). In both active removal cases, the SJA was directed perpendicularly at the surface of the sink from a distance of 30 cm. In the experiment shown in Fig. 4.1-3C, the emission source is placed halfway between the synthetic jet and the adsorbent sink to determine if this orientation (vectoring) lead to faster VOC removal.

SA-normalized removal rates for active flow tests were calculated using equations 4.6, 4.7, and 4.8.

4.3.5. Regeneration

The regeneration experiment, shown in Fig. 4.2, investigated the ability of an AC20 Sm sample to regenerate *in situ,* using an embedded resistance heating element. The heating element was controlled by a microcontroller (Adafruit Metro 328, Adafruit, New York City, NY) attached to a high-voltage relay (Adafruit Power Relay FeatherWing, Adafruit, New York City, NY) and a thermocouple amplifier (Adafruit MAX31855 Thermocouple Breakout Board, Adafruit, New York City, NY) with a k-type thermocouple (PK-1000, Minnesota Measurement Instruments, LLC, Saint Paul, MN, Range: -50°C - 1000°C). A schematic of the test circuit is shown in Fig. 4.3.

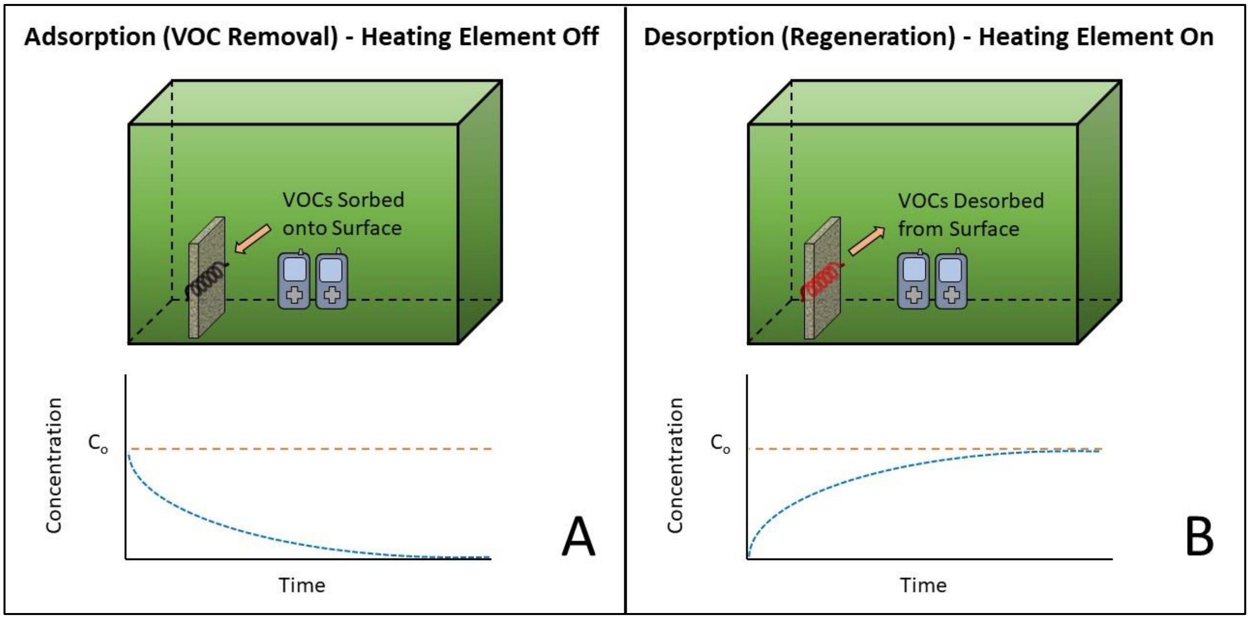

Fig. 4.2. Diagram of regeneration test with embedded heating element.

The regeneration circuit was designed to be easily operated and run off of a standard U.S. electrical outlet. A pulsed 120 V electrical signal was delivered to the heating element during regeneration cycles (Fig. 4.2B), until the thermocouple (located on the surface of the sink) measured 100°C, at which point the relay was turned off. This process was repeated 4 times in 10-15 min during each regeneration cycle. After regeneration, the sink cooled to room temperature and once again began removing VOCs from the air (Fig. 4.2A). This cycle was repeated twice inside the sealed environmental chamber over 24 h, followed by a second injection of acetone and 2 subsequent regeneration cycles over an additional 24 h.

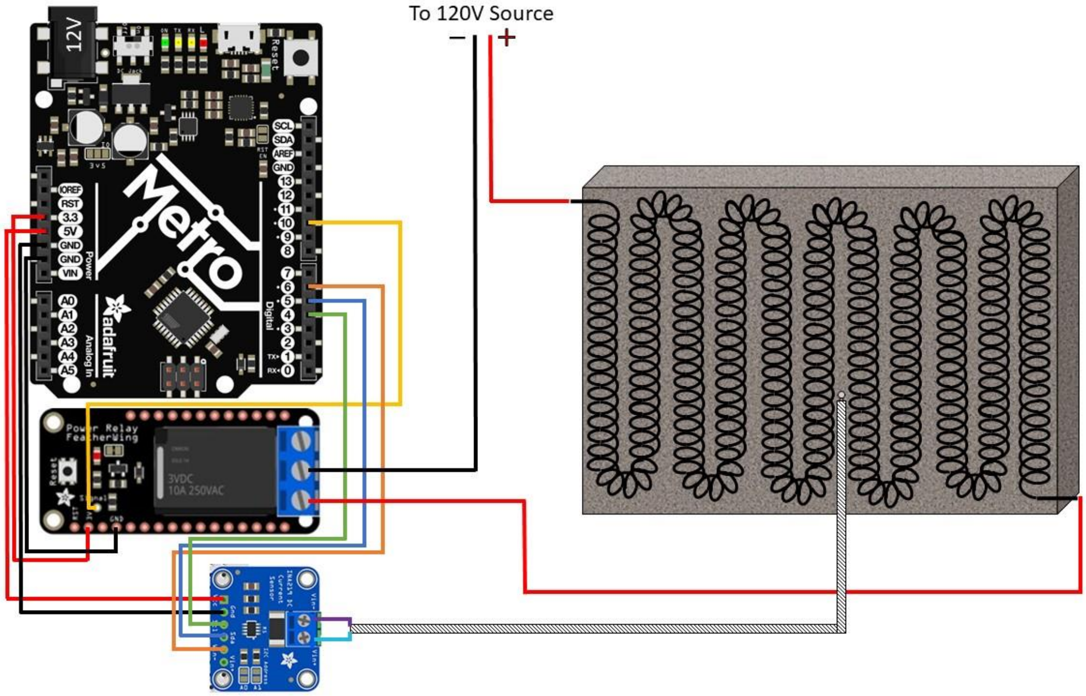

Fig. 4.3. Schematic of thermal regeneration circuit.

4.3.6. VOC Removal Model for Nail Salon Application

A mathematical model, similar to the one described in Chapter 3, was developed to predict VOC concentrations in a nail salon when adsorbent sinks were present under both active and passive flow configurations. The model used a sample of TVOC data from Lamplugh et al. (2019) as the input, and calculated new concentrations based on the adsorption rate and size (i.e. SA or mass) of the adsorbent sink used. TVOC concentrations from the salon (measured with the same PID) were assumed to be from acetone, which was shown to be the primary VOC present in that field study. The correction factor for acetone (1.5608) was applied when converting from ppm to mass-based concentrations. Theoretical VOC removal rates for sinks were calculated for the 8 h sample period using the k_{rem} models determined from equations 4.5 and 4.8. A mass balance was performed at each time-step in order to calculate a new theoretical concentration for the salon:

$$C_{new,i} = C_{field,i} + \frac{[\dot{m}_{i-1}\times(t_i - t_{i-1}) + k_{rem,i-1}\times S_{sorb}\times(t_i - t_{i-1})]}{V_{salon}} \qquad [4.9]$$

where i is the time-step, t is time (min), V_{salon} is the volume of the salon (m^3), $C_{field,i}$ is the VOC concentration (mg m^{-3}) measured during the nail salon field study at i, S_{sorb} is the size of the sorbent sink (either SA or mass), k_{rem} is the normalized removal rate - either $k_{rem,m}$ (equation 4.5) or $k_{rem,SA}$ (equation 4.8), and $\dot{m}$ is the derivative of VOC mass with respect to time (mg min^{-1}) calculated from field study concentration data:

$$\dot{m}_i = \frac{V_{salon}[C_{field,i+1} - C_{field,i-1}]}{t_{i+1} - t_{i-1}} \qquad [4.10]$$

The total theoretical mass of VOCs adsorbed for each case are reported along with average effective ventilation rates. The average effective ventilation rate was calculated using equation 3.8 from Chapter 3:

$$Q_{eff}\left(\frac{m^3}{hr}\right) = \frac{q_{total}\times m_{sorb}}{8\ h\times C_{med}} \qquad [4.11]$$

where q_{total} is the total predicted mass of VOCs adsorbed, per gram of adsorbent (mg g^{-1}), over the 8 h removal period and C_{med} is the median concentration (mg m^{-3}) of VOCs during the same time period.

Q_{eff} was used to estimate the contribution of adsorbents in the indoor environment to air-cleaning operations, and to compare air-cleaning art with traditional ventilation technologies. This metric did not account for other non-VOC air pollutants that may be present indoors, including particulate matter and CO_2, and approximates a constant ventilation rate across all 8 h from a clean source of air. A volume-normalized metric was also considered, which is referred to here as the effective air exchange rate (ACH_{eff}), and was calculated as in Chapter 3:

$$ACH_{eff} = \frac{Q_{eff}}{V_{salon}} \quad [4.12]$$

where V_{salon} is the volume of the test salon (m^3) and ACH_{eff} is given in units h^{-1}.

4.4. Results

4.4.1. Chamber Experiments

4.4.1.1. AC composition testing

Results from dry mass composition experiments are shown in Fig. 4.4. Initial adsorption rates were shown to double between AC00 and both AC20 and AC50 samples in LC tests, however there was no observable difference between adsorption rates of AC20 and AC50 samples. In HC tests, AC00 adsorption rates were approximately half of AC20 adsorption rates (with the exception of the initial data point), and AC50 adsorption rates were found to be substantially greater than AC20 rates over the first 2.5 h.

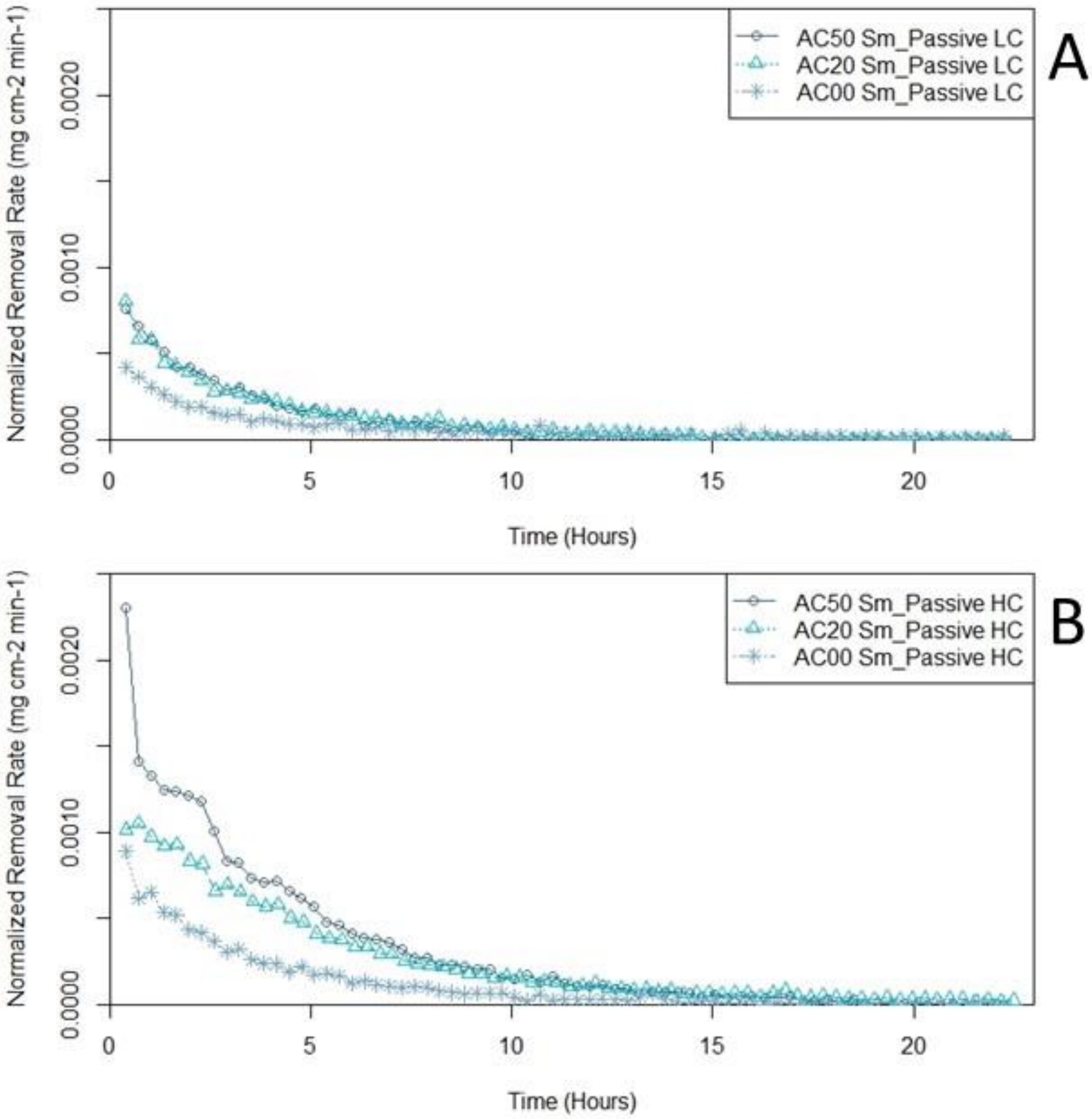

Fig. 4.4. Passive removal rates for Sm AC00, AC20, and AC50 samples at (A) LC and (B) HC.

4.4.1.2. External surface area (constant volume) testing

Removal rates for AC20 Sm, AC20 Md, and AC20 Lg at both LC and HC are shown in Fig. 4.5.

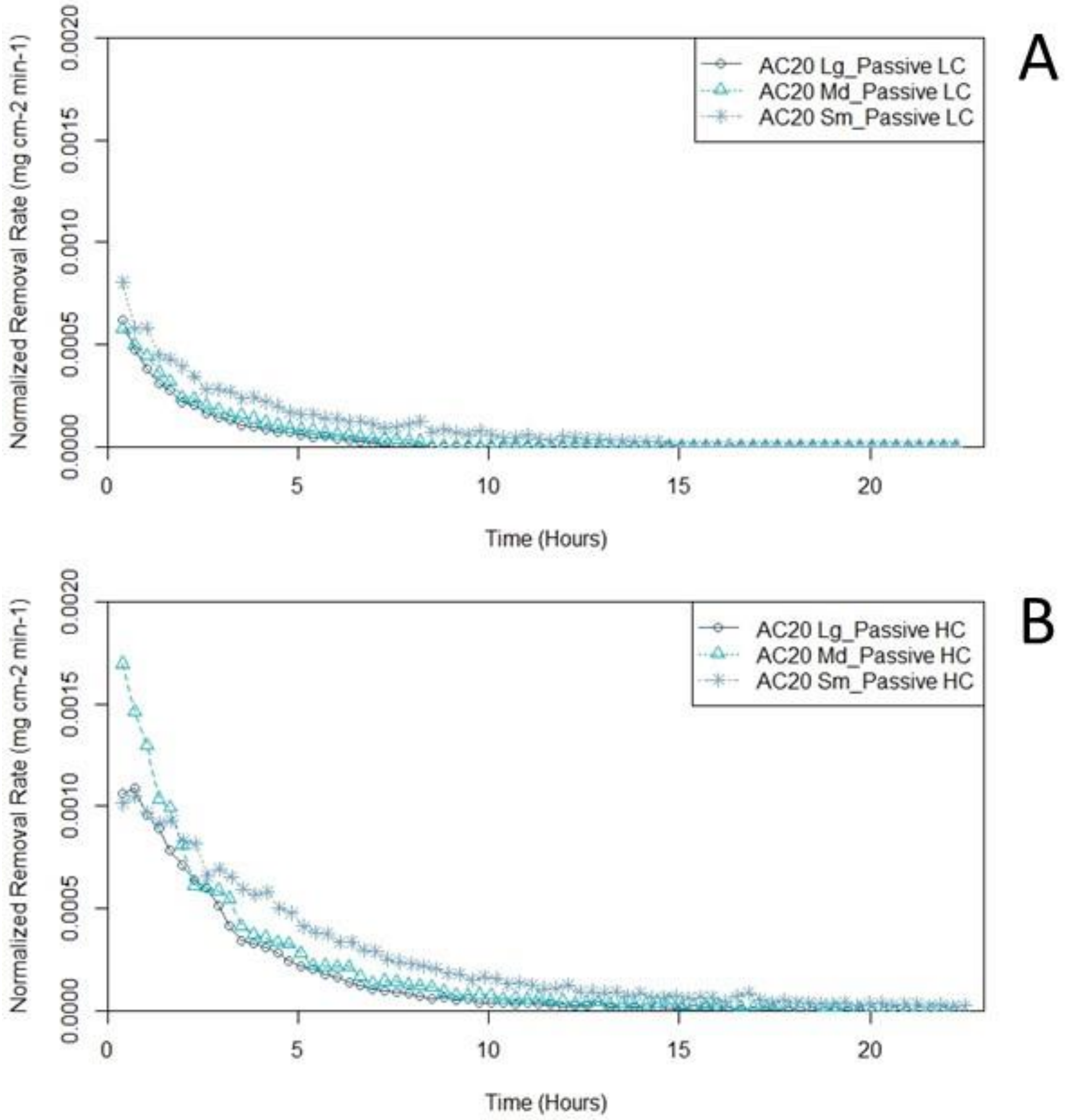

Fig. 4.5. (A) AC20 Sm, (B) AC20 Md, and (C) AC20 Lg samples at LC and HC.

SA-normalized adsorption rates for all three samples were similar, suggesting that the passive removal rate scales fairly linearly with surface area under passive flow conditions.

Fig. 4.6 shows VOC adsorption trends for all passive removal experiments (SA and mass ratio experiments) with AC samples. The y-axis shows concentration at t, normalized by the baseline concentration at t (C/Co). Results show that increasing AC mass ratio and external SA both led to faster acetone removal. SA increases had a greater effect than AC mass ratio increases, with AC20 Lg (100% greater SA than AC20 Sm) demonstrating significantly faster acetone removal than AC50 Sm, which has approximately 100% greater AC than AC20 Sm. This suggests that SA is the dominant optimization parameter for passive VOC adsorption.

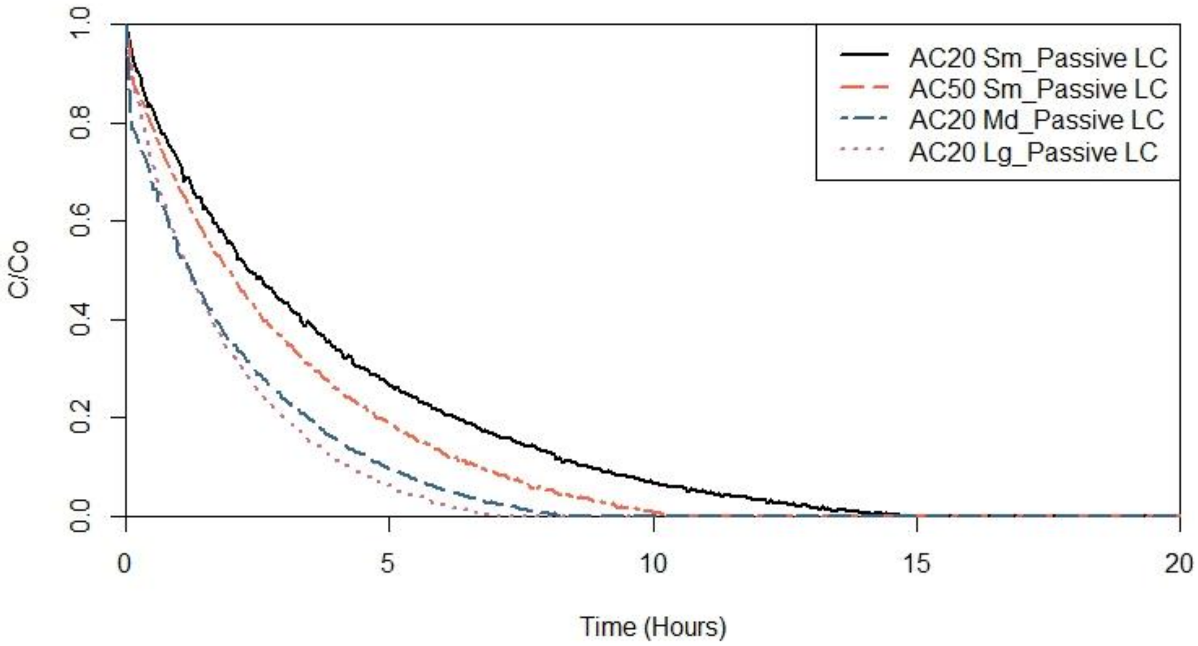

Fig. 4.6. Acetone removal at LC over 20 h by all AC samples under passive flow.

4.4.1.3. Flow conditions (passive vs. active flow)

Fig. 4.7 shows the removal rates from active flow VOC removal tests. Initial removal rates for the passive case (0.0008 mg cm^{-2} min^{-1}) were approximately 2 times lower than either active removal case (0.0015 and 0.0016 mg cm^{-2} min^{-1}). Removal rates for both active flow cases followed nearly identical trends, suggesting that the placement of the VOC emission source does not impact the rate at which gas-phase pollutants are removed from the air. This was confirmed with multiple experiments on different sized samples (Appendix III Supplementary Fig. S2). It was also shown that SA-normalized removal rates under active flow conditions differed depending on the size of the sample tested (Fig. 4.8), with larger samples displaying lower removal rates after normalization. This suggests that active removal rates do not scale linearly with SA, likely because removal is taking place at some depth beneath the outer surface.

Fig. 4.9 shows how passive and active flow removal compared for samples with the same SA. Passive AC20 Sm and AC50 Sm experiments are graphed alongside results from AC20 Sm active flow tests (with and without vectoring). The data show minor differences between vectored and non-vectored trials, but large differences between passive and active flow experiments. This suggests that active flow provides a more substantial enhancement to VOC removal than increased AC, allowing AC20 samples to remove more acetone than samples with 100% more AC.

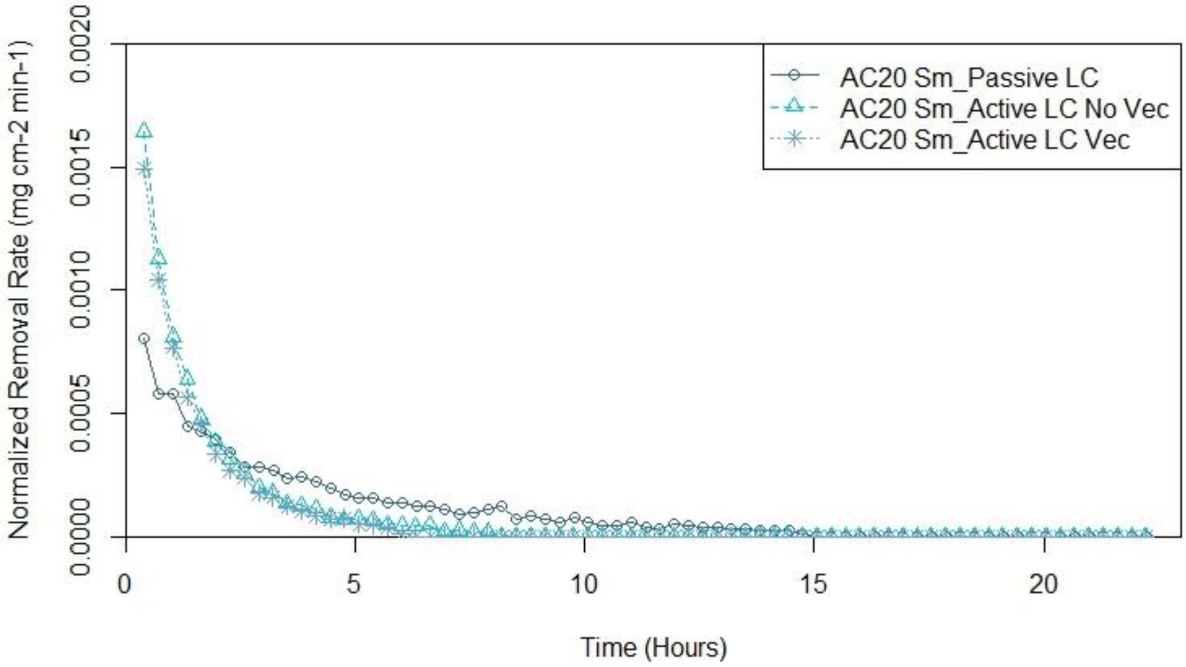

Fig. 4.7. Acetone removal with AC20 Sm samples at LC, passive and active flow, with vectoring (Vec) and without vectoring (No Vec).

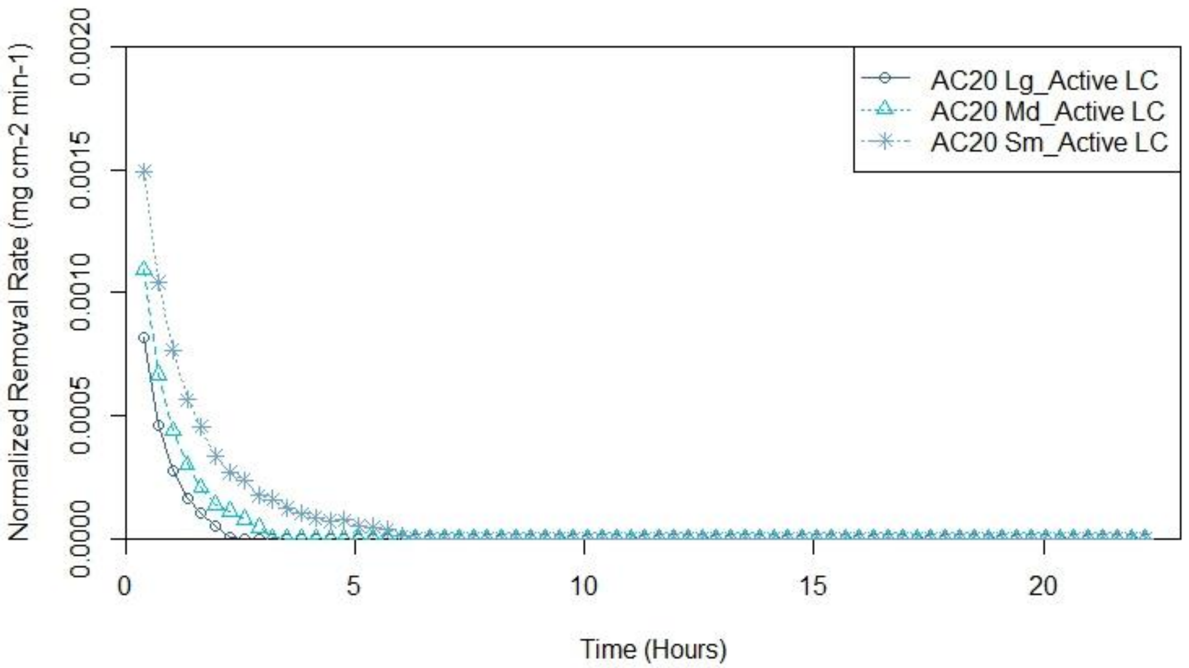

Fig. 4.8. SA-normalized active removal rates for acetone by Sm, Md, and Lg AC20 samples at LC.

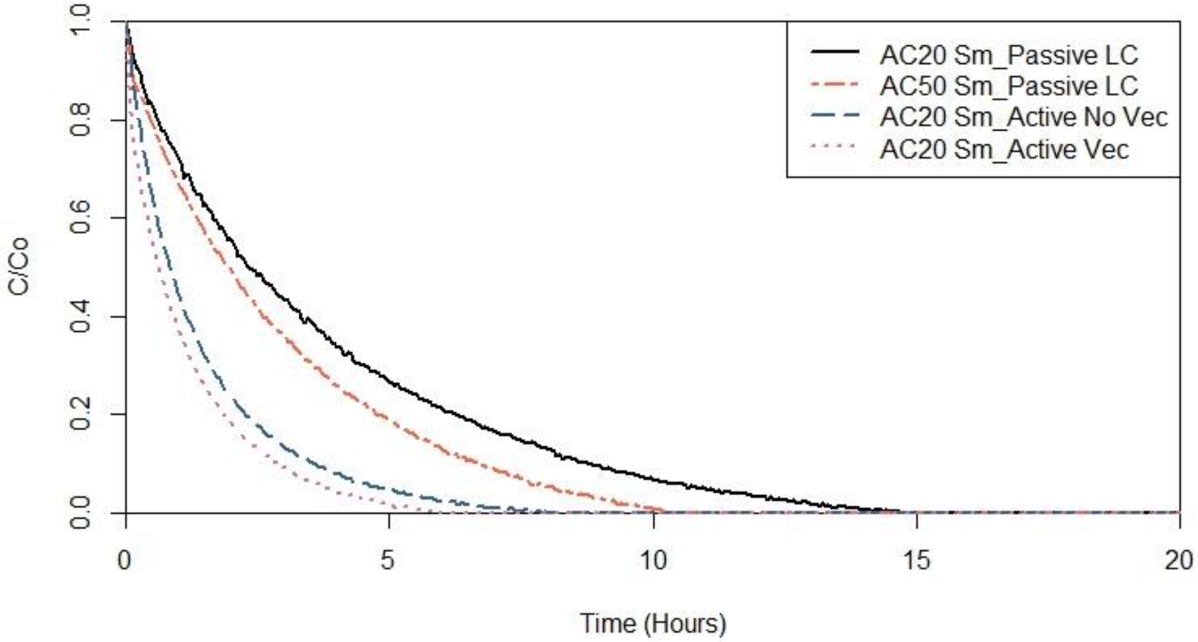

Fig. 4.9. Acetone removal at LC over 20 h by AC samples under passive and active flow.

4.4.2. Regeneration

Fig. 4.10A shows the results of a regeneration experiment performed using an AC20 Sm sample with an embedded resistance heating element. Acetone concentrations were shown to rise during regeneration cycles but did not reach initial concentrations from 0.1 mL injection of acetone (< 30% desorbed). At approximately 24 h, a second volume of acetone (0.12 mL) was injected into the chamber and was also removed by the sample. The sample underwent 2 additional regeneration cycles after the second injection, both of which reached very low concentrations compared with the peak from the second injection (~10%).

Results from this experiment were smoothed using a ~30 min moving average function (Fig. 4.10B), and then SA-normalized removal rates were determined (Fig. 4.10C) for the experiment period. Removal rates were shown to be similar between the first and second acetone injections, although fast, initial removal was reduced following the second injection. Removal rates measured after the second injection were also very close to SA-normalized removal rates previously found for passive removal with AC20 Sm samples (Fig. 4.5A).

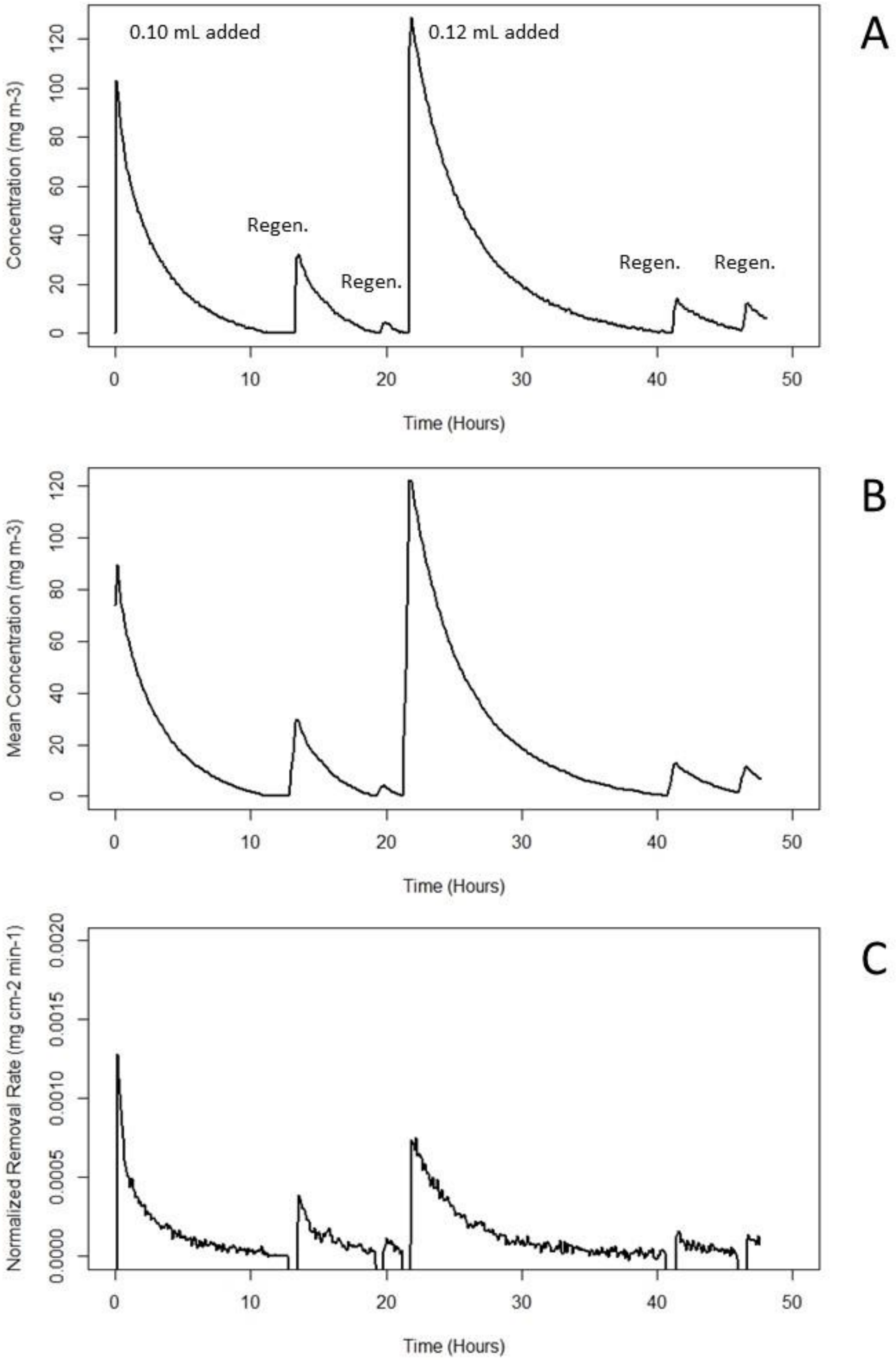

Fig. 4.10. (A) Results from regeneration (regen.) experiment with AC20 Sm sample, (B) Averaged concentration results, and (C) SA-normalized removal rates.

4.4.3. VOC Removal Model for Nail Salon Applications

A box model was used to predict the impact of Air-cleaning Art on VOC concentrations in a typical nail salon. Time-resolved VOC concentration data measured in an actual nail salon during a single-day sampling event (Lamplugh et al., 2019) was used as the input. The volume of the salon used in the model was 1400 m^3. Both mass-normalized and SA-normalized VOC removal rates (from equations 4.5 and 4.8) were used in the model. Appendix III Supplementary Table S1 and Supplementary Fig. S3 show the fit parameters of the removal rates equations used in the box model and the fitted rate data, respectively.

Sinks of masses 10, 50, and 250 kg were used for mass-normalized cases, and sinks of SA 1, 5, and 25 m^2 were used in SA-normalized cases. The total predicted VOC mass removal and effective ventilation rates (Q_{eff} and ACH_{eff}) for each case are shown in Table 4.3. Effective ventilation rates for AC20 Sm samples under active flow conditions ranged from 13.2 m^3 h^{-1} (0.01 ACH) for 10 kg to 173 m^3 h^{-1} (0.12 ACH) for 250 kg, in the mass-normalized case; for the SA-normalized case, effective ventilation values ranged from 9.03 m^3 h^{-1} (0.01 ACH) for 1 m^2 to 143 m^3 h^{-1} (0.10 ACH) for 25 m^2. In both cases (mass or SA normalization), AC20 Sm with active flow was shown to perform 192-272% better than passive AC20 Sm and 142-227% better than passive AC50 Sm in terms of overall mass removal.

Graphs showing the effect of the sinks on VOC concentrations in the salon model are shown in Fig. 4.11. In the left column (Figs. 4.11A, 4.11C, and 4.11E) are results from mass-normalized models, while SA-normalized cases are shown in the right column (Figs. 4.11B, 4.11D, and 4.11F).

Table 4.3. VOC mass removed and effective ventilation rates from adsorption models

Mass-Normalized		**Total VOC Removed (g)**	**Q_{eff} (m3 h^{-1})**	**ACH_{eff} (h^{-1})**
AC20 Sm Passive	10 kg	2.07	4.88	0.00
	50 kg	9.84	23.2	0.02
	250 kg	38.3	90.2	0.06
AC50 Sm Passive	10 kg	3.34	7.86	0.01
	50 kg	15.3	36.1	0.03
	250 kg	51.7	122	0.09
AC20 Sm Active	10 kg	5.62	13.2	0.01
	50 kg	25.4	59.8	0.04
	250 kg	73.6	173	0.12
SA-Normalized		**Total VOC Removed (g)**	**Q_{eff} (m3 h^{-1})**	**ACH_{eff} (h^{-1})**
AC20 Sm Passive	1 m^2	1.41	3.32	0.00
	5 m^2	6.80	16.0	0.01
	25 m^2	28.6	67.4	0.05
AC50 Sm Passive	1 m^2	1.69	3.98	0.00
	5 m^2	8.10	19.1	0.01
	25 m^2	32.9	77.6	0.06
AC20 Sm Active	1 m^2	3.83	9.03	0.01
	5 m^2	17.9	42.2	0.03
	25 m^2	60.7	143	0.10

Only cases of 250 kg or 25 m^2 showed major reductions in VOC concentrations throughout the day, with active flow cases demonstrating the best performance. These results can be compared to results previously presented in Chapter 3, where raw AC was used as the adsorbent in the model. In those cases, removal of VOCs was greater; however, since the mass indicated here is for the entire sink, the mass of AC used in the previous example was 50-80% more. Appendix III Supplementary Fig. S4 includes additional model results, where the effect of the sink is normalized by the mass of AC in the mixture. These results compare more directly with results from Chapter 3.

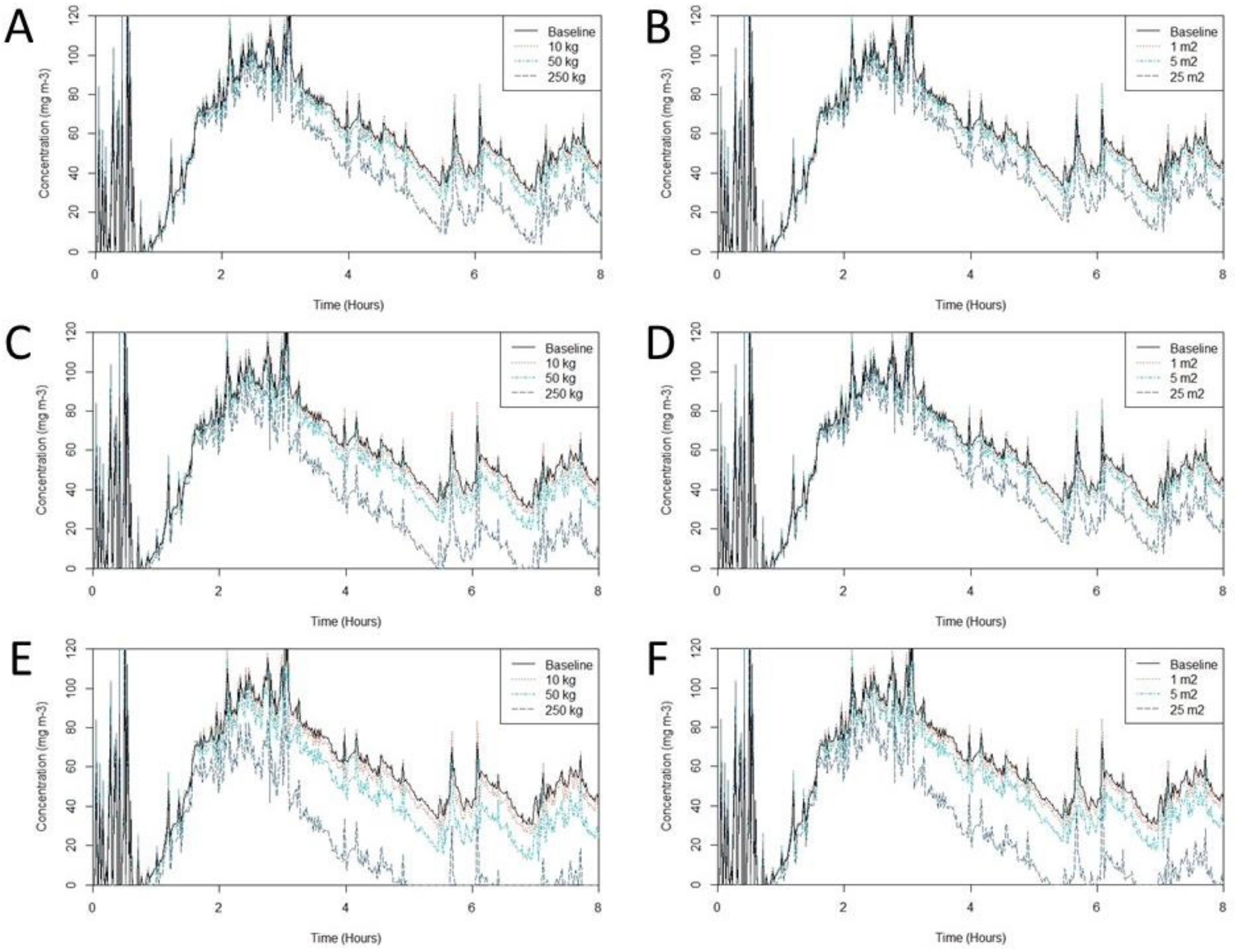

Fig. 4.11. Salon models for (A) AC20 passive flow (mass), (B) AC20 passive flow (SA), (C) AC50 passive flow (mass), (D) AC50 passive flow (SA), (E) AC20 active flow (mass), and (F) AC20 active flow (SA).

4.5. Discussion

Results from optimization experiments showed that flow conditions and external surface area had the greatest impact on removal rates and that, while greater mass ratios of AC enhanced adsorption rates, they had a less pronounced effect than either of the other parameters investigated.

It was demonstrated that *in situ* thermal regeneration of this system with a resistance heating element was mostly ineffective. Of the four regeneration cycles performed in this study, none were able to raise VOC concentrations in the chamber above 30% of the initial concentration. This indicates that the VOC removal process with this material may not be fully reversible under these conditions. Possible reasons for irreversibility include chemisorption as a primary removal mechanism and high adsorption energy for this system (requiring greater amounts of energy to desorb acetone). Further research is needed to resolve which possible mechanism is responsible for the loss of regeneration efficiency observed.

Passive SA-normalized adsorption rates were up to 3 orders of magnitude greater than those previously reported in Ataka et al., (2004), Zuraimi et al. (2018), and Huang et al. (2019), which were 0.0018 mg m^{-2} min^{-1}, 0.0005 – 0.0035 mg m^{-2} min^{-1}, and 0.0021 mg m^{-2} min^{-1}, respectively. This may be due to a difference of adsorbates and reflect a high adsorption affinity for acetone (Wang et al., 2019). It may also be due to different reporting methods, different test conditions (e.g. open vs. closed system), or different gas measurement methods, although the measurement method used in this study has been shown to closely match theoretical predictions based on principles of mass conservation (shown in Chapter 3).

Active flow SA-normalized removal rates were shown to not scale directly with SA, and the dimension of sample thickness was shown to impact this rate; thicker samples demonstrated a higher removal rate per unit area. The use of SA-normalized removal rates is common in research of passive adsorption technology; however, our findings suggest that this value may not adequately represent the removal characteristics of a material when active surface flow is utilized.

Since thickness has been shown to play a role in the adsorption properties of this system, additional research should be performed to determine when the benefits of this parameter begin to experience diminishing returns. Added benefits of sink thickness should be weighed against added material costs to optimize not only the efficiency of the system, but also the economy.

VOC removal models showed that the impact of adsorbent sinks on VOC concentrations in nail salons could be substantial. Effective ventilation rates Qeff and ACHeff for SA-normalized cases ranged from 3.32 m^3 hr^{-1} to 143 m^3 hr^{-1} and 0.00 ACH to 0.10 ACH, respectively. Q_{eff} values for 1 m^2 cases (3.32 - 9.03 m^3 h^{-1} m^{-2}) resemble those previously reported by Ataka et al. (2004) (5.5 - 6.1 m^3 h^{-1} m^{-2}).

The cost of materials used in this study were quite low, with the price of bulk AC as low as 2.5 USD per kg, and the price of plaster 2-10x lower than that. We estimate that the type of sinks described here (20% AC) could be produced for less than 6.5 USD per m^2 in material costs, or approximately 160 USD for a 25 m^2 installation. Since the technology is scalable, the amount of sorbent could be easily be increased to accommodate higher loading in an environment like nail salons, although available mounting surface remains a major constraint.

4.6. Conclusions

Indoor passive VOC removal technology has the potential to alleviate health hazards inside of nail salons. Huang et al. (2019) estimated a 4.84-5.73x10^{-4} reduction in cancer risk to building occupants when micro-carbonized building materials were used to remove formaldehyde. This is approximately the same level of cancer risk that was estimated for nail salon workers in Lamplugh et al. (2019).

The air-cleaning art system tested here was shown to remove VOCs from air in both active and passive flow conditions during controlled testing. Models developed from the removal data also demonstrated that this system could have a significant positive effect on VOC concentrations in the nail salon environment. Regeneration experiments showed that heating of the material *in situ* did desorb some acetone, however, the amount of acetone desorbed was quite low with respect to initial concentrations (< 30%). Additional research should be conducted to determine what factors contributed to irreversibility in this system.

Despite some inconclusive results, the low-cost of the materials used in this technology, as well as potential benefits from predicted VOC reductions, create a strong case for continued research in this area.

CHAPTER 5

CONCLUSIONS, RECOMMENDATIONS, AND FUTURE DIRECTIONS

5.1. Summary Scientific Contributions

The purpose of the research presented in this dissertation was to (1) assess worker exposure to VOCs in Colorado nail salons, (2) determine what risks may be associated with exposure at the VOC levels observed, and (3) explore alternative means of mitigating occupational VOC exposure using low-cost adsorbent materials.

The nail salon exposure study described in Chapter 2 investigated VOC exposure in 6 Colorado nail salons and found that nail salons workers were exposed to high concentrations of VOCs including acetone, ethyl acetate, n-butyl acetate, methyl methacrylate (MMA), and formaldehyde, as well as the aromatic compounds benzene, toluene, benzene, ethyl benzene, and xylenes (BTEX). Comparison with relevant exposure standards found that workers in one salon were exposed to formaldehyde levels over the NIOSH recommended exposure limit of 16 ppb. Workers in two nail salons were also at risk of olfactory epithelial degeneration based on their exposure to MMA above the US EPA inhalation reference concentration (RfC) of approximately 171 ppb.

A simple linear dose-response model found that workers in all nail salons, who worked 20 years or more, faced significant increased risk of squamous cell carcinoma, nasopharyngeal cancer, Hodgkin’s lymphoma, and leukemia ($> 1x10^{-6}$) based on occupational exposure to formaldehyde. Likewise, all workers faced an increased risk of leukemia due to occupational benzene exposure.

The findings of this study present the need for additional research to investigate the incidence of cancer among U.S. nail salon workers through both cross-sectional and longitudinal health studies. Additionally, the results of the study highlight the importance of mitigating VOC exposure in this specific occupational environment.

Chapter 3 detailed a series of controlled experiments aimed at quantifying the VOC content, emission products, and emission rates of common nail care products, as well as VOC removal rates using low-cost adsorbents. A basic mathematical model was developed using input data from the field study in Chapter 2 and the adsorption rate equations obtained from the VOC removal experiments. Results showed that using adsorbents in the nail salon environment could have a substantial, beneficial impact on air quality. Active flow, generated with synthetic jet actuators (SJAs), was found to enhance adsorption processes for both activated carbon and biochar, increasing adsorption rates in some cases by a factor of two. Active flow was found to have a negative effect on acetone adsorption with coco coir. While it is not clear exactly what led to this phenomenon, comparisons with results from BET and BJH material characterization suggest that active flow conditions likely provide the greatest enhancement to adsorption processes for microporous materials like activated carbon (2-3 nm pore width). Effective ventilation rates determined from our box model ranged from 29.3 m^3 h^{-1} (0.02 ACH), for 10 kg of fine AC under passive flow conditions, to 292 m^3 h^{-1} (0.21 ACH) for 250 kg under active flow conditions. This was followed by fine BC and fine CC which ranged from 18.2 m^3 h^{-1} to 213 m^3 h^{-1} and 5.79 m^3 h^{-1} to 182 m^3 h^{-1}, respectively.

Although the findings of Chapter 3 presented a clear justification for using adsorbents to mitigate VOC exposure indoors, they did not present a clear strategy for the implementation of these materials, nor did they include information regarding the useful lifetime of the materials.

These are non-trivial problems that warranted further exploration and were partially addressed in Chapter 4.

The research presented in Chapter 4 investigated the VOC removal capability of a novel, low-cost technology that utilizes AC embedded in common gypsum plaster. VOC removal experiments were conducted in a closed chamber under passive and active flow conditions with acetone as the sorbate. Normalized mass removal rates were calculated from concentration data. Three different optimization parameters were presented and tested: (1) The ratio of AC mass to plaster in the sink mixture, (2) external surface area (SA) of the sorbent sink (tested at constant sample volumes), and (3) flow conditions in the chamber (i.e. passive or active flow). Two different removal rate equations (mass-normalized and surface area-normalized) were determined from experimental data and used in a mathematical model to predict the impact of sorbent sinks in a typical nail salon. Additionally, *in-situ* regeneration of the sink via resistance heating was tested, where the test circuit was controlled by a low-cost, programmable microcontroller.

The performance of sorbent sinks was found to be dependent on both external surface area and sample thickness. Active flow conditions (generated with a synthetic jet) were demonstrated to enhance acetone removal from the air. Model results indicated that sorbent sinks could provide beneficial VOC removal in nail salons but required a SA of approximately 25 m^2. Estimated effective ventilation rates from the model ranged from 3.32-9.03 mg m^{-2} h^{-1}, which was similar to values reported in a previous study (Ataka et al., 2004). Despite the large SA required for sorption, it was estimated that the cost of the sink materials would still make the technology attractive to consumers, particularly if the technology had the added benefit of enhancing aesthetics in the indoor environment. Regeneration tests were inconclusive but indicated that substantial portions of the VOC removal observed may not be easily reversible.

Taken together, the research in Chapters 2, 3, and 4 comprise a full examination of the nail salon VOC exposure issue, from assessment of the problem to development of a potential solution. This work stops short of an actual field evaluation of the proposed technology, but it does establish definitive proof-of-concept that will likely lead to a full-scale trial in the near future. Findings from the three studies have contributed to knowledge in several fields including public health, exposure science, material science, air quality measurement, and building science.

5.2. Recommendations for Follow-Up Research

There were many lessons learned in the course of this research that could be applied to follow-up work, especially the field-testing of novel, air-cleaning adsorbent sinks. Fig. 5.1 shows the minimum recommended sampling plan for a field test of the air-cleaning art intervention. The field testing is broken into two back-to-back sampling periods (pre-testing and post-testing), between which the adsorbent sinks would be installed in the test environment. The pre-testing period establishes a baseline that is used to determine variation in the post-testing period. It was found during the initial exposure study that formaldehyde (HCHO) monitors that use electrochemical sensors demonstrated little-to-no correlation with the established DNPH cartridge sampling method (US EPA TO-11A) when other VOCs were present in high concentrations. Therefore, this type of monitor should be avoided in follow-up nail salon field studies. Depending on resource availability, formaldehyde has also been accurately measured using proton transfer reaction - mass spectrometry (PTR-MS) (Warneke et al., 2011) and cavity ringdown spectroscopy (CRS) (Dahnke et al., 2002; Gorrotxategi-Carbajo et al., 2013), both of which can be operated online for time-resolved data collection. Whole-air samples (WAS) analyzed with GC-MS (US EPA TO-15) should be used to quantify concentrations of other VOC species present in the environment.

Scheduling pre and post-testing periods as closely as possible (in consecutive days or weeks) will help to reduce variability caused by seasonality and other factors. Measured concentrations should also be normalized by the number of salon services performed on each measurement day. Efforts should also be taken to measure or estimate ventilation rates during measurement days, either using CO_2 concentrations as a proxy or by measuring flow velocities in the vents with an anemometer. An optional second post-test measurement period (not shown) should also be considered at 1-2 months past the intervention to capture the long-term effectiveness of the VOC removal system.

Some gas species that were measured in the initial nail salon exposure study such as benzene are sometimes found in high concentrations outdoors. Consequently, performing a second set of outdoor measurements on all test days can help to resolve the source and fate of certain gas species that are of dubious origin.

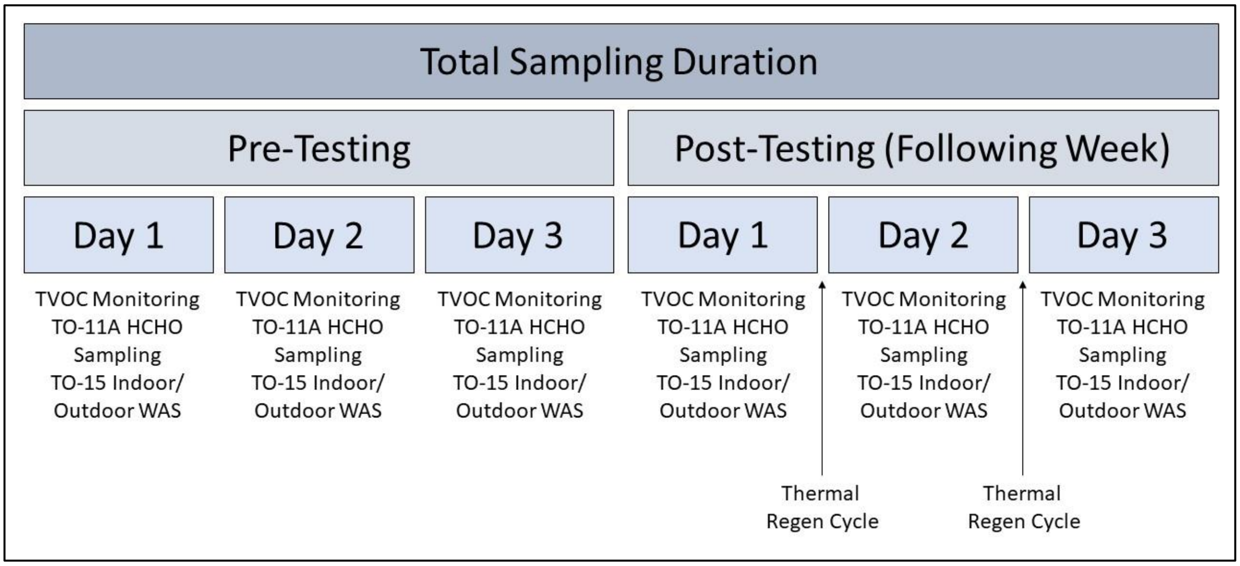

Fig. 5.1. Minimum recommended sampling plan for possible intervention study

Although TVOC data from a PID is not speciated, and therefore inadequate for overall quantitation of VOC concentrations in the nail salon environment, the time-resolved nature of the data is useful in determining the impact that this intervention may have on VOC concentration peaks throughout the business day. Alternatively, other instruments that provide time-resolved VOC concentration data (e.g. PTR-MS and CRS) could be used in place of a PID to capture speciated, time-resolved VOC levels.

Thermal regeneration of the adsorbent sinks should be performed in between each measurement day in the post-testing period using a convective heating appliance like an oven; ideally this would take place immediately prior to the start of business each morning. Additional, VOC measurements (not shown) taken during the regeneration period (outside of business hours) would help to verify that VOC reductions observed between pre and post-test periods are attributable to adsorption by the sinks, rather than other factors.

In addition to field testing the air-cleaning art system, further work should be performed to assess how optimization parameters investigated here affect material properties of the adsorbent sinks. For example, maximizing the amount of activated carbon in the system helps to increase the adsorption capacity of the material; however, the addition of activated carbon also weakens the structure of the gypsum plaster. Using procedures outlined in the European Standard UNE-EN 13279-1 (UNE, 2009), plaster samples with various amounts of activated carbon, similar to the ones used in Chapter 4, could be tested for flexural strength, compressive strength, and Young’s modulus using a common universal testing machine. The same type of testing could be used to determining if and how thermal regeneration processes lead to structural degradation of the sink materials.

Lastly, identifying the factors affecting the regeneration efficiency of air-cleaning art samples is critical to the future success of this project. Additional research should include regeneration tests at a range of temperatures, as well as an investigation of any surface chemistry changes or reaction products that would indicate whether chemisorption is taking place.

5.3. Community-Based Methods, Community Interactions, and Engineering for Developing Communities

Community engagement (CE) and participation has historically been a problem for researchers in fields like health (Wallerstein and Duran, 2010) and engineering (Urmee and Gyamfi, 2014; Bielecki and Wingenbach, 2014; Harsh et al., 2016). In order to enhance our ability to conduct research within the Vietnamese nail salon community, we adopted several aspects of community-based research methodologies used to improve engagement and participation in diverse communities, democratize knowledge, and promote co-learning and empowerment.

Prior to commencing our exposure study, we recruited and trained several undergraduate researchers who were affiliated with the Vietnamese nail salon community in Colorado, USA. Unlike some studies that focus on using community members to perform peer-driven recruitment (Simon and Mosavel, 2010), our goal in recruiting these researchers was to build research capacity within the Colorado nail salon community. Two of these researchers were included as authors in 3 of our related publications; all gained valuable research training and experience that we hope will benefit their communities.

Part of the agreement signed with each salon included a promise to disseminate the findings of the exposure study to salon owners and workers, along with recommendations for improving air quality in participating salons. Salon reports contained VOC concentration data, comparisons to other salons in the study, symptoms reported, and recommendations for improved practices (with links to several published resources in both English and Vietnamese). These reports were delivered to salons in person, with a volunteer Vietnamese translator present. Reports were provided to salon owners and workers in both English and Vietnamese.

Response to the reports was encouraging, and eventually led to a focus group meeting in Spring 2018, in which representatives from half of the participating nail salons from the exposure study met over dinner in a salon owner's home. The meeting covered the results of the exposure study, and included some recommendations for improving occupational air quality, but was primarily focused on gaining valuable insight from community members about how they perceive the exposure "problem", as well as how these businesses typically operate and what solutions may be workable in a potential intervention. At this meeting we discovered that workers and owners were at least somewhat aware of the VOC exposure problem, which they primarily associated with odors. Additionally, they were aware that many common practices like the use of dust masks were ineffective against all pollutants that they encountered; most focus group members also expressed that they generally valued health, and commonly associated health with air quality. In terms of interventions, nail salon owners were most interested in practices and technology that blended with existing salon practices. The majority of focus group members indicated that passive air cleaners and improved mask technology were attractive to them and expressed interest in our air-cleaning art proposal, even indicating preferred aesthetic styles for their salons. We expect that future intervention studies involving this community will benefit from previous engagement, as well as community participation in the planning stage of the research process.

Ultimately, our research group was successful in engaging the Vietnamese nail salon community and at including members of the community in our research efforts. Additionally, the Vietnamese language skills present on our team were necessary to engage community members and conduct research within this industry. Other researchers in this field should consider similar approaches when conducting studies with diverse communities, and, when possible, seek out supplemental training (Harsh et al., 2016) or adopt existing CE and CBPR frameworks (Lavery et al., 2010; Ahmed and Palermo, 2010; Shirk et al., 2012; Ramirez et al., 2012). Furthermore, engineering and physical science departments interested in researching with or designing for diverse and developing communities should first work on introducing sociological concepts into their curriculum (Garff et al., 2014).

5.4. Cross-Disciplinary Art and Science Collaboration

Divisions between art and science in Western culture are large, however these traditional boundaries are cultural products rather than practical necessities (Pearce et al., 2003). Many of history’s greatest scientists were also artists, philosophers, and musicians including Leonardo da Vinci, Alexander Borodin, and Robert Hooke. Consequently, it seems possible that the art/science dichotomy may simply exist as a distinction inherited from previous generations rather than a concrete fundamental difference (Eisner & Powell, 2002). While it is unclear what led to the divergence of arts and sciences as related disciplines, it appears that the introduction of the computer and the subsequent shift to a science and technology driven society may have accelerated it (Pearce et al., 2003).

Despite the modern perception that art and science are unrelated, or the popular scientific belief that form follows function, the value of aesthetics in engineering technology seems highly intuitive. Several studies of web surveys and digital user interfaces have shown that aesthetics have a significant impact on user experience including perceptions of ease of use and usefulness (Li & Yeh, 2010; Casey & Poropat, 2014; Lazard et al., 2015). Scientists have also identified artists’ abilities to (1) provide lateral thinking about technology and science, (2) socialize and humanize technologies, (3) challenge dominant structures, and (4) engage in actual invention (Peace et al., 2003).

Potential reasons that art and science collaborations remain limited include notions of “discipline-as-identity” and the fact that reward structures in both art and science disciplines do not support serious art/science collaboration, reducing phrases like “inter-disciplinary” to clichés and catchphrases (Pearce et al., 2003). Another deterrent to this type of collaboration is the fact that academic papers that feature broad collaboration from non-heterogeneous subject areas are often viewed as lower quality and less impactful (Franceschet & Costantini, 2010).

In Chapter 4 of this dissertation, we present a novel, low-cost adsorbent sink platform, which we refer to as “air-cleaning art”. Although the samples used for testing do not appear as art (Fig. 5.2A), the materials tested are made from traditional art media (gypsum plaster), which in the right hands can easily be transformed into the highly aesthetic art piece shown in Fig. 5.2B.

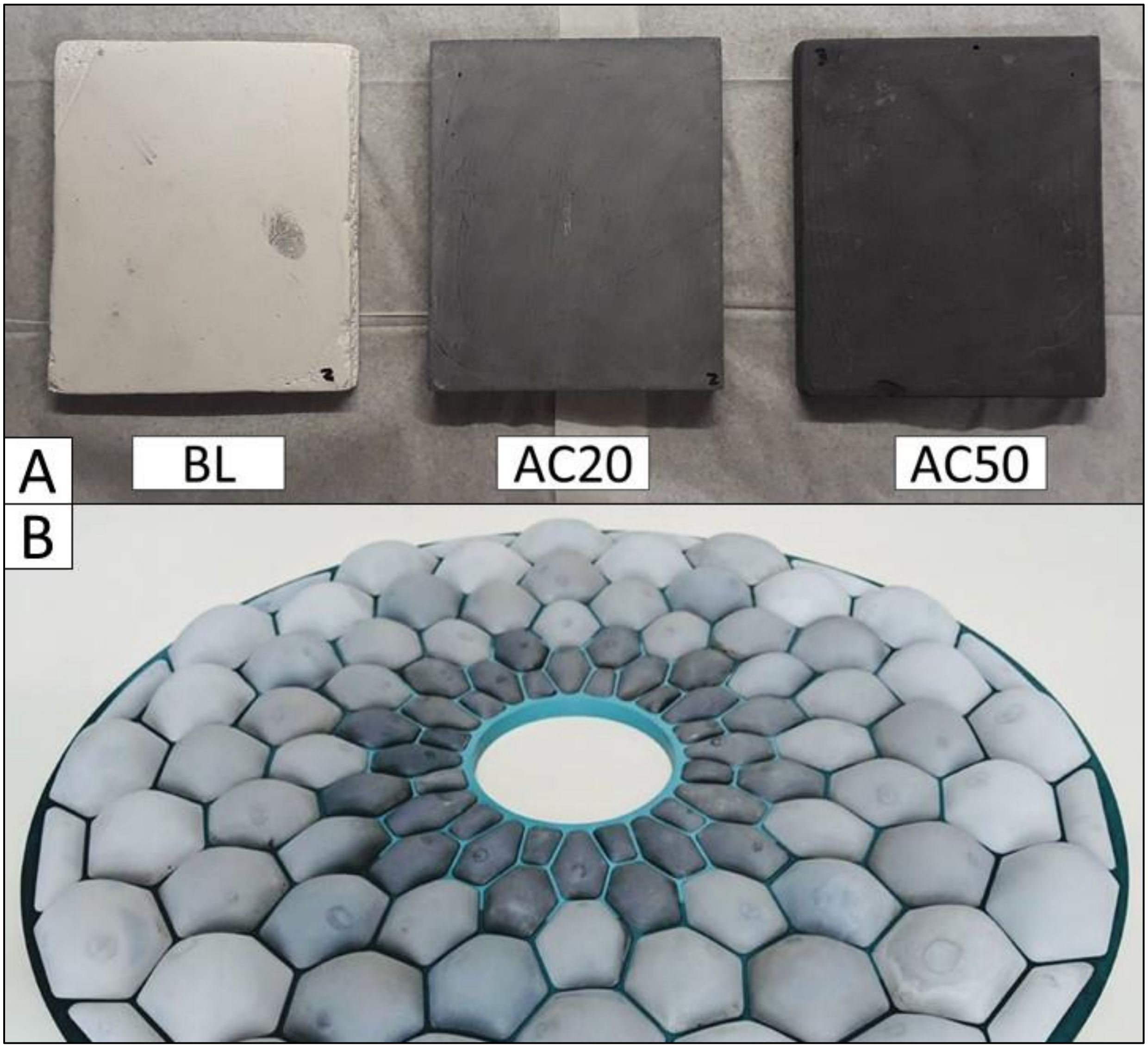

Fig. 5.2. (A) Adsorbent sink material used in test samples and (B) Adsorbent sink materials used in art.

The work presented in Chapter 4, as well as the art piece shown in Fig. 5.2B involved a collaboration with between the CU Boulder Department of Mechanical Engineering and the CU Boulder Department of Art and Art History. The goal of the project was to develop a passive VOC removal system capable of cleaning the air inside of nail salons through adsorption processes rather than ventilation. Air-cleaning art pieces were developed to be aesthetically pleasing, and to enhance both the look and the feel (air quality) of nail salons. The interdisciplinary collaboration was designed to combine the form and function aspects of the respective disciplines (Art and Engineering) to develop a VOC removal system that was simple, elegant, and effective.

The project yielded practical proof-of-concept (Chapter 4), as well as several sleek, modern designs for future use and implementation. Designs were brought back to stakeholders in the Colorado nail salon community, who expressed their general approval and invited our research team back for future intervention testing. In this work, the individual strengths of both art and science disciplines complemented each other to enhance project outcomes, resulting in improved functionality and end-user satisfaction.

Successful collaborations of this kind have far-reaching implications, not only in terms of enhancing research products, but also in addressing issues beyond the scope of traditional engineering (e.g., technology adoption, user interaction, and human behavior). It is important that, as some problems become increasingly trivial, we focus effort on the human aspects of science and engineering, rather than pursuing function and efficiency into the realm of diminishing return. In light of this, many physical science disciplines would benefit from increased collaboration with truly disparate fields of study and an overall broadening of perspective.

5.5. Scientific Contributions

Although previous studies documented VOC exposure in this type of occupational environment (Quach et al., 2011; Alaves et al., 2013; Zhong et al., 2019), prior to the nail salon exposure study, reported here, there had been no research which estimated long-term health risk for U.S. nail salon workers. This was an important contribution to the body of work surrounding occupation VOC exposure in nail salons, in that it provided comparisons and metrics that were arguably more accessible than those presented in previous publications. Since its online publication, in March 2019, the results of this study have been circulated through various media outlets to locations as far as Hong Kong and Indonesia (Jiashan, 2019; Iskandarsjah, 2019). We hope that this work continues to attract public interest and leads to actions that improve working conditions in salons.

Despite some previous research concerning passive, adsorbent-based air cleaners, no other study had previously attempted to develop a truly deployable adsorbent sink with *in situ* regeneration or aesthetic appeal. While the results of this work were not entirely conclusive, we did demonstrate limited proof of concept and present model results that suggest this type of intervention could be useful in reducing VOC exposure in salons.

Because of its unique framing of the issue, as well as its novel approach to addressing the underlying problem, we believe the research presented in this dissertation can be considered entirely original, and potentially quite valuable to this area of study.

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APPENDIX I - OCCUPATIONAL EXPOSURE TO VOLATILE ORGANIC COMPOUNDS AND HEALTH RISKS IN COLORADO NAIL SALONS

Supplementary Tables and Figures

Supplementary Tables:

Table S1. Lower Limit of Quantitation (LLOQ) values for each compound measured during personal exposure sampling.

Compound	LLOQ (ppb)
Acetone	72
MEK	60
Ethyl Acetate	51
MMA	57
n-Butyl Acetate	49
Benzene	53
Toluene	39
Ethylbenzene	55
Xylenes	54

Table S2. Formaldehyde results from collocation experiment with DNPH-Silica cartridges (US EPA Method TO-11A) and electrochemical monitors.

Salon	TO-11A 8-h Average (ppb)	Electrochemical 8-h Average (ppb)
Salon 1	11.0	340
Salon 2	8.17	3
Salon 3	5.33	0
Salon 4	13.1	60
Salon 5	21.5	180
Salon 6	7.31	110

Table S3. p-values from statistical analysis of worker health surveys

	Nose Irritation	Throat Irritation	Lung Irritation	Skin Irritation	Eye Irritation	Headache	Nausea	Cough	Increased Pulse	Confusion	Shortness of Breath	Chest Tightness
Age	0.8352	0.7687	NA	0.7834	0.4974	0.3645	NA	0.0794	NA	0.6107	0.2715	0.2715
Yrs. Worked	0.8906	**0.0019***	NA	0.8266	0.4277	0.7455	NA	0.4725	NA	0.9785	0.7442	0.7442
Hours/Wk.	**0.0261***	0.2976	NA	0.6312	0.4888	0.0832	NA	0.3968	NA	**0.0003***	0.5793	0.5793
Acetone Max	0.1203	0.7286	NA	0.9581	0.7181	0.8377	NA	0.3663	NA	**0.0409***	0.9258	0.9258
Acetone Min	0.0742	0.9700	NA	0.5448	0.6281	0.9372	NA	0.2137	NA	0.9660	0.7471	0.7471
MEK Max	0.6020	0.6059	NA	0.0852	0.0853	0.3167	NA	0.0855	NA	0.0855	0.0855	0.0855
MEK Min	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Eth.Ace. Max	0.7165	0.0530	NA	0.7280	0.9332	0.0820	NA	0.2341	NA	0.4259	0.6819	0.6819
Eth.Ace. Min	0.1338	0.3338	NA	0.7295	0.9137	0.6722	NA	0.0613	NA	0.7043	0.8629	0.8629
MMA Max	0.4529	**0.0006***	NA	0.3771	0.3288	0.3523	NA	0.6649	NA	**0.0385***	0.5735	0.5735
MMA Min	0.3458	0.0999	NA	0.6347	0.3559	0.3997	NA	0.7854	NA	**0.0198***	0.6755	0.6755
But.Ace. Max	0.9855	0.6693	NA	0.0907	0.1314	0.8487	NA	0.1128	NA	0.7568	0.6227	0.6227
But.Ace. Min	0.6975	0.4215	NA	**0.0302***	0.1415	0.9419	NA	**0.0044***	NA	0.0672	0.5523	0.5523
Day 1 PE[1]	0.3067	0.8265	NA	0.4951	0.8091	0.4661	NA	0.4724	NA	**0.0122***	0.5082	0.5082
Day 2 PE[2]	0.0998	0.9069	NA	0.1906	0.3261	0.5820	NA	0.1262	NA	0.2266	0.5202	0.5202
Formaldehyde	0.9103	0.3632	NA	0.3524	0.4667	0.6111	NA	0.8320	NA	0.0663	0.4313	0.4313
Benzene	0.4042	0.2803	NA	0.4701	0.3766	0.3524	NA	0.6346	NA	**0.0235***	0.7174	0.7174
Toluene	0.6631	0.9636	NA	0.3851	0.2418	0.3865	NA	0.7586	NA	**0.0232***	0.3562	0.3562
Ethylbenzene	0.4231	0.8727	NA	0.1369	0.2869	0.7097	NA	**0.0016***	NA	**0.0011***	0.8285	0.8285
Xylene	0.4280	0.8760	NA	0.0808	0.1989	0.5669	NA	**0.0007***	NA	**0.0005***	0.7229	0.7229
BTEX	0.6658	0.8356	NA	0.3302	0.2097	0.3900	NA	0.7292	NA	0.0996	0.3063	0.3063

*Statistically significant ($p < 0.05$), [1]Total Day 1 Personal Exposure VOC concentration, [2]Total Day 2 Personal Exposure VOC concentration

Note: “Max” refers to the larger of the concentrations of an analyte measured on two separate sampling days, while “Min” refers to the smaller.

Supplementary Figures:

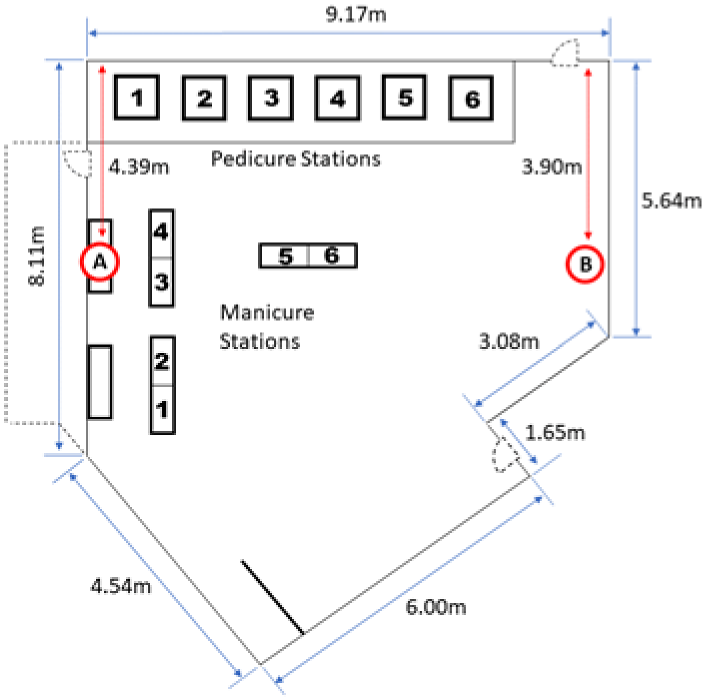

Fig. S1. Typical salon floor plan (Salon 6) with dimensions and sampling locations A and B.

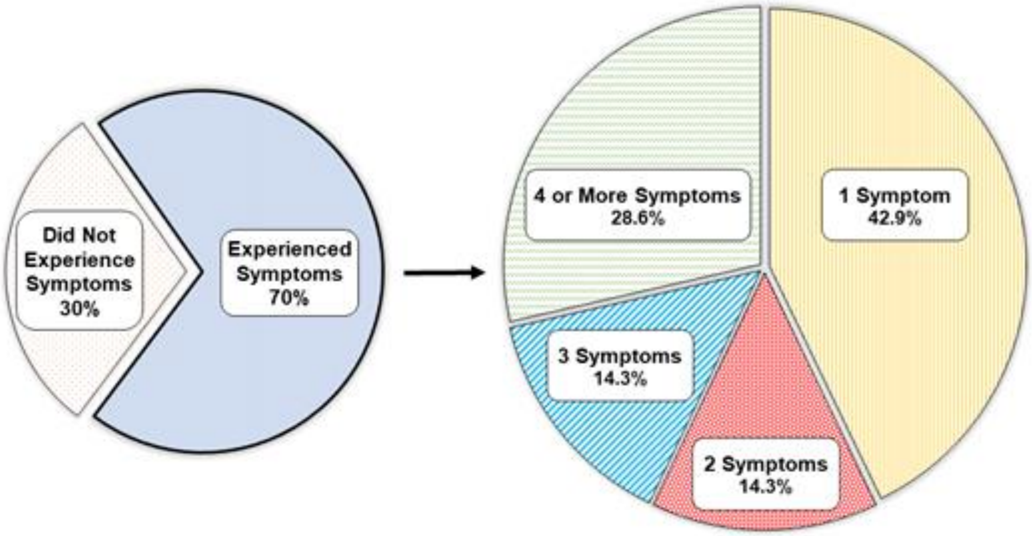

Fig. S2. Symptoms experienced by nail technicians in the study. (Left) Percentage of total workers (n=20) experiencing health-related symptoms. (Right) Breakdown of symptomatic workers based on number of symptoms experienced.

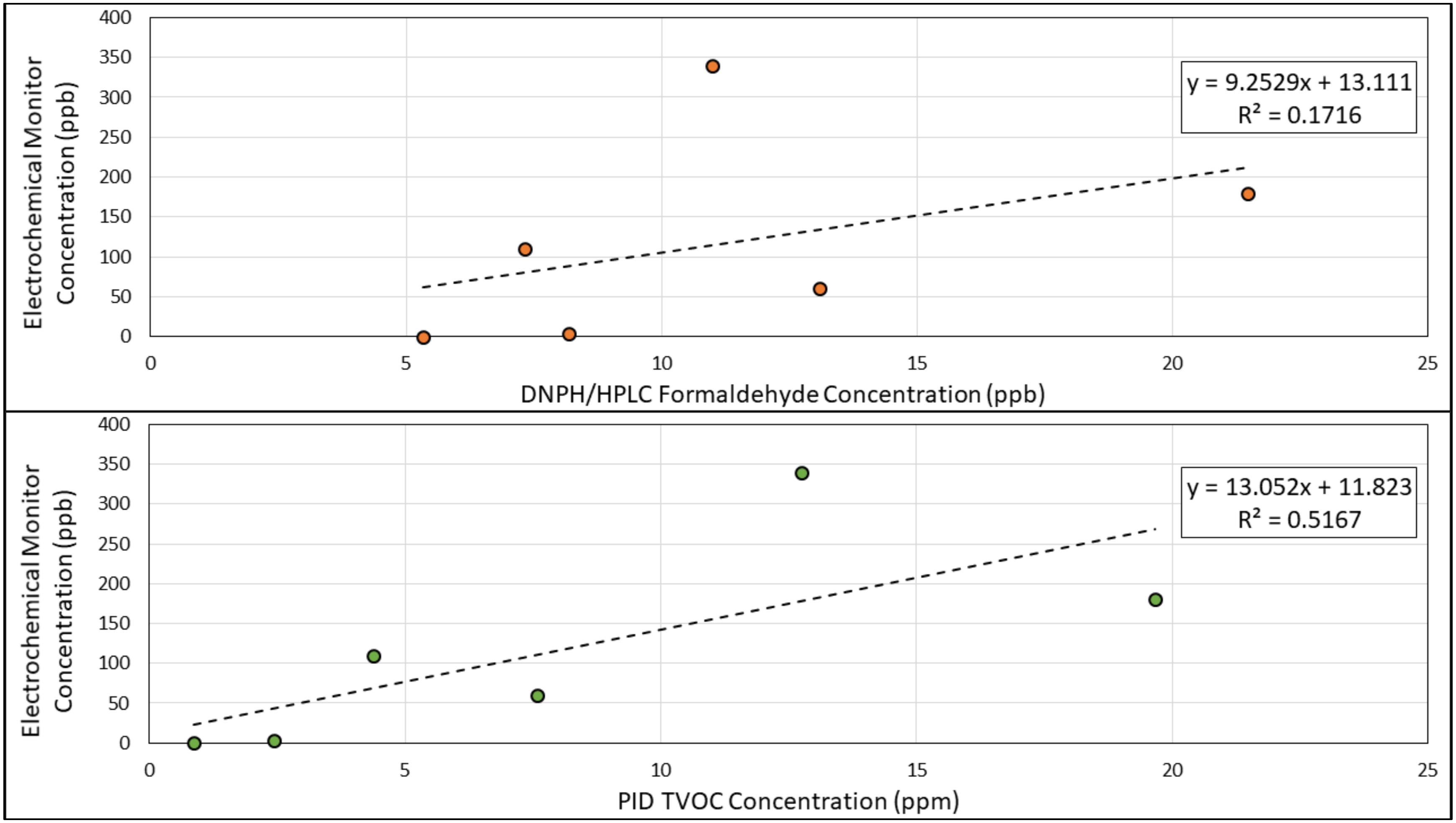

Fig. S3. Correlation plots of: (Top) Average electrochemical formaldehyde measurements and average US EPA Method TO-11A formaldehyde measurements with DNPH-Silica cartridges; (Bottom) Average electrochemical formaldehyde measurements and average TVOC measurements taken with a Photo-Ionization Detector (PID).

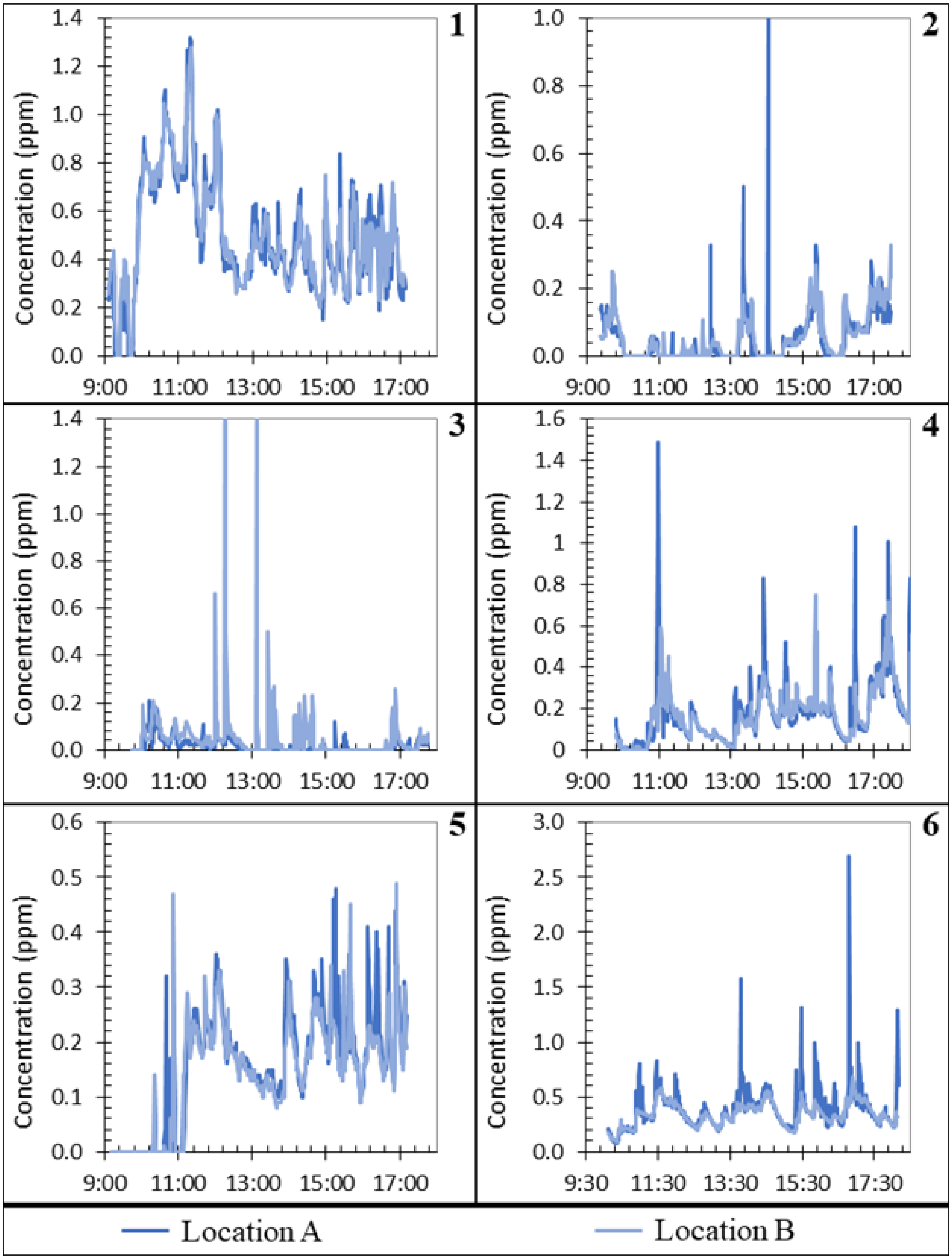

Fig. S4. Comparison of electrochemical formaldehyde measurements at locations A and B on one day in each salon.

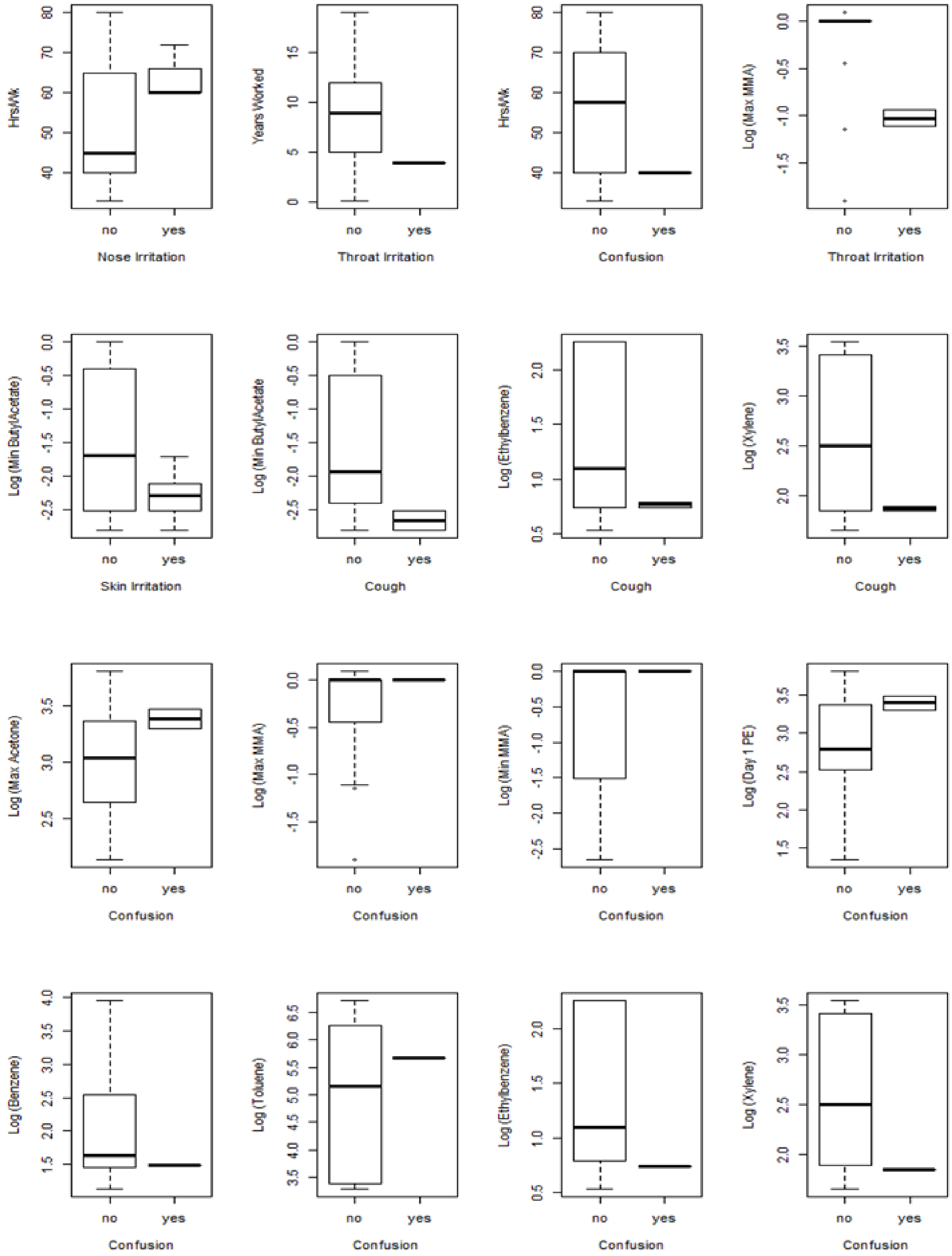

Fig. S5. Boxplots from significant associations ($p < 0.05$) between health-related symptoms and exposure factors.

APPENDIX II – VOC EMISSIONS FROM NAIL SALON PRODUCTS AND EFFECTIVE REMOVAL USING AFFORDABLE ADSORBENTS AND SYNTHETIC JETS

Supplementary Tables and Figures

Supplementary Tables:

Table S1. Model fitting values and correlations

Passive Flow		**a**	**n**	**R^2**	**Spearman ρ**
Fine CC	LC	3.167E-5	1.176E+0	0.718	0.856
	MC	3.167E-5	1.176E+0	0.780	0.925
	HC	3.167E-5	1.176E+0	0.949	0.943
Fine BC	LC	3.098E-5	4.447E-1	0.680	0.935
	MC	3.098E-5	4.447E-1	0.678	0.920
	HC	3.098E-5	4.447E-1	0.862	0.971
Fine AC	LC	5.124E-5	3.261E-1	0.874	0.941
	MC	5.124E-5	3.261E-1	0.863	0.956
	HC	5.124E-5	3.261E-1	0.969	0.990
Active Flow		**a**	**b**	**R^2**	**Spearman ρ**
Fine CC	LC	9.852E-6	9.091E-1	0.843	0.839
	MC	9.852E-6	9.091E-1	0.740	0.823
	HC	9.852E-6	9.091E-1	0.400	0.446
Fine BC	LC	4.635E-5	8.231E-1	0.869	0.917
	MC	4.635E-5	8.231E-1	0.825	0.968
	HC	4.635E-5	8.231E-1	0.874	0.983
Fine AC	LC	1.234E-4	9.862E-1	0.966	0.969
	MC	1.234E-4	9.862E-1	0.982	0.985
	HC	1.234E-4	9.862E-1	0.975	0.989

Supplementary Figures:

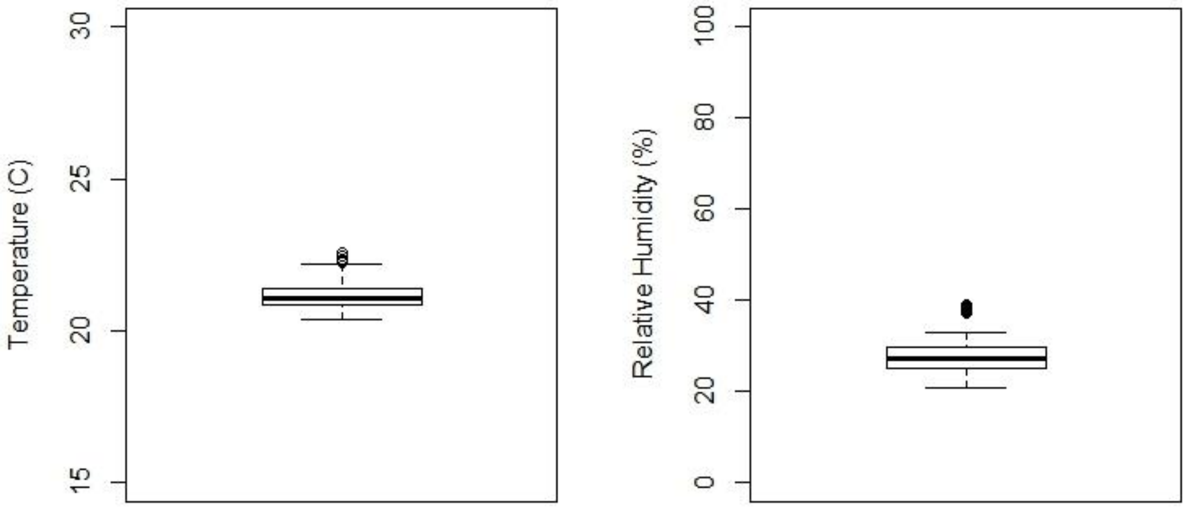

Fig. S1. All temperature and RH data collected during Chapter 3 emission and removal testing (n=55,452).

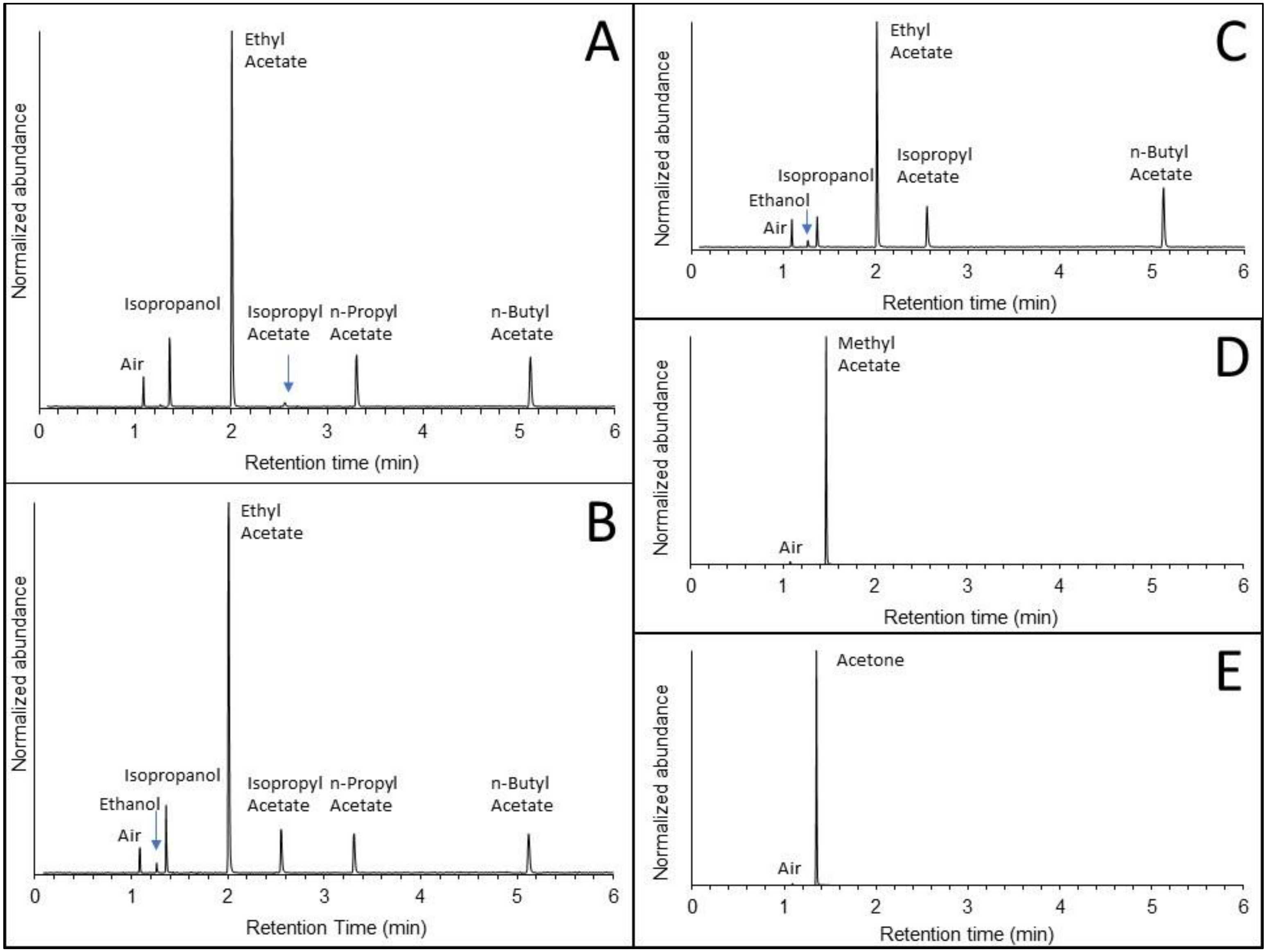

Fig. S2. Chromatograms from headspace analyses of (A) NP-1, (B) NP-2, (C), NP-3, (D) PR-1, and (E) PR-2

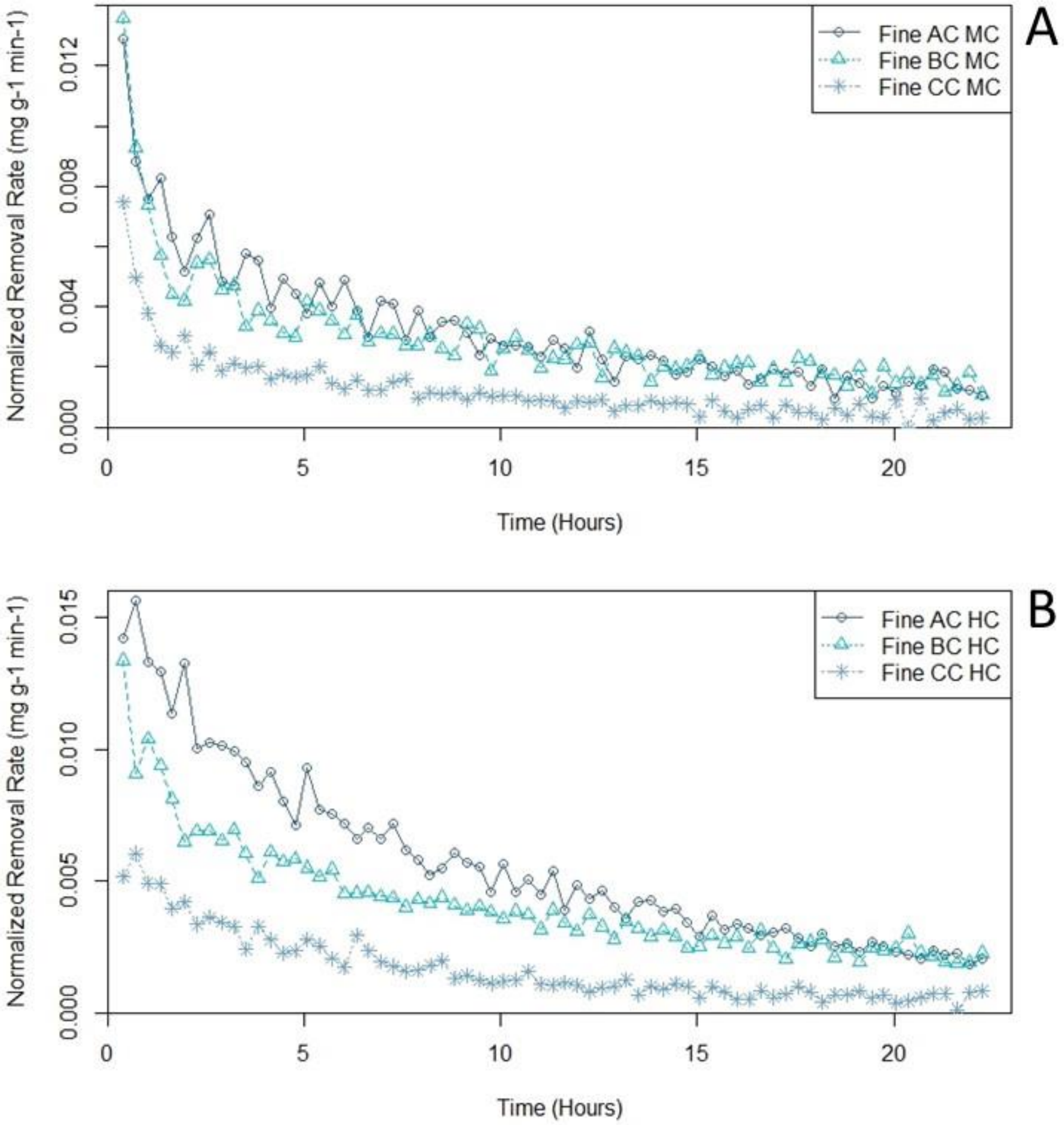

Fig. S3. Adsorption rates of fine CC, BC, and AC at (A) MC and (B) HC across 22.5 h.

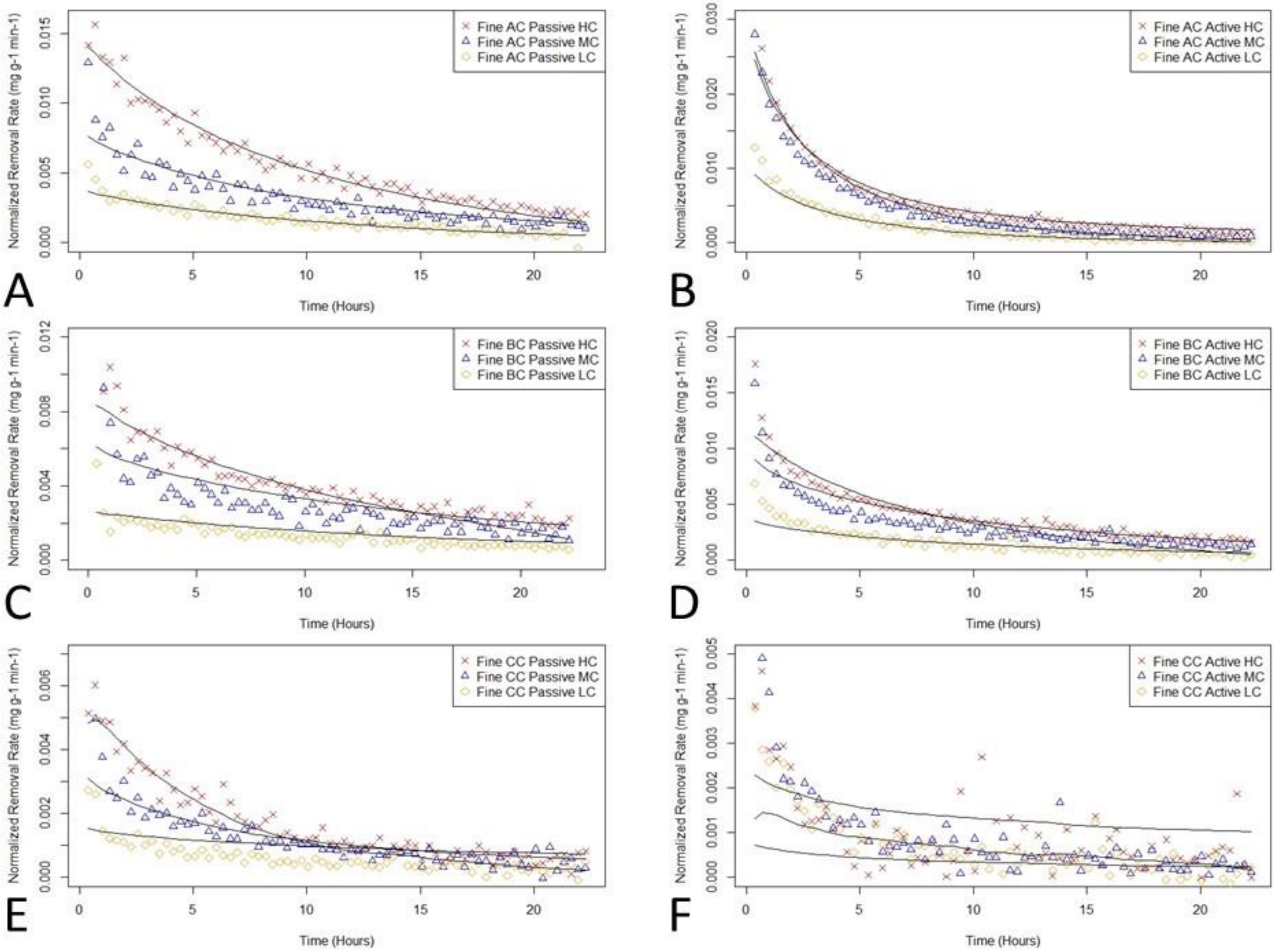

Fig. S4. Fitted removal rate data for fine grain materials: (A) AC Passive Flow, (B) AC Active Flow, (C) BC Passive Flow, (D) BC Active Flow, (E) CC Passive Flow, and (F) CC Active Flow.

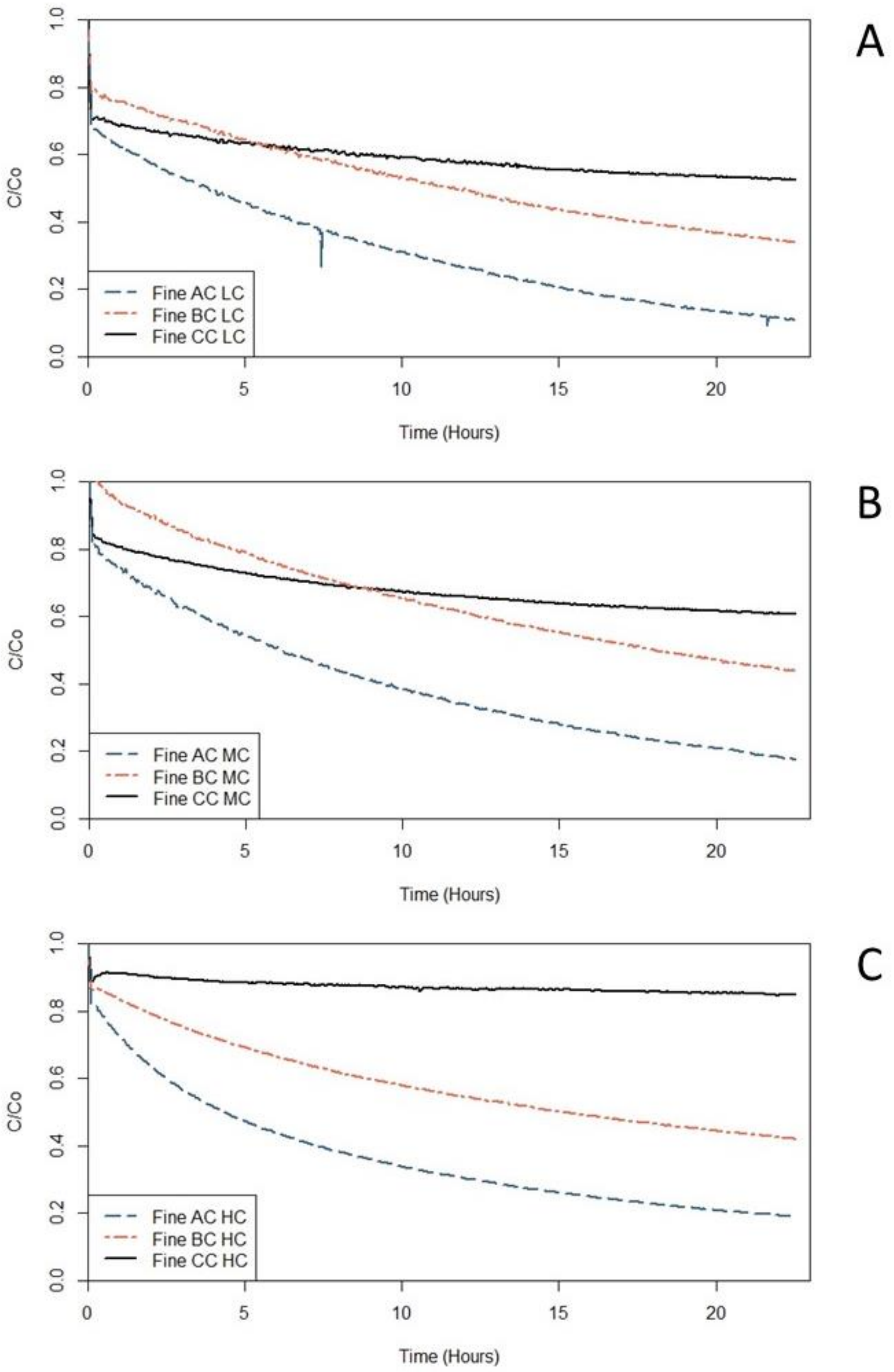

Fig. S5. Passive VOC removal of fine CC, BC, and AC at (A) LC, (B) MC, and (C) HC across 22.5 h.

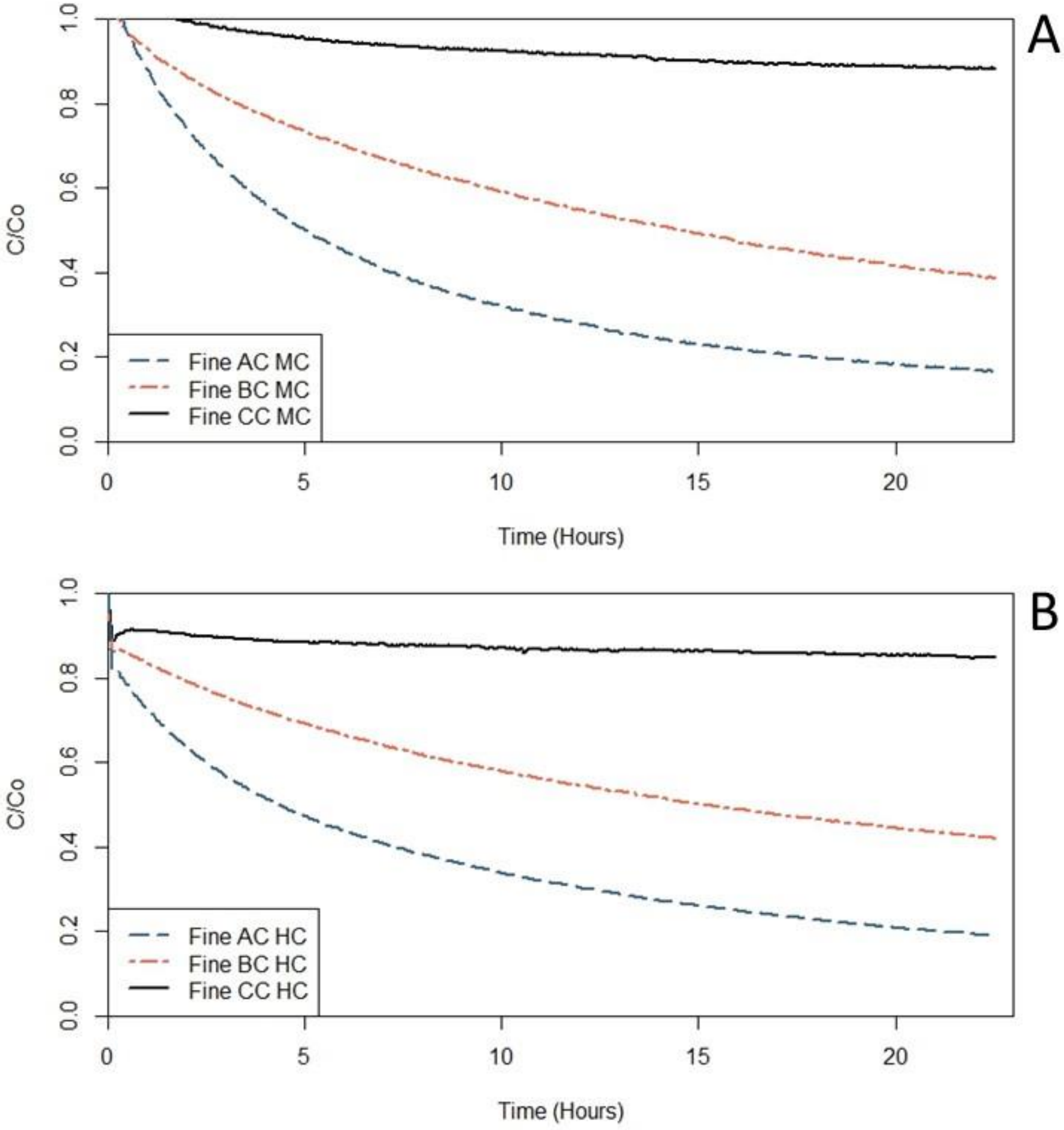

Fig. S6. Active VOC removal of fine CC, BC, and AC at (A) MC and (B) HC across 22.5 h

APPENDIX III – VOC REMOVAL IN THE NAIL SALONS USING NOVEL, LOW-COST SORBENT SINKS: AIR-CLEANING ART.

Supplementary Tables and Figures

Supplementary Tables:

Table S1. Model fitting values and correlations

Mass-Normalized		**a**	**n**	**R^2**	**Spearman ρ**
AC20 Sm	LC	8.027E-5	2.039E-1	0.973	0.997
Passive	HC	8.027E-5	2.039E-1	0.989	0.993
AC50 Sm	LC	1.288E-5	1.045E-1	0.989	0.999
Passive	HC	1.288E-5	1.045E-1	0.971	0.997
AC20 Sm	LC	3.300E-5	6.727E-1	0.996	1.000
Active	HC	3.300E-5	6.727E-1	0.999	0.951
SA-Normalized		**a**	**n**	**R^2**	**Spearman ρ**
AC20 Sm	LC	5.432E-6	2.039E-1	0.980	0.997
Passive	HC	5.432E-6	2.039E-1	0.989	0.993
AC50 Sm	LC	6.449E-6	1.045E-1	0.987	0.999
Passive	HC	6.449E-6	1.045E-1	0.971	0.997
AC20 Sm	LC	2.233E-5	6.727E-1	0.974	1.000
Active	HC	2.233E-5	6.727E-1	0.999	0.951

Supplementary Figures:

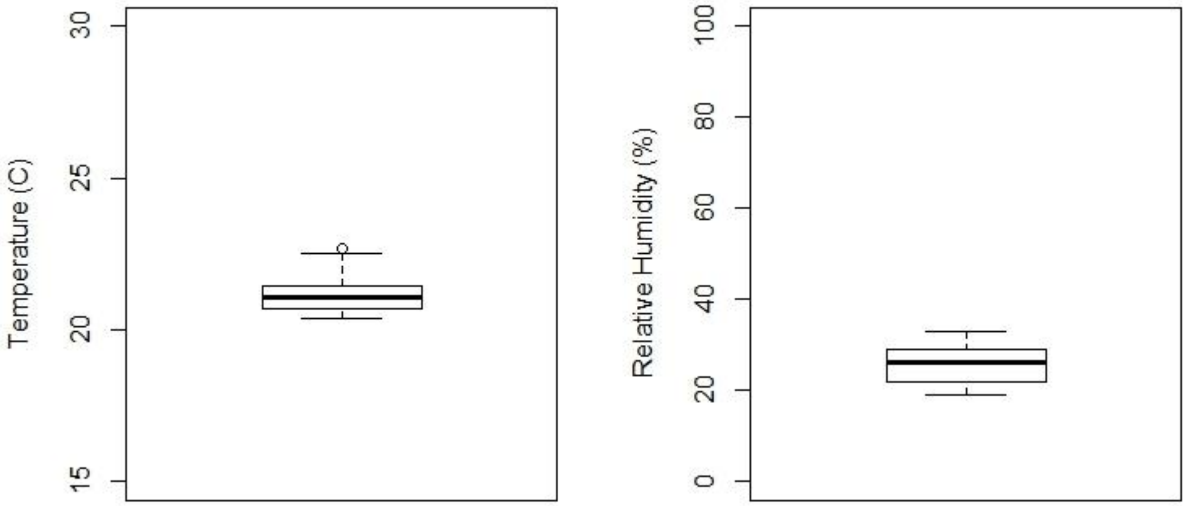

Fig. S1. All temperature and RH data collected during baseline and removal testing (n=23,931)

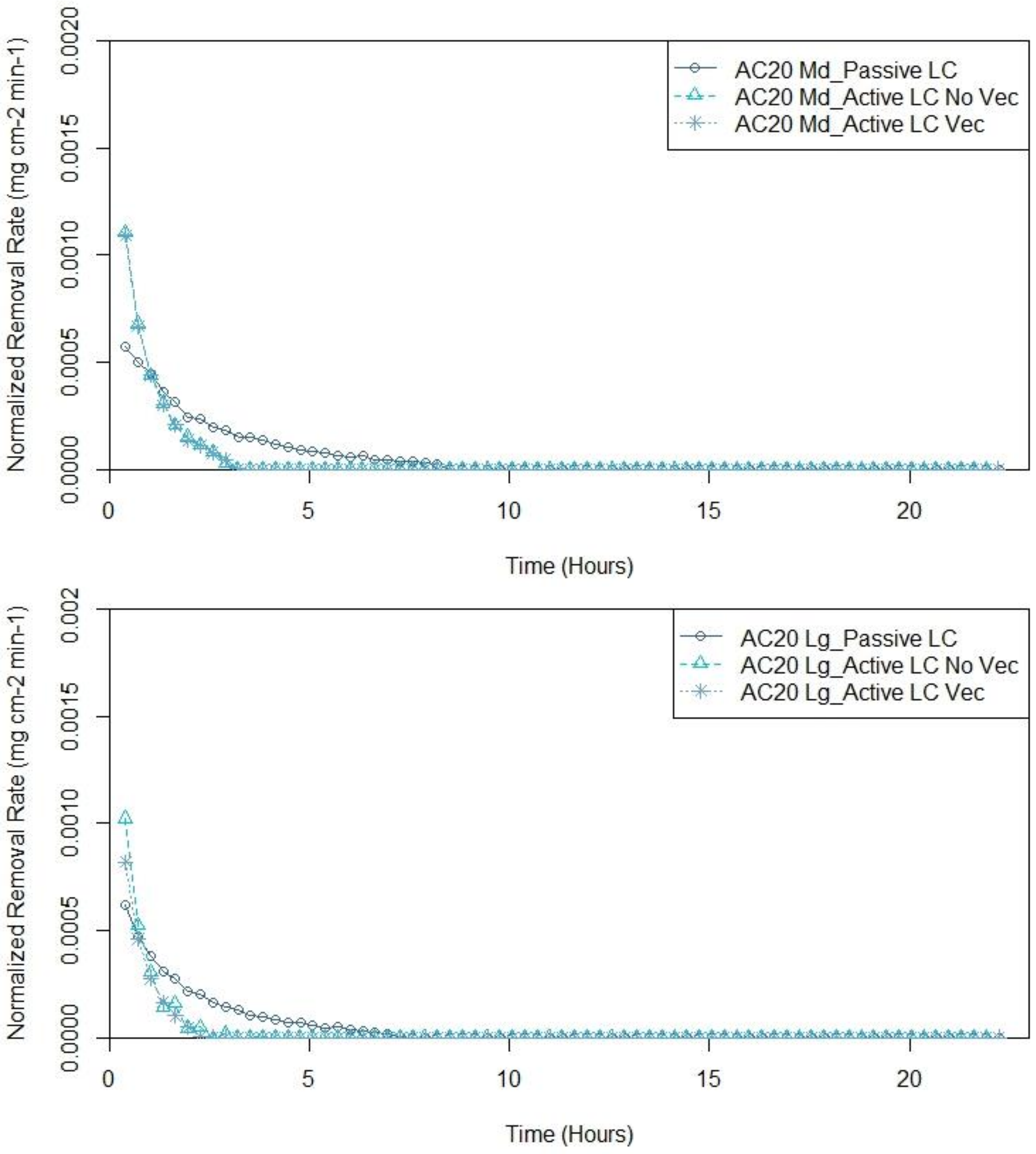

Fig. S2. Acetone removal with AC20 Md and Lg samples at LC, passive and active flow, with vectoring (Vec) and without vectoring (No Vec).

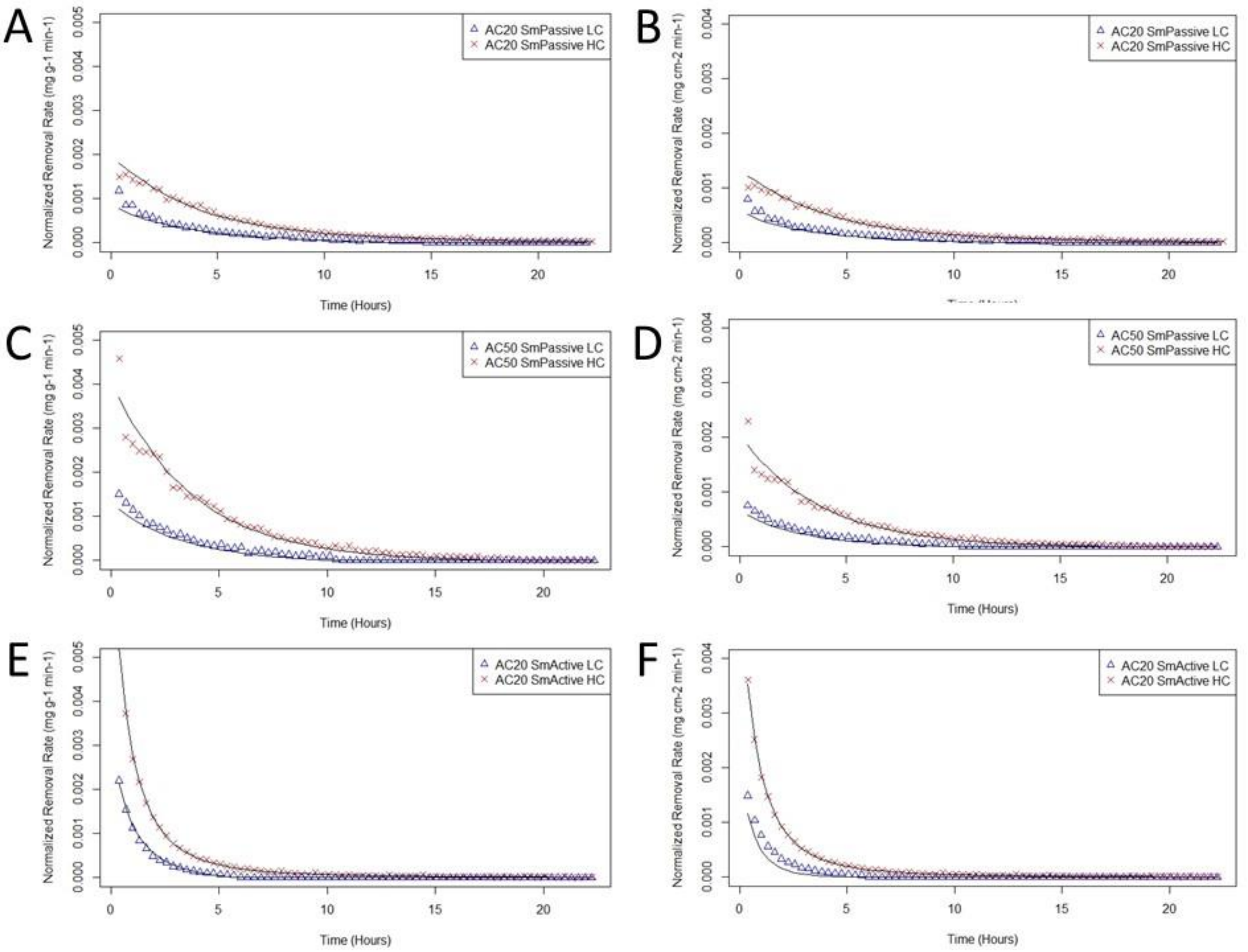

Fig. S3. Fitted removal rate data for sorbent sinks: (A) AC20 Sm Passive (mass), (B) AC20 Sm Passive (SA), (C) AC50 Sm Passive (mass), (D) AC50 Sm Passive (SA), (E) AC20 Sm Active (mass), and (F) AC20 Sm Active (SA).

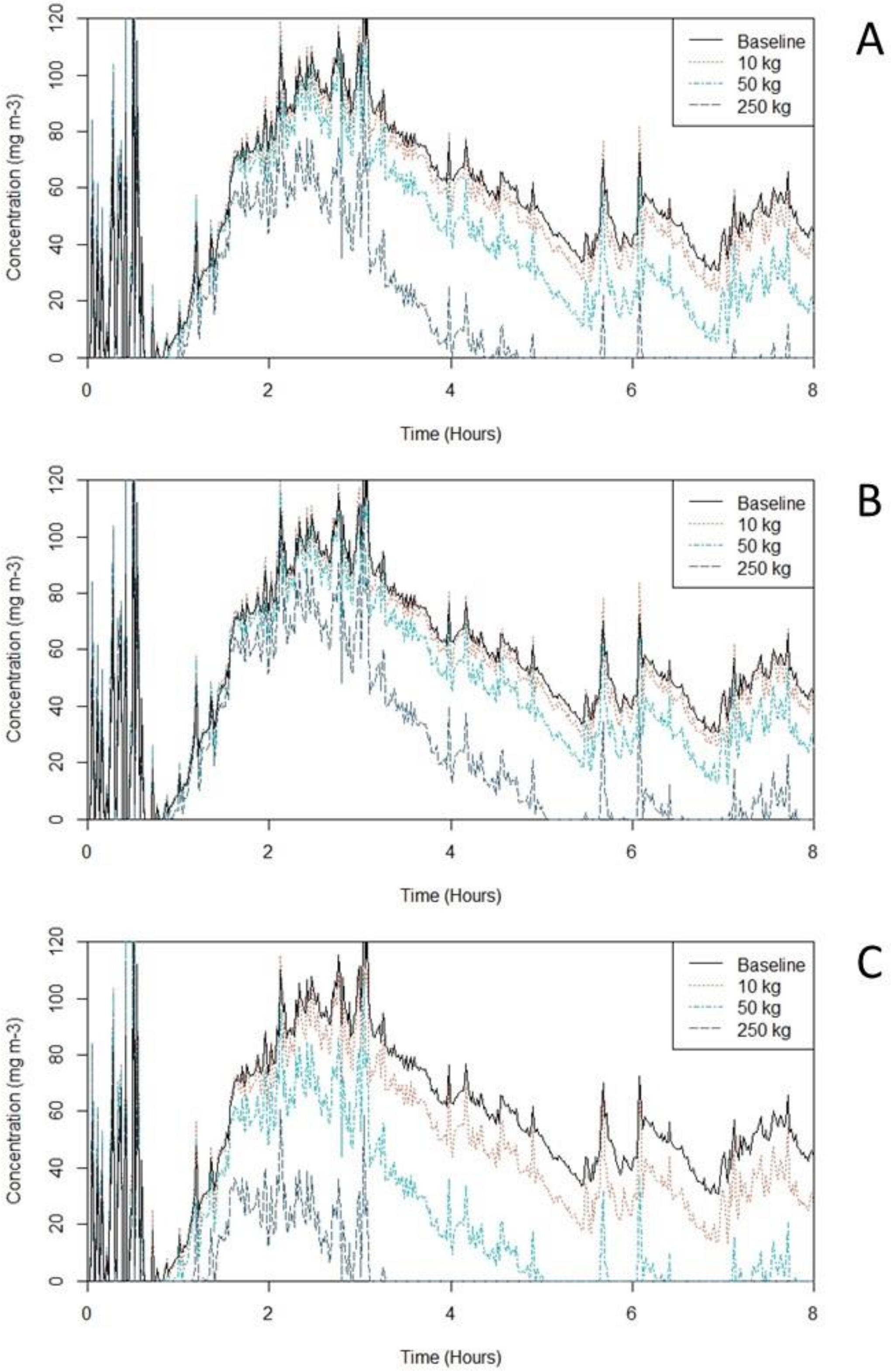

Fig. S4. Model results for (A) AC20 Sm Passive, (B) AC50 Sm Passive, and (C) AC20 Sm Active, normalized by AC mass in sink.