Indoor Air Quality Investigations on Particulate Matter, Carbonyls, and Tobacco Specific Nitrosamines

by

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ABSTRACT

Americans spend upwards of 90% of their time indoors, hence indoor air quality (IAQ) and the impact of IAQ on human health is a major public health concern. IAQ can be negatively impacted by outdoor pollution infiltrating indoors, the emission of indoor pollutants, indoor atmospheric chemistry and poor ventilation. Energy saving measures like retrofits to seal the building envelope to prevent the leakage of heated or cooled air will impact IAQ. However, existing studies have been inconclusive as to whether increased energy efficiency is leading to detrimental IAQ. In this work, field campaigns were conducted in apartment homes in Phoenix, Arizona to evaluate IAQ as it relates to particulate matter (PM), carbonyls, and tobacco specific nitrosamines (TSNA).

To investigate the impacts of an energy efficiency retrofit on IAQ, indoor and outdoor air quality sampling was carried out at Sunnyslope Manor, a city-subsidized senior living apartment complex. Measured indoor formaldehyde levels before the building retrofit exceeded reference exposure limits, but in the long term follow-up sampling, indoor formaldehyde decreased for the entire study population by a statistically significant margin. Indoor PM levels were dominated by fine particles and showed a statistically significant decrease in the long term follow-up sampling within certain resident subpopulations (i.e. residents who reported smoking and residents who had lived longer at the apartment complex). Additionally, indoor glyoxal and methylglyoxal exceeded outdoor concentrations, with methylglyoxal being more prevalent pre-retrofit than glyoxal, suggesting different chemical pathways are involved. Indoor concentrations reported are larger than previous studies. TSNAs, specifically N'-nitrosonornicotine (NNN), 4-(methyl-nitrosamino)-4-(3-pyridyl)-butanal (NNA) and 4-

(methylnitrosoamino)-1-(3-pyridyl)-1-butanone (NNK) were evaluated post-retrofit at Sunnyslope Manor. Of the units tested, 86% of the smoking units and 46% of the non-smoking units had traces of at least one of the nitrosamines.

DEDICATION

I would like to dedicate this work to my husband Ryan, my parents, and my family, who have given me continual emotional support throughout my graduate education. This work is also dedicated in remembrance of my grandmothers, Alma Swiney and Deloris Frey, both of whom always believed in me and inspired me to persevere. Thank you for your love and encouragement, both now and for the great journey ahead.

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CHAPTER 1

INTRODUCTION AND BACKGROUND

Importance of monitoring and improving indoor air quality (IAQ)

The Earth's atmosphere is predominately composed of nitrogen, oxygen, and argon; however the constituents in the remaining 0.038% of our atmosphere have an enormous impact on the earth's climate, global ecosystems, and human health. Air pollution is a growing concern across the globe and can be caused by both biogenic and anthropogenic sources. The Clean Air Act was passed to enable the US Environmental Protection Agency to monitor, regulate, and reduce air pollution. While there are many classifications of pollutants, this research focuses on particulate matter (PM), aldehydes, dicarbonyls, and nitrosamines.

Biogenic air pollution includes volatile organic carbons (VOCs) from plant life and PM from wildfires and volcanoes. Anthropogenic sources can include vehicle emissions, industrial processes, construction, energy production, and agricultural practices (Seinfeld and Pandis, 2012). As air pollution is ubiquitous, it is alarming that it has been linked to approximately 2 million premature deaths per year (WHO, 2002). With rising health care costs, preventative measures and ensuring the safety of our environment has become paramount. Poor air quality has been shown to negatively impact health in many ways. Most commonly, the airways are affected, leading to coughing, sneezing, and shortness of breath. Other short-term symptoms of poor air quality include headaches, dizziness, and fatigue. Long term exposure is also hazardous, leading to cases of respiratory disease, heart disease, and cancer (Dockery et al., 1993; Li et al., 2003; Viegi et al., 2004; Mitchell et al., 2007).

Currently, outdoor pollution is carefully monitored and mitigated. The National Ambient Air Quality Standards (NAAQS) regulating ambient concentrations of particles in the United States include 24-hour average standards for PM_{10} (particles 10 μm in diameter or less) and $PM_{2.5}$ (particles 2.5μm in diameter or less) at 150 and 35 $\mu g/m^3$, respectively (USEPA, 2012a). Additionally, an annual $PM_{2.5}$ standard of 12 $\mu g/m^3$ has recently been included by the EPA, due to increasing health concerns of fine particle exposure (USEPA, 2012b). While there are also national standards for carbon monoxide, lead, nitrogen dioxide, ozone, and sulfur dioxide, the EPA does not set regulations for aldehydes and carbonyls in outdoor air (USEPA, 2012a).

Even though outdoor air pollution is hazardous, the indoor environment is the most common environment humans are exposed to and more research is needed in the area of indoor air quality (IAQ). It is becoming common knowledge that Americans spend upwards of 90% of their time indoors, whether at home, at work, or during leisure activities (US EPA, 1989; Wallace et al., 2006). As with outdoor pollution, one of the greatest concerns is the impact of indoor pollution on human health. Sources of indoor pollution differ from outdoor pollution, with many of the emissions coming directly from human activities. Indoor emission of pollutants can be from both primary and secondary sources. Primary sources of indoor air pollution include combustion of fuels, cooking activities, cleaning products, smoking, and building materials (Crump and Gardiner, 1989; Abt et al., 2000; Afshari et al., 2005; Paoletti et al., 2006; Wallace et al., 2006). Secondary sources are the result of chemical reactions that occur inside, often due to the presence of ozone, NO_x, or radicals (Crump and Gardiner, 1989; Munger et al., 1995; Mitchell et al., 2007). Both primary and secondary pollutants affect air quality in the

indoor and outdoor environments. An assessment of toxins in the indoor environment identified nine priority hazardous chemicals: acetaldehyde, acrolein, benzene, 1-3 butadiene, 1,4-dichlorobenzene, formaldehyde, naphthalene, nitrogen dioxide, and $PM_{2.5}$ (Logue et al., 2011). A better understanding of these reactions and their relationship to human activities will help to mitigate production.

In addition to air pollution, climate change and energy reduction measures have become global issues and will affect the planet in many ways. In order to reduce energy waste, a common approach has been to seal the building envelope to prevent the leakage of heated or cooled air, often referred to as "weatherization". Some energy efficiency retrofits are currently being federally subsidized and, if well executed, could both reduce energy consumption and improve indoor air quality (Fisk, 2000; Manuel, 2011).

While all humans can experience the negative health effects of indoor air pollution, children and the elderly are the least likely to spend time outdoors, which in part makes them the most vulnerable subpopulations to indoor pollution exposure, compared to working adults and the general population (Lee et al., 2002; Williams et al., 2000). Low-income communities are also vulnerable populations, having limited access to educational material, limited income for "green" upgrades, higher rates of outdoor pollution, and a greater potential for the unintended implications of weatherization and energy-efficiency retrofits (Adamkiewicz et al., 2011).

Recently, the US EPA requested a panel of experts to evaluate the current state of indoor air quality in regards to the possible effects of climate change (Institute of Medicine, 2011; Spengler, 2012). Public health, energy conservation, and pollution were among the topics of scientific discussion. Increased CO_2, NO_x, and ozone in the

atmosphere, combined with elevated temperatures and fluctuating humidity, can cause an increase in chemical reaction rates and secondary pollutants. Unfortunately, this report found that some of the actions taken to mitigate climate change (such as reducing ventilation rates) may actually intensify harmful indoor environmental conditions, unless federal agencies and building professionals can refine protocols and testing standards (Institute of Medicine, 2011; Spengler, 2012).

In addition to mitigating outdoor pollution, the EPA is also concerned with the health implications of indoor pollution exposure. Unlike outdoor pollution and indoor exposure in the work environment, no federal government entities have authority to regulate indoor air quality in homes (US EPA, 1994); however regulations have been established in other countries and by state entities. The California EPA and Health Canada have established standards for formaldehyde: 8-h Reference Exposure Level (REL) of 7 ppb (California EPA, 2007) and 40 ppb (Health Canada, 2006). Several other exposure levels established by other countries and agencies are summarized by Salthammer et al. (2010) and partially represented here, in Table 1.1.

Table 1.1

Indoor Formaldehyde Exposure Guidelines

Country/Organization	Year	Concentration (ppb)	Concentration ($\mu g/m^3$)	Duration (avg. over time)
Canada – Health Canada	2005	100	123	1-h (Acute)
	2006	40	50	8-h
China – Ministry of Health	2003	80	100	1-h
UK – COMEAP[(a)]	2004	80	100	0.5-hr
USA – OEHHA[(b)]	1999	76	94	1-h (Acute)
(California)	2004	27	33	8-h
	2005	2	3	Annual (Chronic)
	2007	7	8	8-h
	2007	44	55	1-h (Acute)
World Health Organization	1987	80	100	0.5-hr

[(a)] Committee on the Medical Effects of Air Pollutants (COMEAP)
[(b)] California Environmental Protection Agency, Office of Environmental Health Hazard Assessment (CA-EPA, OEHHA)

It is interesting to note that California is the only state in the USA that has determined limits for indoor formaldehyde exposure. Neither the federal government nor other state entities have established reference exposure levels for indoor air. As can be seen from Table 1.1, as more information is collected about the health impacts of formaldehyde exposure, the guidelines have more stringent. For example, the 1-hour acute REL has been reduced from 76ppb in 1999 to 44ppb in 2007 in California.

In addition to formaldehyde exposure, CA-EPA has established limits for acetaldehyde: 80 ppb chronic (annual) REL, 160 ppb 8-hr REL, and 260 ppb 1-hr acute REL. The main concern with acetaldehyde exposure is the negative effect on the upper respiratory tract, especially for asthmatics. Other non-cancer effects of acute exposure

include irritation the eyes, skin, and lungs (California EPA, 2008). Acetone is another carbonyl that has been shown to have health effects for long-term exposure; however the exposure limits are three orders of magnitude higher than acetaldehyde and it is rare to see concentrations large enough in a home environment. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for acetone is 250 ppm as a time-weighted average for up to 10 hour work shift over a 40 hour work week (NIOSH, 1994). No regulations have been applied to glyoxal or methylglyoxal, as the carcinogenicity of these compounds have not been determined (NIOSH, 2013).

In an editorial article for the journal Indoor Air, four priorities of a healthy indoor environment were described. In order to ensure improved air quality, indoor emissions of pollutants should be minimized, moisture should be controlled, areas should be properly ventilated, and outdoor pollution infiltration should prevented. In essence, these are the goals of the indoor air quality community (Nazaroff, 2013). In order to be effective at achieving these four goals, more information is needed in regards to what the sources of indoor pollutants are, what constitutes proper ventilation, and how to best reduce infiltration. Contributing to the body of indoor air quality research, the present thesis will focus on the presence of indoor particulates and toxins, the common emission sources of these pollutants, and the effect of energy efficiency construction on the indoor environment.

Particulate matter in the indoor environment

Particulate matter in the indoor environment is of great concern because of the known associations with declining health and mortality (Dockery et al., 1993; Viegi et

al., 2004; Mitchell et al., 2007). Not only can ambient outdoor particles infiltrate the indoor environment, but many sources of PM exist within our homes and workplaces. As previously mentioned, particles are often characterized and defined by their size, specifically the aerodynamic diameter. Particles 10 μm in diameter or less are denoted as PM_{10} and particles 2.5μm in diameter or less are denoted as $PM_{2.5}$. These two size distributions are most commonly used to describe particle pollution and have different health impacts. Coarse particles ($PM_{10\text{-}2.5}$) can irritate the eyes, nose, throat, and upper respiratory tract. Fine particles ($PM_{2.5}$) are smaller and can infiltrate deep into the lungs and, in some cases, can enter the bloodstream. People with existing lung conditions, such as asthma or emphysema, as well as children and the elderly are more vulnerable to particle exposure than healthy adults (Williams et al., 2000; Koenig et al., 2005). A study of 19 children with asthma found that indoor and outdoor $PM_{2.5}$ exposure affected the lungs in different ways. Lung function was tracked and it was found that particles generated from indoor sources were correlated with decreased lung function, but particles generated from outdoor sources showed the opposite trend and increased markers for airway inflammation were detected, highlighting the complexity of health effects of PM on vulnerable populations (Koenig et al., 2005).

Sources of indoor PM_{10} can include pet dander, dust, and mold. Sources of $PM_{2.5}$ are commonly the result of combustion, including the use of candles, incense, fire places, and cigarettes. In a study of PM exposure on North Carolina residents, mean PM exposure levels increased by 25-50 $\mu g/m^3$ while participants were cooking or cleaning, and increased by more than 1500 $\mu g/m^3$ when using fireplaces or burning food (Wallace et al., 2006). In addition, two of the participants were exposed to second hand smoke,

which yielded an increase of 2.5 and 3.5 times mean PM exposure. As human activities have been identified as a common source of indoor particles, Abt, et al. (2000) conducted a study in four Boston homes and used modeling to determine the contribution of both human activities (including cooking, cleaning, movement, and washing) and outdoor sources on total indoor particle concentrations. While cooking, cleaning and human movement had a strong influence on PM greater than 2 μm, outdoor concentrations were found to contribute to all PM sizes, from 0.02 to 10 μm in diameter. For particles greater than 1 μm, cleaning and human movement caused resuspension at a rate that increased with particle size. However, cleaning was negatively associated with $PM_{0.2\text{-}0.5}$, most likely do the coagulation of those small particles onto coarse particles. This study found more indoor sources of coarse PM than fine PM, with highest emission rates correlating with cooking, movement, and cleaning (Abt et al., 2000).

In addition to studies in real environments, laboratory chamber studies have also revealed the extent to which human activities impact PM production. The benefits of chamber studies include the ability to control important factors such as temperature, relative humidity, and air exchange. Afshari, et al. (2005), tested 13sources of indoor fine and ultrafine (particles less than 0.1μm) PM and measured the resulting concentrations with an optical particle counter. The sources include two types of candles, air freshener spray, ironing (with and without steam), second-hand smoke, vacuuming (with and without dust bag), an electric heater, an electric radiator, an electric stove, a gas stove, and frying meat. Size ranges of <0.1, 0.3-0.4, 0.4-0.5, 0.5-0.6, and >1.0 μm were observed. Ultrafine particle concentrations greatly exceeded fine particle concentrations for every source by at least 3 orders of magnitude. The highest observed concentration of

ultrafine PM was the result of burning pure wax candles (241,000 particles/cm^3) and the lowest observed concentration of ultrafine PM was the result of ironing without steam (550 particles/cm^3). Interestingly, initial fine particle concentration for the pure wax candle was quite low while the candle was lit, but had a dramatic increase when the candle was extinguished. In general, maximum concentration peaks were achieved quickly after the activity began, but decay rates varied greatly by activity (Afshari et al., 2005).

Environmental tobacco smoke (ETS) is one of the most recognizable types of indoor pollution and has been shown to cause respiratory disease in both smokers and nonsmokers. Paoletti, et al. studied the influence of ETS on PM characterization in a variety of environments. PM_{10} concentrations were measured outdoors, inside and office, and in a designated smoking area and the averages were found to be 81, 39, and 144 $\mu g/m^3$, respectively. During smoking activity, $PM_{2.5}$ mass concentration was measured to be 267 $\mu g/m^3$. The effects of smoking accounted for 28-44% of the coarse PM and 78-95% of the fine PM measured. It was also found that the coarse carbonaceous component of ETS was limited to the smoking area while fine carbonaceous components were present in the surround areas, even 7 days after the smoking event (Paoletti et al., 2006).

Aldehydes, carbonyls and nitrosamines in the indoor environment

The compounds of greatest concern in our environment are volatile organic compounds, or VOCs. VOCs are organic molecules with high vapor pressures and are ubiquitous in our environment, having both biogenic and anthropogenic sources. Particularly, concentrations of certain VOCs, such as formaldehyde and acetaldehyde, are

being monitored. Recent studies have shown that VOC concentrations are consistently higher indoors compared to outdoor environments (USEPA, 2004).

Carbonyls are a subset of organic compounds in which a carbon has a double-bonded oxygen attached. Aldehydes, have this double bond on a terminal carbon and ketones have this double bond on an interior carbon (i.e., also bonded to two other carbons). A dicarbonyl, such as glyoxal and methylglyoxal have two separate carbons double bonded to oxygen atoms. The presence of this class of molecule is important for two reasons: health impacts of exposure to extreme concentrations and the propensity to form secondary organic aerosols (Schwier et al., 2010). Formaldehyde (HCHO) is the smallest aldehyde and is widely recognized as a harmful chemical. HCHO has been identified as a potential carcinogen by the US EPA (group B1, US EPA, 1999), and classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC, 2012).

In the atmosphere, carbonyls are often generated from the oxidation of hydrocarbons. Formaldehyde is a common precursor of hydroxide (OH) and methylglyoxal is a common precursor of peroxyacetylnitrate (PAN). Additionally, glyoxal and methylglyoxal are considered tracer compounds for the oxidation of hydrocarbons such as isoprene and terpenes (Munger et al., 1995). On the biological level, glyoxal and methylglyoxal have raised concerns involving genotoxicity and mutagenic properties (Ueno et al., 1991; Ankrah and Appiah-Opong, 1999; Murata-Kamiya and Kamiya, 2001; O'Brian et al., 2005; Thronally, 2008; Desai et al., 2010) and have been linked to dermatitis in workers who have been regularly exposed to the compounds (Elsner et al., 1990; Uter et al., 2001; Aalto-Korte et al., 2005).

Sources of carbonyls differ for each species and can be biogenic or anthropogenic and indoor carbonyls can have different formation pathways than in nature. An investigation of indoor aldehydes and ketones in the UK revealed common sources for 13 compounds. Tobacco smoke, car exhaust, building materials, and various scented sprays all released detectable levels of formaldehyde. However, tobacco smoke yielded substantially more acetaldehyde and acrolein than formaldehyde. Air testing performed near motor vehicle tailpipes favored acetaldehyde, furfuraldheyde, and formaldehyde. The perfumes tested showed variable amounts of formaldehyde, acetaldehyde, benzaldehyde, and acrolein. Hairspray, on the other hand, only had one detectable carbonyl: acetaldehyde. Building materials such as particle board, insulation, and carpets all contained formaldehyde and low levels of acetaldehyde. Other notable compounds include acetone/propanal (insecticide) and non-quantifiable levels of anisaldehdye and methylglyoxal (air freshener sprays). Based on formaldehyde testing both inside and outside of various buildings, infiltration was not considered a significant source of indoor carbonyls in this study (Crump and Gardiner, 1989).

While it is known that formaldehyde and other toxins are emitted from common indoor furniture and carpeting, it is sometimes difficult to explicitly identify the source of the emission. Shinohara, et al. (2009) utilized passive flux samplers and DNPH-coated silica cartridges connected to pumps for the determination of emission rates of carbonyls in a Japanese apartment. It was determined that the carpet, ceiling, walls, and outdoor air contributed 24, 20, 22, and 18%, respectively, to the total formaldehyde concentration in the indoor environment (61.5 $\mu g/m^3$) while the door, flooring, and desk contributed less than 6% combined. Acetaldehyde was relatively low in abundance, only 13.5 $\mu g/m^3$, but

still larger than the outdoor concentration. Surprisingly, acetone was found in the indoor environment at 93.7 $\mu g/m^3$ while it was not detectable outside or on any of the passive flux samplers. The source of acetone was hypothesized to be from the breath of the four occupants in the room during sampling (Shinohara et al., 2009).

Though VOCs and carbonyls are ubiquitous in our atmosphere and readily formed by reactions involving tropospheric ozone, many studies have shown indoor/outdoor ratios of aldehydes to be greater than one, thus prevalent in our indoor environments. A study of six homes in New Jersey yielded mean I/O ratios of 1.38 to 7.20 for 8 different aldehyde compounds, the greatest value belonging to formaldehyde (Zhang et al., 1994). This study also found that the total concentration of the 9 aldehydes tested was 19.12 ± 10.88 ppb and 62.57 ± 21.75 ppb for the outdoor and indoor concentrations, respectively, with formaldehyde accounting for 60% of the outdoor and 87% of the indoor aldehydes tested.

While formaldehyde and acetaldehyde are considered primary emissions, some dicarbonyls are formed from other processes and are secondary emissions. For example, the ozonolysis of limonene is one formation pathway for methylglyoxal. A recent study by Rossignol, et al. quantified and identified the products formed by use of indoor cleaning products. Among the 22 carbonyls detected in the gas and particle phases are glyoxal and methylglyoxal (Rossignol et al., 2013).

A wide scale study, RIOPA (Relationships of Indoor, Outdoor and Personal Air), investigated air quality in over 200 non-smoker homes in Los Angeles, CA, Houston, TX, and Elizabeth, NJ (Liu et al., 2006). The database created shares valuable information about indoor, outdoor, and personal air quality for toxins and PM related to

multiple parameters, including air exchange rates, human activities, and home design factors. In this study, the most prevalent carbonyls in the indoor environment were formaldehyde and acetaldehyde, with median concentrations of 20.1 and 18.6 $\mu g/m^3$, respectively. Acetone, glyoxal, and methylglyoxal were also detected, having median concentrations of 8.08, 2.53, and 2.75 $\mu g/m^3$, respectively. Outdoor air samples were also test: formaldehyde, acetaldehyde, acetone, glyoxal, and methylglyoxal had outdoor median concentrations of 6.42, 5.44, 4.19, 1.81, and 2.05 $\mu g/m^3$, respectively. Of the 10 total carbonyls evaluated, 9 had greater concentrations indoors, acrolein being the only molecule which had greater outdoor concentrations, thus supporting evidence that the important emission sources of aldehydes are favored in indoor environments. Source strengths were also estimated, again with formaldehyde and acetaldehyde having the largest median values of 3.9 mg/h and 2.6 mg/h, respectively. Glyoxal and methylglyoxal source strengths, on the other hand, were quite low at <1 mg/h in 95% of the homes studied (Liu et al., 2006).

Another group of compounds of great health concern are tobacco-specific nitrosamines (TSNAs). These compounds are formed from the nitrosation of nicotine and are often carcinogenic (Caldwell et al., 1991; Brunneman et al., 1996; Hecht, 1998; Hecht, 2004). TSNAs have been detected in water, air, and surface samples and are the result of first-hand smoke (via urine excretions from smokers into wastewater systems), second-hand smoke (via gas phase reactions), and third-hand smoke (via surface reactions with ambient HONO) to name a few (Sleiman et al., 2010; Wu et al., 2014).

Specifically, the N-nitrosamines discussed here are N'-nitrosonornicotine (NNN), 4-(methyl-nitrosamino)-4-(3-pyridyl)-butanal (NNA) and 4-(methylnitrosoamino)-1-(3-

pyridyl)-1-butanone (NNK). In surface studies conducted in vehicle in which smoking occurred, NNA and NNK were detected at concentrations ranging from 1 to 5 ng/cm^2 (Sleiman et al., 2010). Very few studies have been able to quantify NNA concentrations, but NNN and NNK have been identified in air samples as early as the 1970s and concentrations have been found to range from n.d.-22.8 and 1.4-29.3 μg/m^3, respectively (Hoffmann et al., 1979; Brunnemann et al., 1996). These molecules can also be detected in human urine and saliva, and can be biomarkers for environmental tobacco smoke and lung tumors (Hecht et al., 1978a; Hoffmann et al., 1987; Anderson et al., 2001).

Ventilation and infiltration of outdoor pollutants

Two of the top four indoor air quality priorities involve ventilation and infiltration. While infiltration focuses on outdoor pollution coming in, ventilation is important to remove indoor pollution from enclosed environments. Studies have shown that an increased risk of allergies, respiratory illnesses, and other poor air quality health symptoms can be associated with low ventilation rates (Sundell et al., 2011). Additionally, in multi-unit buildings, such as apartment complexes and duplexes, air pollution can be transferred between units (Bohac et al., 2011).

Ventilation and air exchange play a large role in the chemistry of the indoor environment. If a space has a high ventilation rate, then the ability for molecules to interact with other molecules is limited. In contrast, reduced ventilation rates and low air exchange increases residence times and chemical concentrations become greater in the limited, defined volume. Outdoor air is not confined to a specific volume, which reduces direct exposure. This is one reason indoor exposure levels are stricter than outdoor regulations. To add to the complexity of the system, ventilation can also influence the

transport of pollution from indoors to outdoors and vice versa. While it is beneficial to increase the transport of indoor pollutants to the outdoor environment, one hopes to reduce the pollution from traveling from outdoors to indoors. Calculating the impact of ventilation on indoor air quality becomes complex, and can be modeled in either a steady-state or dynamic environment. Experimentally, air exchange rates are most often determined by the release and monitoring decay of SF_6. Weschler, et al. (2000), conducted a study utilizing both models and experimentally determined exchange rates. The outcome revealed that reactions that have reaction rates similar to the air exchange rate have increased product concentrations as ventilation rates are decreased, even when a steady-state is not achieved (Weschler et al., 2000). This highlights the need to maintain ample ventilation in environments where indoor pollution sources are common, thus reducing the impacts of chemical reaction products.

In most buildings, the potential for outdoor pollutions to infiltrate the indoor environment is expected. This is most apparent when chemicals with no known indoor sources are detected. Many studies, however, find that the concentration of indoor aldehydes and particles are much higher than outdoor concentrations and have numerous indoor emission sources, thus reducing the chance that infiltration is a significant contributor to indoor air pollution (Zhang et al., 1994).

Though this is true in many regions, a study of four nonsmoking homes in Boston found that outdoor particles substantially contributed to indoor PM concentration, especially in the $PM_{0.02-0.3}$ size range. Penetration efficiencies were greatest for $PM_{0.1-0.2}$ while penetrations efficiencies of the larger particles decreased as particle size increased due to losses from diffusion, impaction, and deposition. It was found that 20-43% of

indoor PM_{2-10} was contributed from outdoor sources, while 63-92% of indoor $PM_{0.02-0.3}$ could be attributed to outdoor sources (Abt et al, 2000). It is important to note that the median indoor/outdoor ratios for this study ranged from 0.56 to 1.24, slightly favoring outdoor particle concentrations.

The infiltration of secondhand smoke into the indoor environments of non-smokers has also been evaluated. Bohac, et al. conducted research in which air sealing and ventilation improvements were utilized in an attempt to reduce or eliminate inter-unit air exchange between smoking and nonsmoking residents' apartments. Ventilation systems were improved to maintain a continuous exhaust flow of 42 m^3/hour or greater and the median air leakage reduction for all units studied was 18%. Though improvements resulted in a reduction of inter-unit flow in 24 out of 35 units, contamination concentrations of non-smokers' units was only reduced by 30% (Bohac et al., 2011). This becomes an important factor in multiunit buildings, where indoor air pollution exposure not only a function of an individual's activities, but also that of their neighbors' activities.

Impacts of energy efficiency on indoor air quality (IAQ)

Energy consumption and energy conservation are gaining attraction as important international concerns. Demand for electricity in buildings was a major contributor to the 58% growth in electricity production (from 1985 to 2006). With 40% of all energy being used in buildings, energy efficiency is becoming critical. In 2005, it was found that heating and cooling account for 43% of the energy used in a home (US DOE, 2008). In 2009, the federal government granted about $5 billion dollars to states to use toward making homes more energy-efficient (Manuel, 2011). In order to reduce energy waste, a

common approach is to seal the building envelope to prevent the leakage of heated or cooled air, often referred to as “weatherization”. However, lowering ventilation rates can cause an increase in toxin concentrations, as has been discussed in the previous section (Weschler et al., 2000; Fisk, 2000).

Apart from sealing the building envelope, energy efficiency retrofits include updating HVAC (heating, ventilation, and air conditioning) systems, installing of exhaust fans, energy saving appliances, and insulated windows. Ventilation systems and exhaust fans can have a positive impact on PM, especially in the kitchen, as long as it exits the building, as opposed to just being circulated within the indoor environment. Thermal windows and doors help reduce infiltration, drafts, and condensation that leads to microorganism growth. In general, well executed energy efficiency retrofits can lead to better and more productive indoor environments (Fisk, 2000).

Goals and Objectives

The present work explores the indoor air quality (IAQ) at low-income senior living center in Phoenix, AZ before and after an energy-efficiency retrofit. Though IAQ can be defined and evaluated with many parameters, the focus was specifically on the concentrations of particulate matter, carbonyls, and tobacco-specific nitrosamines (TSNAs). Field samples were collected over a period of three years, during the summer months of 2010, 2011, and 2012. This project was a subset of a large collaboration lead by Principal Investigator Dr. Sherry Ahrentzen (University of Florida) to examine how the building modifications funded by the American Recovery and Reinvestment Act of 2009 (ARRA) Green Retrofit Program impacted indoor environmental quality (IEQ) and heath of elderly residents.

The first field campaign occurred between June 10 and July 12, 2010, before any construction of the energy-efficiency retrofit began, in order to obtain baseline IAQ. Particulate matter, formaldehyde, and acetaldehyde concentrations were analyzed. The results and observations for this first panel have been submitted for publication and are discussed in Chapter 2.

The second and third campaigns were conducted immediately after construction was completed from late April through September 2011 and one year later from June through early August 2012, respectively. Particulate matter, formaldehyde, acetaldehyde, and acetone concentrations were analyzed and short and long term trends identified. These results and observations have been submitted for publication and are discussed in Chapter 3.

Using samples from the first and third panels (2010 and 2012), additional analysis was used to identify glyoxal and methylglyoxal in the indoor and outdoor environments. Indoor/outdoor ratios, concentrations, and correlations with human activity are discussed in Chapter 4.

During the third panel in 2012, additional collection techniques were utilized to determine the presence of TSNAs in the indoor environments of both smokers and non-smokers. Additionally, samples were collected in 2014 in the car and home of a heavy smoker. Discussion of the results is detailed in Chapter 5.

Chapter 6 provides an overall summary of the present work and offers suggestions for future research.

CHAPTER 2

CHARACTERIZATION OF INDOOR AIR QUALITY AND RESIDENT HEALTH IN AN ARIZONA SENIOR HOUSING APARTMENT BUILDING[1]

Introduction

With urban populations spending a majority of their time indoors, understanding the sources of indoor pollutants with the ultimate goal of mitigating exposure is a vital concern (Lee et al., 2002; Wallace et al., 2006). Of particular interest is the control of pollutants that can impact people who are most vulnerable to exposure including children, the elderly, and those with existing respiratory disease. Further, limited access to healthcare may limit intervention to overcome any health burden on low-income populations affected by air pollution. For this reason, low income seniors are amongst those most impacted by, and least able to respond to, health burdens from indoor pollution (Williams et al., 2000).

With rising energy costs and concern about the impact of fossil-fuel based energy on climate, energy efficiency retrofits have become more common with billions of dollars from numerous sources available to implement energy savings in buildings. One common, low-cost/high-return approach to saving energy is sealing the building envelope to reduce building leakage with the goal of lowering the amount of make-up air that must be conditioned and the associated energy used for air handling. However, this sealing of the building envelope may trap pollutants released from indoor sources leading to increased exposure to pollutants for residents (Jones, 1999; Fisk, 2000). Identifying

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common indoor pollutant sources in multi-unit residential buildings may help in the design and implementation of more effective energy efficiency interventions, which may include retrofits in association with different approaches to building ventilation, filtration and air cleaning.

Particulate matter, or PM, is of great concern to the EPA because of the impact on heart and lung health (Dockery et al., 1993). Particles with an aerodynamic diameter less than 10 micrometers have the potential to pass through the throat and nose and into the lungs. Additionally, epidemiological studies have linked increased outdoor PM exposure to increased mortality and exacerbation of existing respiratory diseases (Wallace, 1996; Li et al., 2003; Englert, 2004; Davidson et al., 2005). While much of the research studying health impacts of indoor air pollution has focused on volatile organic compounds, biological aerosols or radon (Jones, 1999; Bernstein et al., 2008), there is growing evidence of the impact of indoor PM on health (Koenig et al., 2005). While there are no established acceptable limits of indoor PM levels, the National Ambient Air Quality Standards (NAAQS) regulating ambient concentrations of particles in the United States over 24-hour averaging periods include standards for PM_{10} and $PM_{2.5}$ at 150 and 35 micrograms/meter^3, respectively. An annual $PM_{2.5}$ standard of 12 $\mu g/m^3$ has recently been modified by the EPA, due to increasing health concerns of fine particle exposure (USEPA, 2012).

Formaldehyde is a pollutant of concern due to its prevalence indoors and its association with chronic and acute health effects. It is found in the additives used in wood-based building products and furnishings, such as particleboard (Hodgson et al., 2002; Destaillats et al., 2006; Singer et al., 2006; Destaillats et al., 2011; Sidheswaran et

al., 2013). Acute formaldehyde exposures may lead to sensory irritation symptoms (eye, nose and throat), as well as irritation of the upper respiratory system, nasal obstruction, pulmonary edema and dyspnea. Chronic exposures have been linked with allergic sensitization, asthma symptoms, histopathological changes in respiratory epithelium, and decrements in lung function (LBNL, 2008; Salthammer et al., 2010; California EPA, 2007). In addition, formaldehyde is listed by the US EPA as a probable carcinogen (group B1, US EPA, 1999a), and the World Health Organization has classified formaldehyde as a human carcinogen (Cogliano et al., 2005). A recent assessment listed formaldehyde among the top five indoor pollutants leading to chronic health effects in US residences (Logue et al., 2012). Several health-based exposure levels for formaldehyde have been established by regulatory agencies. In the US, the California Environmental Protection Agency established an acute Reference Exposure Level of 44 ppb and an 8-h Reference Exposure Level (chronic exposure) of 7 ppb (California EPA, 2007). Similarly, Health Canada has established an 8-h exposure limit of 40 ppb based on respiratory symptoms in children (Health Canada, 2006). Several other exposure levels established by other countries and agencies are summarized by Salthammer, et al. (2010).

With this background, we report a study characterizing a city-subsidized apartment complex for seniors in Phoenix, Arizona. The building is characterized by concentrations of indoor PM and volatile aldehydes. While there are many contaminants of concern in the indoor environment, few can be tested in short time periods in a minimally invasive way. PM, formaldehyde, and acetaldehyde were chosen due to their high chance of detection, known impacts on human health, and availability of standards for comparison. In addition, PM is often used to investigate the impacts of environmental

tobacco smoke while formaldehyde can indicate the release of pollutants from building materials. Associations between occupants' behavior, self-reported health conditions, and IAQ (i.e. which sources or individual behaviors are linked to high measure PM and aldehydes) are evaluated.

Materials and Methods

Sampling campaign and health survey. A study was conducted at a local apartment complex, operated by the City of Phoenix Housing Department, for seniors who qualify for subsidized rent. Originally built in the early 1970's, this three-story apartment building contains 116 identical units. Air samples were collected in the self-contained apartment units with simultaneous measurements of indoor air pollutants (PM and aldehydes) in the living room and kitchen, and outdoor pollutant concentrations on the balcony of each unit. All units have 619 ft^2 of livable space and are identical in interior layout and are all-electric homes (i.e. no fireplaces, gas stoves, etc.) with individual packaged terminal air conditioning (PTAC) units.

At the same time as air quality testing, a health survey of over 100 questions was given to the residents to solicit information about personal habits and health conditions of the apartment occupants. This questionnaire consisted of open-ended and fixed-response questions developed from applicable portions of the National Health Interview Survey (NHIS) and from the Behavioral Risk Factor Surveillance System (BRFSS) for Arizona as well as questions about personal habits and perceived air quality. Questions most relevant to this article involve smoking and cleaning behaviors, pet ownership, methods of odor reduction, and respiratory health. Performing the air quality measurements and

administering the questionnaire simultaneously decreased the impact that a resident's activities (i.e. cooking, smoking) can have on IAQ measurements.

The indoor air quality testing, presented here, is a subset of a larger-scale study in which cost efficiency and health benefits are also being analyzed (Ahrentzen et al., 2013). The larger study takes benefits such as reduced falls, quality of life, and fewer trips to the doctor into account, while the air quality portion mainly focuses on respiratory diseases and perception of air quality. A total of 72 apartments with 77 residents were studied during the program between June 10 and July 12, 2010. One-hour air quality samples were collected in each unit between the hours of 9am and 5pm. Repeated testing in a subset of units (7% replicate) ensured that no time-of-day bias impacted collected data. The summer season was selected for sampling as local hot weather would result in the apartment units being sealed (i.e. windows closed) with air conditioning running. This ensured consistency between units and enabled the isolation of the impact of resident behavior on IAQ. Residents were asked not to cook, smoke or clean for 2 hours prior to air quality measurements, in order to minimize introducing strong transient sources that would impact the air quality measurements. While one-hour sampling periods are relatively short and may be more susceptible to transient emission events, the sampling plan was carefully designed in order to minimize the impact of resident activity during sampling, thus reducing the potential impact of individual activities on indoor air quality. In addition, this sampling plan maximized the number of participants to ensure sufficient apartments for potential follow-up analysis. Short-duration samples allowed coordinating for a large number of units over the month-long sampling period, obtaining a

representative data set for the building by testing units on different floors, wings, and orientations.

Particulate matter measurements. Indoor air quality sampling included real-time measurement of PM using a TSI DustTrak DRX (model 8533, TSI, Inc., Shoreview, MN) sampler. This instrument contains a light-scattering laser photometer to detect various particle sizes, including PM_1, $PM_{2.5}$, PM_4, PM_{10} and PM-total. The maximum size measured for the PM-total is approximately 15 microns based on manufacturer specifications. Three samplers were deployed to the apartment kitchen, living room, and balcony to simultaneously collect particle data over a one hour period during which the resident was given the health survey. By sampling both indoor and outdoor air, we are able to calculate indoor/outdoor ratios with the goal of quantifying the impact of infiltration of outdoor particles verses indoor sources on indoor air quality. Dusttraks were labeled and used in a consistent manner among units, were calibrated prior to the study, and tested for reproducibility by collocated sampling. While Dustraks have been shown to overestimate PM compared to gravimetric measurements, the use of a consistent sampling platform was designed to minimize bias due to sampling technique (Jenkins et al., 2004).

Aldehyde measurements. Samples of indoor and outdoor formaldehyde and acetaldehyde were collected using commercial samplers containing dinitrophenylhydrazine (DNPH)-coated silica gel (Sep-Pak XPoSure Aldehyde Sampler, # WAT047205, Waters Corp., Milford, MA). The cartridges were preceded by an ozone scrubber (Sep-Pak Ozone Scrubber, # WAT054420, Waters Corp., Milford, MA) to eliminate ozone from the incoming air. Air was drawn through the samplers by means of

pumps operating at ~2 L min^{-1} (determined with a precision better than ±3%). Samples were collected over 1-hour periods using portable gas pumps (Universal XR Pump, Model PCXR4, SKC Inc., Eighty Four, PA). The sampling flow of each pump was calibrated in the laboratory before and after the sampling period using a bubble flow meter and a primary air flow calibrator (Gilibrator-2, Sensidyne, St. Petersburg, FL). Three samples were collected simultaneously with and in close proximity to the PM samplers in the living room, kitchen, and balcony.

After collection, each DNPH cartridge was capped, labeled and stored at 4 ^{o}C until it was extracted and analyzed. Acetonitrile extracts were analyzed by High Performance Liquid Chromatography (HPLC) with UV detection at 360 nm following a US method (US EPA, 1999b). The concentration value reported in each case corresponded to a time-integrated average over the sampling period. Calibration curves for quantification were determined with authentic standards of the dinitrophenylhydrazones of formaldehyde and acetaldehyde (Sigma-Aldrich). The detection limit for each volatile carbonyl was typically 10 ng or lower, corresponding to air concentrations < 0.1 ppb. Laboratory and field blank samples (at least three laboratory and six field blanks) were also analyzed, showing non-detectable values of the three analytes.

Results and Discussion

Occupant questionnaire outcomes. To characterize the demographics of the apartment units sampled, key variables expected to impact sources of air pollution in the apartment (i.e. smoking, use of candles, etc.) as well as those with self-reported existing respiratory disease that might lead to residents taking active steps to mitigate indoor

pollution, are summarized in Table 2.1. The demographics of those residents who participated in our study aid in the interpretation of the indoor air quality data. Eleven to thirteen percent of residents reported an existing respiratory disease (i.e. asthma or emphysema), 14% owned pets, and 64% used something to change the smell of the air at least once a week (candles, incense, air freshener, or other such as scented plug-ins, Lysol-type sprays, and carpet fresheners).

Table 2.1

Questionnaire Response Counts. Participant responses to indoor source and respiratory health related questions. Questions were framed has "Do you have" or "Do you use" each of the following:

	Smokers (N=16)			Nonsmokers (N=56)		
	Yes	No		Yes	No	Don't Know
Emphysema	6	10		2	53	1
Asthma	3	13		6	50	0
Pets	6	10		4	52	0
Bug spray	5	11		12	44	0
Candles	4	12		6	50	0
Incense	3	13		2	54	0
Air freshener	10	6		28	28	0

Particulate Matter. For initial comparison, measured levels of indoor PM often far exceeded measured outdoor concentrations, an indication of the importance of indoor PM sources for the units participating in the study. As can be seen in Table 2.2, indoor particle concentrations averages are higher and more widely variable than outdoor PM concentration averages, though part of the difference may be due to varying particle morphology between indoor and outdoor PM, which alters instrument response. When comparing living room PM_{10} to outdoor PM_{10}, there is a mean difference of 42 ($\mu g/m^3$) (paired t-test: $t=2.665$, $p<0.01$) and a low correlation of 0.29 ($p<0.05$). The differences

between measured particle concentrations in the kitchen and living room for each unit are not statistically significant (values had a linear regression correlation of 0.993), therefore we will use the living room data to be representative of indoor PM levels.

Table 2.2

Particulate Matter Concentrations. Particulate matter concentrations for the living room, kitchen, and balcony (outdoor). Samples collected in the summer months of 2010.

	Mean ($\mu g/m^3$)	Median ($\mu g/m^3$)	Range ($\mu g/m^3$)	Standard Deviation	Standard Mean Error
Living Room: $PM_{2.5}$	62	13	845	137	16
Living Room:PM_{10}	66	17	844	137	16
Living Room: PM_{15}	80	32	847	136	16
Kitchen: $PM_{2.5}$	53	14	707	113	13
Kitchen: PM_{10}	58	18	707	113	13
Kitchen: PM_{15}	71	34	714	113	13
Balcony: $PM_{2.5}$	20	13	122	21	2
Balcony: PM_{10}	24	17	121	21	3
Balcony: PM_{15}	28	20	123	22	3

The mean indoor/outdoor (I/O) ratios for $PM_{2.5}$ and PM_{10} for all units studied are 3.0 (σ=5.6) and 2.5 (σ=4.8), respectively. The difference of the means from unity is statistically significant ($t= 2.945$, $p<0.005$ and $t = 2.699$, $p<0.01$, respectively). The median I/O ratio is 1.0 for both $PM_{2.5}$ and PM_{10}. However, if participant data are separated by those who smoke and those who do not, the impact of smoking as a PM source is clearly evident. The mean values of the I/O ratios for non-smoking participants are 1.4 (σ=2.1) and 1.1 (σ=0.8) and the median values are 1.0 and 0.9 for $PM_{2.5}$ and PM_{10}, respectively. In addition, the difference of the means from unity is not statistically significant. Smoking participants have mean I/O ratios of 8.5 (σ=9.5) and 7.4 (σ=8.3) and median I/O ratios of 4.9 and 4.5, respectively and the difference of the means from unity

is statistically significant ($t = 3.169$, $p<0.006$ and $t = 3.057$, $p<0.008$, respectively). Variances assumed unequal, the differences in the mean I/O ratios for units where residents report smoking versus those units where residents do not report smoking is statistically significant (independent samples t-test: $t=3.00$ and $t=3.01$, $p<0.01$). Figure 2.1 shows the relationship between measured indoor $PM_{2.5}$ and PM_{10} and the log of the respective I/O ratio, with data points differentiating between units occupied by residents who smoke and those who do not. From this plot, it is clear that the units with the most elevated ratio of indoor to outdoor PM also have the highest concentrations of indoor PM and tend to be occupied by persons who reported that they smoke.

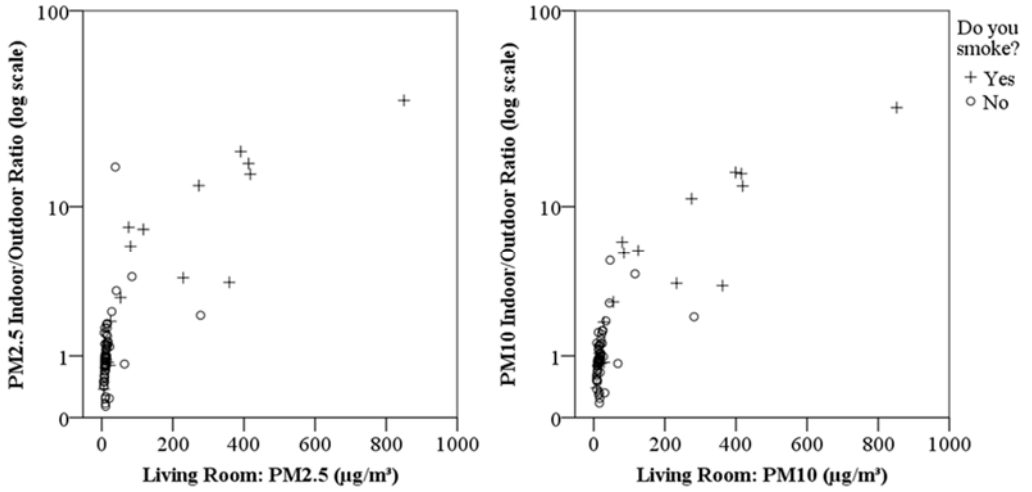

Figure 2.1. Concentration vs. Indoor/Outdoor Ratio, $PM_{2.5}$ (left) and PM_{10} (right). Circles are nonsmoking units and plus signs are smoking units.

Figure 2.2 summarizes all data collected in the study for particle concentrations at each monitoring location broken down by particle size for fine ($PM_{2.5}$) and coarse PM ($PM_{10} > x > PM_{2.5}$). Figure 2.2 shows that the majority of particle mass are measured in the fine particle fraction, which may indicate the importance of particle sources like

combustion as opposed to pet dander and other mechanical entrainment of dust, which typically produce coarse mode particles.

The data also suggests that infiltration of outdoor particles is not expected to be the dominant source of indoor particles, based on the relative concentration of particles. This is evident in both Figures 2.1 and 2.2, with the average I/O ratios being greater than 1 and balcony PM concentrations being much lower than the elevated indoor PM levels in units in which residents smoke. For these reasons, it is important to focus on the potential sources of indoor particles in the home, including smoking and use of air fresheners, candles, and incense.

As previously mentioned, the NAAQS regulating outdoor concentrations of particles in the United States is set at a 24-hour average concentration of 150 $\mu g/m^3$ for PM_{10} and 35 $\mu g/m^3$ for $PM_{2.5}$ as well as an annual $PM_{2.5}$ limit of 12 $\mu g/m^3$. While not directly applicable to indoor PM concentrations, this is used as a screening level to identify units where the indoor PM levels might be considered to directly impact health. In Table 2.3, we report the number of units that exceed each of these three standards.

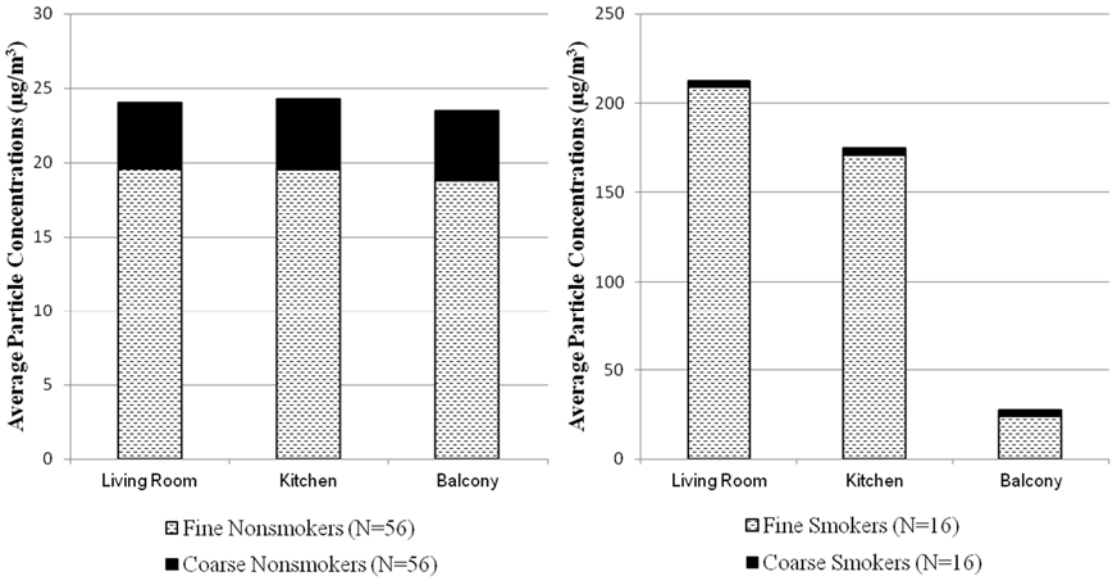

Figure 2.2. Fine (dashed lines) and coarse (solid black) particle concentrations in the living room, kitchen, and balcony (outdoor) for residents who report they do not smoke (left) and those that report they do smoke (right). Note the differences in scale.

Table 2.3

Units exceeding NAAQS. Number of units with PM concentrations above and below the EPA National Ambient Air Quality Standards, split by occupant reported smoking habits.

		Do you smoke?	
		Yes	No
PM_{10} in Living Rooms	Less than 150 µg/m^3	9	55
	Greater than 150 µg/m^3	7	1
$PM_{2.5}$ in Living Rooms	Less than 35 µg/m^3	5	51
	Greater than 35 µg/m^3	11	5
	Less than 12 µg/m^3	2	32
	Greater than 12 µg/m^3	14	24

Smoking had a clear impact on indoor PM levels in the units in which residents indicated that they smoke (N=16). Mean values of living room PM_{10} were 213 ± 58 µg/m^3 for smokers versus 24 ± 5 µg/m^3 for non-smokers (N= 56). Mean values of living

room $PM_{2.5}$ were 209 ± 58 $\mu g/m^3$ for smokers versus 20 ± 5 $\mu g/m^3$ for non-smokers. Apart from smoking, elevated indoor PM can originate from combustion sources (i.e. candles and incense), air fresheners, or the presence of pets, and each of these sources has been shown in prior research to impact PM concentrations inside the home (Géhin et al., 2008). In Figure 2.3, the outlying data points correspond to units occupied by participants who reported using air fresheners, candles, and/or incense. Among nonsmokers, the most commonly indicated potential source of indoor particles was air fresheners (N=28 out of 56). Though nonsmoking units in which products were used to change the smell in their homes (N=33) have a higher average PM compared to nonsmoking units where no additional potential PM source was reported as used (N=23), this difference was not statistically significant ($t = 1.3$, $p<0.2$). The average PM_{10} concentration for units occupied by a non-smoker who also reported none of these alternative sources of PM (i.e. use of candles, incense, or air fresheners or owning a pet) was 17 $\mu g/m^3$ while units occupied by nonsmokers reporting one or more of these alternative sources had a mean PM_{10} of 24 $\mu g/m^3$.

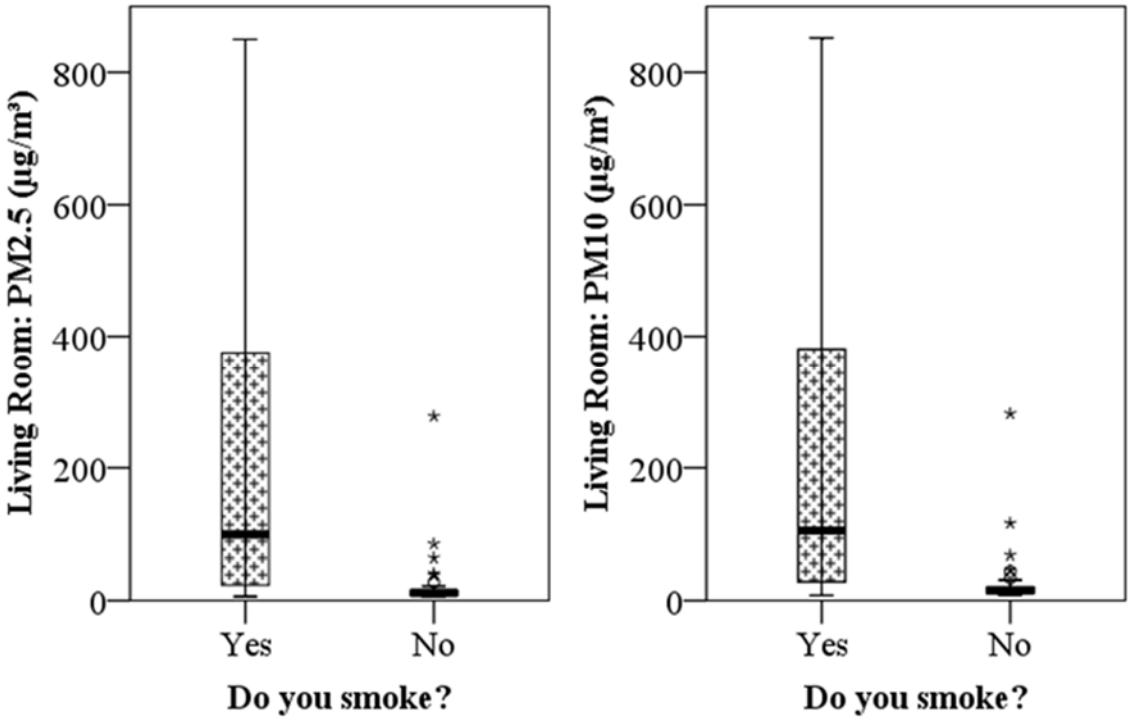

Figure 2.3. $PM_{2.5}$ (left) and PM_{10} (right) concentrations ($\mu g/m^3$), separated by smokers (N=16) and nonsmokers (N=56). The bold line within the box indicates the median. The top and bottom of the boxes indicate the 75th and 25th percentile, respectively. Asterisks and circles denote outliers.

One potential hypothesis to test is that persons with existing respiratory problems may mitigate sources of indoor pollutants to limit their exposure to particles in the home. Based on the data collected as part of our current study, this hypothesis is not supported. Occupants who indicated that they had either emphysema or asthma had higher average particle concentrations than those who did not have these respiratory problems. Units occupied by participants reporting emphysema had a mean [median] PM_{10} level of 154 [57] $\mu g/m^3$ versus 56 [16] $\mu g/m^3$ (no report of emphysema) but these differences were not statistically significant ($t = 1.5$, $p<0.2$). Occupants reporting asthma had a mean [median] PM_{10} level of 98 [18] $\mu g/m^3$ versus

61 [16] µg/m^3 (no report of asthma) but these differences were also not statistically significant (t = 0.7, p<0.5). These results are likely complicated by the correlation between persons reporting respiratory disease and those who smoke as 75% of persons with emphysema and 33% of persons with asthma are smokers compared to the entire study population where only 22% smoke.

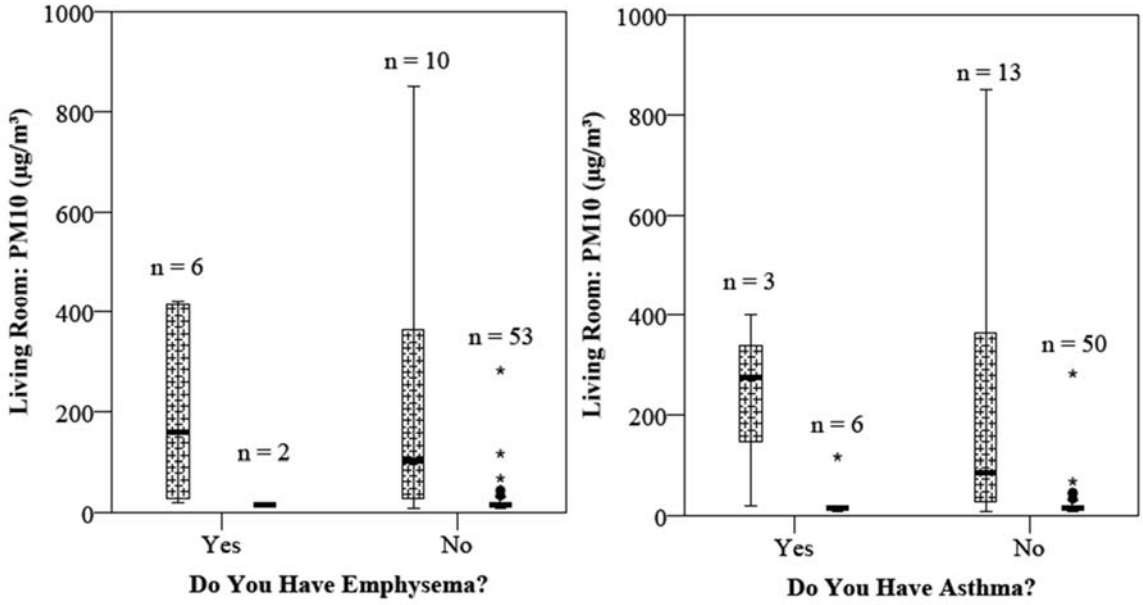

Figure 2.4. PM_{10} concentrations and respiratory problems separated by smokers (texture) and nonsmokers (solid black). N indicates the number of samples for each group. The bold line within the box indicates the median. The top and bottom of the boxes indicate the 75th and 25th percentile, respectively. Asterisks and circles denote outliers.

Aldehyde measurements. Table 2.4 summarizes formaldehyde and acetaldehyde concentrations measured in the living room, the kitchen, and the balcony. We also illustrate the cumulative frequency of the data in Figure 2.5. Indoor formaldehyde concentrations spanned the range 10 to 80 ppb, with a median of 36.9 ppb in the living room and 38.8 ppb in the kitchen. No major differences were

observed between the two indoor samples, which are highly correlated due to their close proximity (paired sample correlation=0.857, $p<0.001$).

Median formaldehyde concentrations were much higher than the 8-h reference exposure level (REL) established by the California EPA (7 ppb), comparable to the 8-h REL proposed by Health Canada (40 ppb), and were slightly lower than the California 1-h REL (44 ppb) (California EPA, 2007; Health Canada, 2006). By contrast, acetaldehyde levels were below the health-based exposure levels (the California EPA 8-h REL is 160 ppb and 1-h REL is 260 ppb for acetaldehyde). Median acetaldehyde levels for the living room and kitchen are 17.2 and 18.4 ppb, respectively.

The formaldehyde levels measured in this study were significantly higher than those described in surveys conducted in US commercial buildings and homes. Hodgson and Levin (2003) reported a median formaldehyde level of 17 ppb in North American residences, with a 95 %-ile of 61 ppb. Offermann (2009) determined a median of 29 ppb formaldehyde in new homes in California. Liu (2006) found indoor median formaldehyde and acetaldehyde levels to be 20.1 and 18.6 $\mu g/m^3$, respectively. The higher levels observed in the studied building are likely associated with the combination of strong sources (e.g., building materials, occupant activities) and relatively low air exchange rates during the summer season.

Table 2.4

Volatile aldehyde concentrations and indoor/outdoor ratios

	Formaldehyde			Acetaldehyde		
	living room	**kitchen**	**outdoor**	**living room**	**kitchen**	**outdoor**
Concentration (ppb) [(a)]						
Median all units, N=72	36.9	38.8	4.3	17.2	18.4	1.9
Mean all units, N=72	38 ± 12	40 ± 11	4.8 ± 1.9	20 ± 9	20 ± 9	2.0 ± 1.0
Mean non-smoking units, N=56	38 ± 12	41 ± 11		18 ± 7	19 ± 9	
Mean smoking units, N=16	36 ± 11	36 ± 8		24 ± 13	21 ± 12	
Indoor/Outdoor (I/O) ratio						
Median I/O all units, N=72	8.6	9.0		9.0	9.7	
Mean I/O all units, N=72	7.9	8.3		10	10	

(a)The experimental error corresponds to one standard deviation of the data.

In this study, the median outdoor concentration was 4.3 ppb for formaldehyde and 1.9 ppb for acetaldehyde, consistent with values previously reported in the literature for similar studies (Hun et al., 2010; Offermann et al., 2009). The high indoor/outdoor (I/O) concentration ratios ($8 < I/O < 10$) reported in Table 2.4 indicate the prevalence of indoor sources for these pollutants. The difference of the means from unity is statistically significant ($t = 18.026$, $p<0.001$ and $t = 17.466$, $p<0.001$, for formaldehyde and acetaldehyde, respectively).

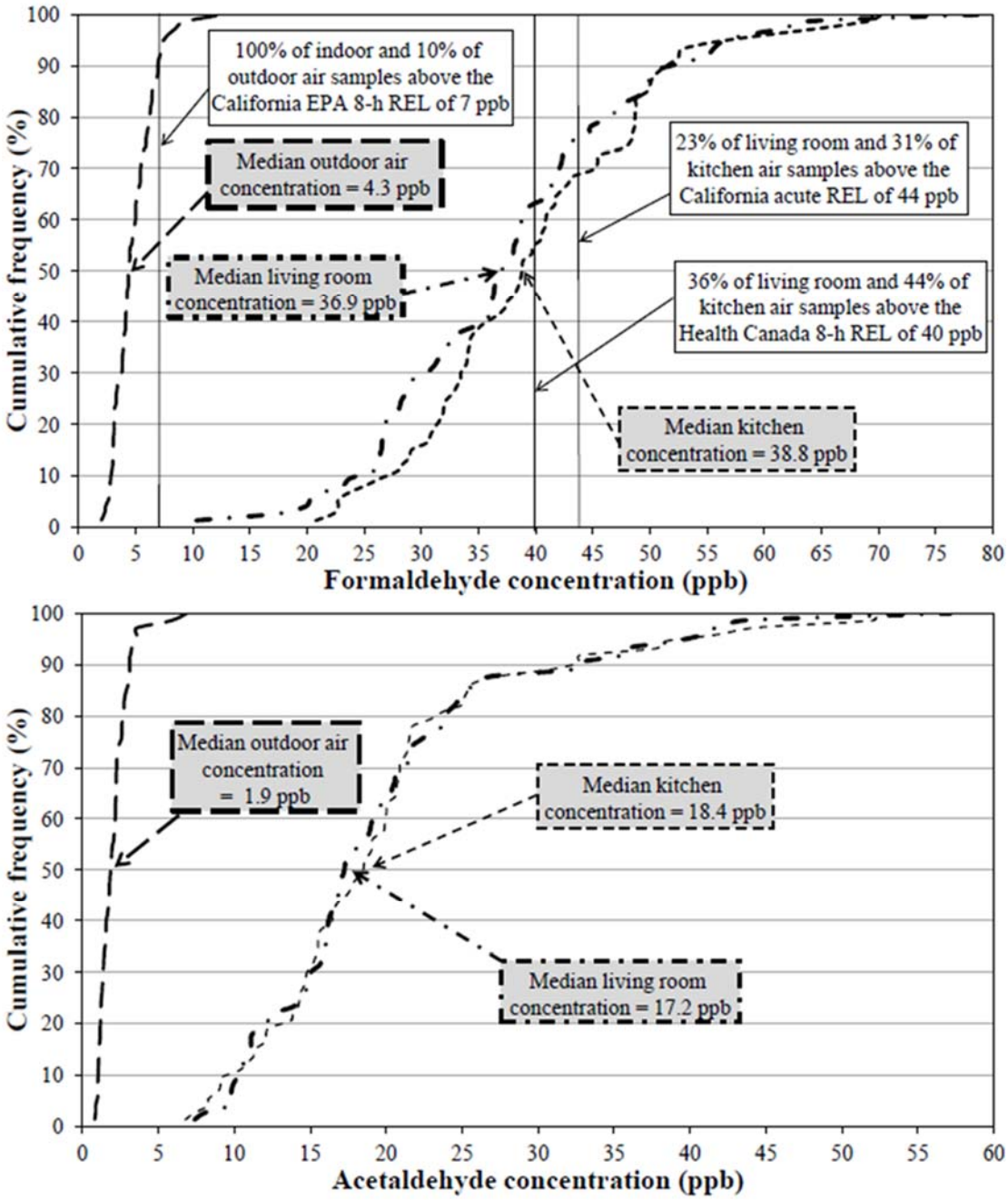

Figure 2.5. Cumulative frequency of formaldehyde concentrations (top) and acetaldehyde concentrations (bottom) measured in the living room (dash-dot), kitchen (short dash) and outdoors (long dash).

The distribution of formaldehyde and acetaldehyde concentrations across subsets of smoking and non-smoking apartments is shown in Figure 2.6. In contrast to the strong

influence of smoking on PM levels, there was no statistically significant difference in volatile aldehyde levels between units where residents report smoking versus units where residents do not report smoking ($t = -0.66$, $p<0.6$ and $t = -1.82$, $p<0.10$ for formaldehyde in the living room and kitchen, respectively). Formaldehyde mean concentrations were in the range 35 – 41 ppb (comprising both indoor measurements), with standard deviation between 8 and 12 ppb. Units in which residents indicated they smoked showed slightly lower levels of formaldehyde than non-smoking units; however, the differences (between 2 and 5 ppb) were smaller than the standard deviation of the data. Similarly, acetaldehyde mean indoor levels were in the range 18 – 24 ppb with standard deviations between 7 and 14 ppb. Acetaldehyde levels in smoking apartments were higher by a small margin of 3 to 5 ppb, which was also smaller than the standard deviation of the data and not statistically significant ($t = 2.10$, $p<0.04$ and $t = 0.8$, $p<0.5$ for the living room and kitchen, respectively).

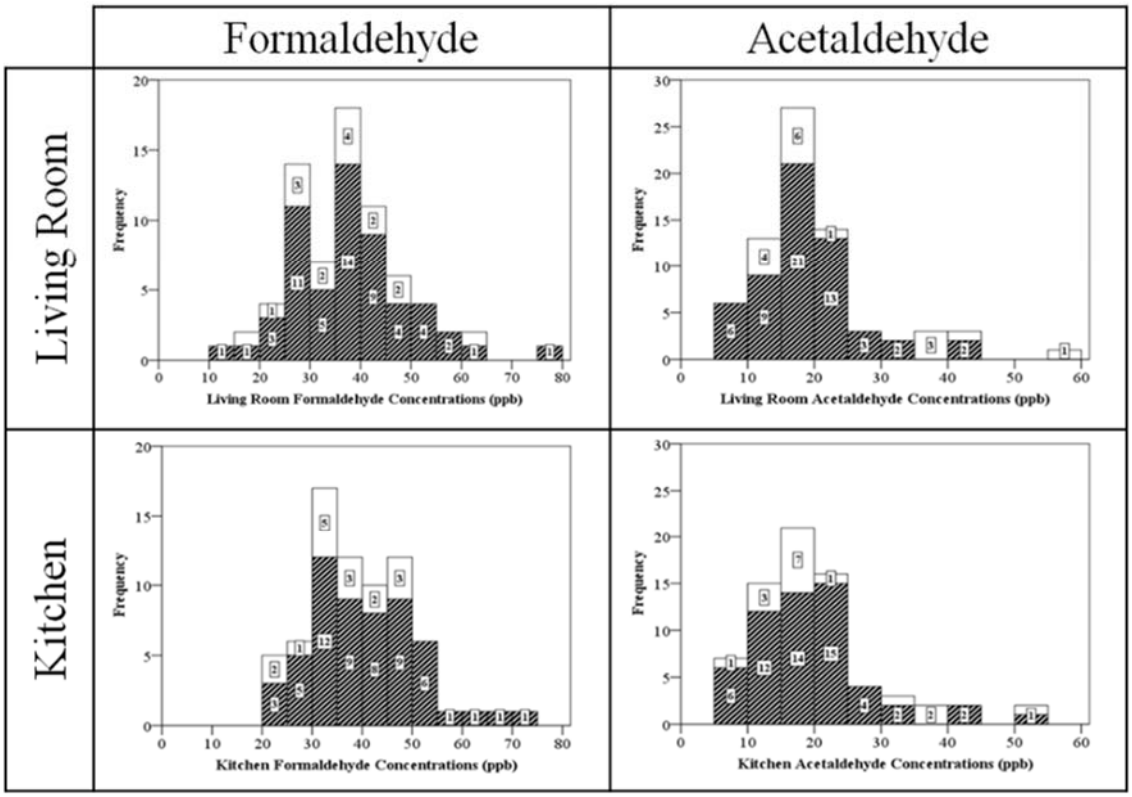

Figure 2.6. Distribution of indoor formaldehyde and acetaldehyde concentrations in smoking and non-smoking apartments corresponding to (top) living room, and (bottom) kitchen. The blank sections indicate smoking units and the textured sections indicate nonsmoking units.

Conclusions

The present work reports key indoor air quality parameters, including PM levels and aldehyde concentrations, for a low-income senior apartment complex. The air quality sampling was combined with a health questionnaire to garner information on the personal habits and general health of residents. With over 70 residences sampled, this large data set describes associations between occupants' behavior, indoor air quality and health, and provides a foundation for the subsequent evaluation of the impact of different

interventions (e.g., building retrofits, increased ventilation, filtration, air cleaning) on indoor air quality.

The initial results indicate that elevated indoor particle concentrations are directly linked to residents who smoke; however residents were only asked if they smoked, not if they smoke indoors. Data do not indicate that outdoor particles are infiltrating to the indoor environment. While smoking impacted indoor PM levels, there was no statistically significant difference on indoor aldehyde levels for residents who smoked compared to those that reported they did not smoke. For all units, formaldehyde levels were greatly elevated with 36% of living room samples and 44% of kitchen samples exceeding the Health Canada REL for chronic exposure to formaldehyde, of 40 ppb. No statistically significant correlation was found between measured indoor PM and aldehyde concentrations.

Although this study allowed us to sample many units, one hour sampling leads to some research limitations. For example, while data presented here represent typical concentrations in the summer, it may not hold true for the fall, winter, and spring seasons. Additionally, even though cross contamination between different units could impact measured indoor air quality, as has been shown by Bohac, et al. (2011), air exchange between units was not quantified in this study. This could be an important factor if the environmental tobacco smoke of one neighbor was infiltrating the unit of a nonsmoker, thus increasing particle concentrations. Another limitation is that no longer term (day-long or week-long) indoor air samples were collected.

CHAPTER 3

THE EFFECTS OF AN ENERGY EFFICIENCY RETROFIT ON INDOOR AIR QUALITY[2]

Introduction

As the topic of energy efficiency in buildings is further explored, there are many concerns pertaining to the long term effects of these changes. The need for reduced energy consumption, driven by rising energy costs and the desire to eliminate dependence on fossil fuels, has become a national priority. A common approach to this problem is to seal the building envelope, reducing air leakage and unnecessary usage of heating and cooling units. However, by reducing ventilation rates, pollutants could become trapped and increased exposure to toxins becomes a concern (Jones, 1999; Fisk, 2000; Weschler and Shields, 2000).

The risk of increased exposure lies in the statistic that Americans spend up to 90% of their time indoors, whether at work , school, or in their homes (US EPA, 1989; Wallace et al., 2006). Mitigating exposure and understanding how the indoor pollutants are created and sustained is of utmost importance (Lee et al., 2002; Wallace et al., 2006). The most vulnerable populations affected are children, the elderly, and people with existing respiratory diseases. In addition, low-income populations are less likely to have access to indoor air pollution intervention information, making low-income seniors a population most impacted and least able to respond to the burdens of a toxic indoor environment (Williams et al., 2000).

[2] Accepted for publication as Frey, S.E., Destaillats, H., Cohn, S., Ahrentzen, S., and Fraser, M.P. (2014). The effects of an energy efficiency retrofit on indoor air quality. *Indoor Air*.

Therefore, a combination of increased time spent indoors and the increase of energy efficiency building practices has created the need to assess the impact of renovations on indoor environmental quality and human health. The U.S. Department of Housing and Urban Development promotes energy conservation and healthy home environments and has funded research on the potential impacts of "green" building methods on both indoor environments and resident health (US HUD, 2009). It has been suggested that "green" housing solutions may actually be detrimental to resident health, by not taking into account low-risk building materials and neglecting indoor air quality during the design process (Wargo, 2010). However, a recent study illustrated the potential for overall improvements in indoor air quality when retrofit measures are implemented with the simultaneous aims of saving energy and improving indoor environmental quality (Noris et al., 2013). Here, we evaluate impacts on indoor air quality as it relates to particulate matter and volatile carbonyl concentrations, specifically formaldehyde, acetaldehyde, and acetone.

The US EPA considers particulate matter, or PM, as a major concern due the ability of particles with diameters less than 10 micrometers (PM_{10}) to pass through the throat and nose and into the lungs. This, in turn, has an impact on both lung and heart health (Dockery et al., 1993; Pope and Dockery, 2006). There have also been many studies connecting outdoor PM exposure to increased mortality rates and respiratory diseases (Li et al., 2003; Englert, 2004; Davidson et al., 2005; Fann et al., 2012). Due to these findings, National Ambient Air Quality Standards (NAAQS) were set to regulate annual ambient concentrations of PM_{10} at 150 $\mu g/m^3$ and $PM_{2.5}$ at 35 $\mu g/m^3$. No limits

have been established for indoor PM levels, even though more evidence of indoor PM exposure being linked to negative health effects are surfacing (Koenig et al., 2005).

Carbonyls, especially formaldehyde, are ubiquitous in the indoor environment, and have been associated with both chronic and acute health effects. The main sources of indoor formaldehyde include the degradation of additives used in wood based building materials, furniture, and sealants as well as combustion and chemical reactions common to the indoor environment (Hodgson et al., 2002; Destaillats et al., 2006; Singer et al., 2006; Destaillats et al., 2011; Sidheswaran et al., 2013). Potential health concerns include irritation to the eyes, nose, throat, and lungs. Chronic exposure to formaldehyde has also been shown to lead to asthma symptoms, allergic sensitization, and overall reduction of lung function (LBNL, 2008; Salthammer et al., 2010; California EPA, 2007). Formaldehyde has been listed among the top five indoor pollutants causing chronic health effects in US residences (Logue et al., 2012), has been identified as a potential carcinogen by the US EPA (group B1, US EPA, 1999a), and classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC, 2012). Acceptable exposure levels for formaldehyde determined by various countries have been summarized by Salthammer et al. (2010). In 2007, the California EPA established an 8-hour Reference Exposure Level (REL) of 7 ppb and an acute REL of 44 ppb. Health Canada, however, has 8-hour REL of 40 ppb, over five times higher than the CA EPA requirements (2006). In 2010 the World Health Organization released a less stringent guideline of 80 ppb for both short-term and long-term risks (WHO, 2010).

This research is a subset of a larger study evaluating the overall impact of an energy efficiency retrofit on a vulnerable population, including cost effectiveness and

health benefits (Ahrentzen et al., 2013). Here, particulate matter and volatile carbonyl concentrations are the benchmark for measuring how the retrofit affects the indoor air quality both immediate post-renovation and 1 year following renovation. We seek to understand what sources and behaviors may impact increased PM and aldehyde exposure. We also examined whether indoor air quality improvements resulted in changed health conditions or health-related behaviors (such as improved sleep).

Material and Methods

Sampling campaign and health survey. A study was conducted at a local apartment complex, operated by the City of Phoenix Housing Department, for seniors who qualify for subsidized rent. Originally built in the early 1970's, this three-story, 116-unit structure underwent unit renovations and energy efficiency improvements in spring and early summer of 2011. The HVAC system for each apartment included a through-wall package terminal air conditioner (PTAC) unit, a bathroom exhaust fan, a range hood exhaust fan, and doors and windows. The retrofit of each apartment included upgrades in PTAC units, both exhaust fans, and installation of energy efficient, double pane exterior windows and sliding glass balcony doors. Other improvements included installation of low VOC flooring, new cabinetry (natural oak product), paint (zero VOC), low VOC carpet and carpet pad (Green Label Plus Certified), Energy Star kitchen appliances (refrigerator, electric range, microwave, and garbage disposal), and the addition of a bedroom ceiling fan.

Researchers tested air quality in the self-contained apartments a total of three times: in the summers of 2010, 2011, and 2012. Panel 1, before the renovation, was conducted during the summer of 2010. Panel 2 was conducted immediately after

construction was completed from late April through September 2011. One year later, Panel 3 was conducted from June through early August 2012. For air quality sampling, a total of 72 apartments were studied in Panel 1, which have been reported separately (Frey et al., 2014). A total of 54 and 53 units were studied in Panel 2 and 3, respectively. However, only 47 units participated in all three panels, corresponding to an attrition rate of 35%. Since the research design was a longitudinal panel study examining the changes in each resident's apartment over time, data from residents in the first panel who did not participate in later panels were eliminated from the analyses. This type of research design, however – in which each apartment is its own control group – allowed us to examine improvements or changes from the first to subsequent panels by using paired t-tests and fixed-effects regression models, which worked effectively with this smaller sample size.

Simultaneous measurements of indoor air pollutants, particulate matter and volatile carbonyls were collected in the living room and kitchen, and outdoor pollutant concentrations on the balcony of each unit. All units have 619 ft^2 of livable space and are identical in interior layout and are all-electric homes (i.e. no fireplaces, gas stoves, etc.) with individual through-wall package terminal air conditioner (PTAC) units. One-hour samples were collected in each unit between the hours of 9am and 5pm. Repeated testing in a subset of units (7 % replicate) ensured that no time-of-day bias was present. The summer season was selected for sampling as local hot weather would result in the apartment units being sealed (i.e. windows closed) with air conditioning running. During instrument setup and sampling, residents did not cook, smoke, or clean.

At the same time as air quality testing, a health survey of over 100 questions was given to the residents to solicit information about personal habits and self-reported health conditions. Performing the air quality measurements and questionnaire simultaneously ensured that resident activities (i.e. cooking, smoking) did not bias the data and would not be present during sampling.

The indoor air quality testing, presented here, is a subset of a larger-scale study in which cost efficiency and health benefits of the renovations were also analyzed (Ahrentzen et al., 2013). Additional information about temperature, humidity, air leakage, and the health questionnaire can be found in that report. While one-hour sampling periods are relatively short and may be more susceptible to short-term sources, the sampling plan was carefully designed in order to minimize the impact of resident activity during sampling, thus reducing that risk. In addition, the sampling plan and the panel survey research design maximized the number of participants to account for an expectedly high attrition rate among a low-income elderly population over a two-year period. Short-duration samples allowed coordinating for a large number of units over the month-long sampling period obtaining a representative data set for the building. Though cross contamination across different units could impact the results of this study (e.g., due to all units sharing common vertical exhaust ducts), it was not quantified in this study. In addition, because ventilation rates were not tracked during sampling, changes in concentrations could be due to either changes in sources or changes in ventilation rates.

Particulate Matter measurements. Indoor air quality sampling included real-time measurement of PM using TSI DustTrak DRX aerosol monitors (model 8533, TSI, Inc., Shoreview, MN) sampler. This instrument contains a light-scattering laser

photometer to detect various particle sizes, including PM_1, $PM_{2.5}$, PM_4, PM_{10} and PM-total. The maximum size measured for the PM-total is approximately 15 microns based on manufacturer specifications. Three samplers were deployed to the apartment kitchen, living room, and balcony to simultaneously collect particle data over a one hour period during which the resident was given the health survey. By sampling both indoor and outdoor air, we are able to calculate indoor/outdoor ratios with the goal of quantifying the impact of infiltration of outdoor particles verses indoor sources on indoor air quality. Dusttraks were labeled and used in a consistent manner among units, were calibrated prior to the study, and tested for reproducibility by collocated sampling. While Dustraks have been shown to overestimate PM compared to gravimetric measurements, the use of a consistent sampling platform was designed to minimize bias due to sampling technique (Jenkins et al., 2004 and Wallace et al., 2011).

Carbonyl measurements. Samples of indoor and outdoor formaldehyde, acetaldehyde and acetone were collected using commercial samplers containing dinitrophenyl hydrazine (DNPH)-coated silica gel (Sep-Pak XPoSure Aldehyde Sampler, # WAT047205, Waters Corp., Milford, MA). The cartridges were preceded by an ozone scrubber (Sep-Pak Ozone Scrubber, # WAT054420, Waters Corp., Milford, MA) to eliminate ozone from the incoming air. Air was drawn through the samplers by means of pumps operating at ~2 L min^{-1} (determined with a precision better than ±3%). Samples were collected over 1-hour periods using portable gas pumps (Universal XR Pump, Model PCXR4, SKC Inc., Eighty Four, PA). The sampling flow of each pump was calibrated in the laboratory before and after the sampling period using a bubble flow meter and a primary air flow calibrator (Gilibrator-2 Sensidyne, St. Petersburg, FL).

Three samples were collected simultaneously with and in close proximity to the PM samplers in the living room, kitchen, and balcony of each unit.

After collection, each DNPH cartridge was capped, labeled and stored at 4 ^{o}C until it was extracted and analyzed. Acetonitrile extracts were analyzed by High Performance Liquid Chromatography (HPLC) with UV detection at 360 nm following a US EPA method (US EPA, 1999). The concentration value reported in each case corresponded to a time-integrated average over the sampling period. Calibration curves for quantification were determined with authentic standards of the dinitrophenylhydrazones of formaldehyde, acetaldehyde and acetone (Sigma-Aldrich). The detection limit for each volatile carbonyl was typically 10 ng or lower, corresponding to air concentrations < 0.1 ppb. Laboratory and field blank samples (at least three laboratory and six field blanks) were also analyzed, showing non-detectable values of the three analytes.

Reported health measures. The resident survey created and used in this study contained over one hundred fixed-response and open-ended questions pertaining to health conditions, resident assessments of the environmental quality of their apartments, and household activities and behaviors relevant to environmental quality. The health-related questions were derived from standardized instruments developed by the Centers for Disease Control: the National Health Interview Survey (NHIS) and the Behavioral Risk Factor Surveillance System (BRFSS). The same questions were asked of residents at each panel. Pertinent to the analyses presented here were questions regarding: smoking behavior; use of cleaning and odor-masking products; an index of respiratory conditions

(derived from single questionnaire items pertaining to snoring, asthma, emphysema, hay fever, bronchitis, sinusitis); index of quality of health/life (derived from three questionnaire items); index of emotional distress (derived from six standardized questionnaire items; see Pikonis et al., 2011); and sleep (number of hours).

Results and Discussion

While the effectiveness of the retrofit is beyond the scope of this particular manuscript, energy and water savings have been quantified. To summarize, the retrofit of Sunnyslope Manor resulted in a reduction of 12.6% in water consumption and 19.4% in electricity consumption based on analysis of 39 months of metered electrical and water use between July 2009 and September 2012 (Ahrentzen et al., 2013).

Data analyses procedures. As mentioned previously, the particulate matter (PM) and aldehyde concentrations of each resident's kitchen, living room and balcony were recorded. However, because linear correlations between an apartment's kitchen and living room PM data were 0.90 or higher, measurements were combined from these rooms into one composite measure (by averaging room-level data) to represent the unit.

Trends are evaluated as the change of conditions between Panels 1 and 2, labeled the "Short Term" and between Panels 1 and 3, labeled the "Long Term" where only units that participated in both Panels are included in the statistical analysis. Given the panel research design, we used fixed effects models when comparing differences in an apartment's conditions between panels (all statistics presented will be fixed effects regressions, unless otherwise noted).Since we did not have a control group but did have a longitudinal panel research design, these models were quite appropriate to the panel nature of our study, where each individual's apartment acts as his or her own control.

There are two basic data requirements for using fixed effects methods (Allison, 2005), both of which were addressed in our study: (1) the dependent variable must be measured for each unit on at least two occasions and those measurements must have the same metric; and (2) the predictor variable must change in value across those two occasions for some substantial portion of the sample.

Sample characteristics. The questionnaire given to residents during testing was essential to characterize the demographics of the apartment units sampled. Most units (88%) were occupied by a single individual. Average age of residents at the beginning of the study was 73 years; and 65% reported at least one respiratory health problem at the first panel. The average length of stay of living in the apartment was 5.5 years.

Behavioral questions most relevant to the data reported here are summarized in Table 3.1. In addition, this resident behavior information aids in the interpretation of the indoor air quality data collected; and a summary of participant behavioral data is presented in Table 3.2 below.

Table 3.1

Examples of relevant questions asked of residents during air sampling. This is a subset of a questionnaire of over 100 questions.

Relevant Questionnaire Inquiries
Do you smoke?
Do you use bug sprays?
Do you use anything to change the smell of the air in your home more than once per week?
If yes, does that include candles? Incense? Air freshener? Or Other?

Table 3.2

Questionnaire responses for each panel, number of responses (percentage)

	Total Units	Smoker	Use Insecticide	Change smell of air
Panel 1	72	16 (22%)	17 (24%)	46 (64%)
Panel 2	53	9 (17%)	19 (36%)	34 (64%)
Panel 3	53	11 (21%)	1 (2%)	33 (62%)

Particulate Matter. Mean and median indoor concentrations, as well as indoor outdoor ratios, can be found in Table 3.3. Based on all indoor/outdoor ratios being greater than 1, measured levels of indoor PM often far exceeded measured outdoor concentrations, an indication of the importance of indoor PM sources for the units participating in the study. Though indoor particle concentration averages are higher, they are also widely variable compared to outdoor PM concentrations, though part of the difference may be due to varying particle morphology between indoor and outdoor PM, which alters instrument response. When comparing Panel 1 indoor PM_{10} to outdoor PM_{10}, there is a mean difference of 42 ($\mu g/m^3$) (paired t-test: $t=2.665$, $p<0.01$) and a low correlation of 0.29 ($p<0.05$). This trend is also found in Panels 2 and 3. However, as the bias of PM mass concentrations have been reported with the use of light-scattering instruments, the focus will be on the relative change of PM concentrations between panels.

Table 3.3

Means and medians for particulate matter concentrations and indoor/outdoor ratios for all three panels. Panel 1 (N=72) from 2010, Panel 2 (N=53) from 2011, and Panel 3 (N=53) from 2012.

		$PM_{2.5}$			PM_{10}		
		Indoor concentrations (µg/m³)	Outdoor concentrations (µg/m³)	Indoor/Outdoor Ratio	Indoor concentrations (µg/m³)	Outdoor concentrations (µg/m³)	Indoor/Outdoor Ratio
N=72	Panel 1 Mean	58 ± 125	20 ± 21	3.0	62 ± 125	24 ± 21	2.5
	Panel 1 Median	13	13	1.1	18	17	1.0
N=53	Panel 2 Mean	67 ± 145	17 ± 13	2.8	74 ± 146	26 ± 18	2.9
	Panel 2 Median	20	13	1.6	25	19	1.5
N=53	Panel 3 Mean	37 ± 87	10 ± 5	2.9	41 ± 87	16 ± 7	2.2
	Panel 3 Median	19	10	1.9	22	15	1.5

The ranges of PM_{10} concentration were 8-783, 13-1375, and 11-600 µg/m^3 for Panels 1, 2, and 3, respectively. The best way to visualize these concentrations and changes between the short and long term is through a cumulative frequency plot, as seen in Figures 3.1 and 3.2.

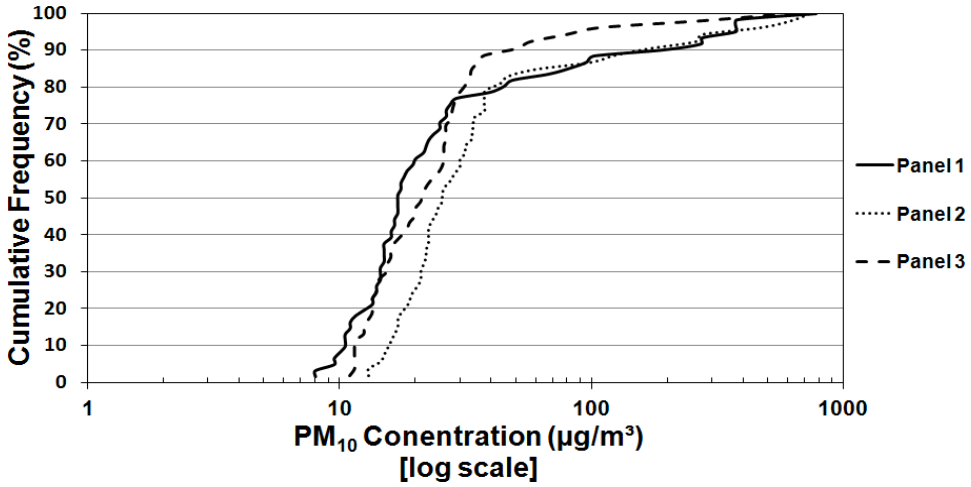

Figure 3.1. Cumulative frequency plot of PM_{10} concentrations from Panel 1 (solid), Panel 2 (dot), and Panel 3 (dash).

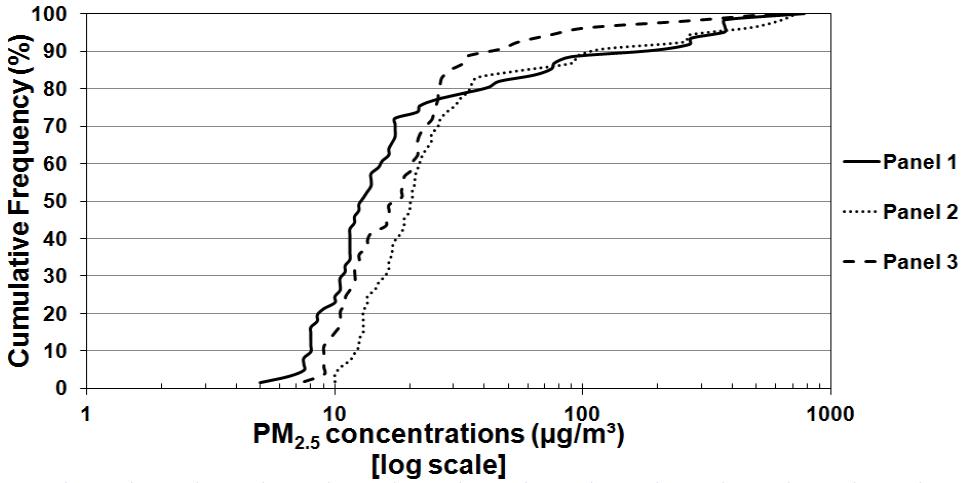

Figure 3.2. Cumulative frequency plot of $PM_{2.5}$ concentrations from Panel 1 (solid), Panel 2 (dot), and Panel 3 (dash).

While mean PM counts did show changes over time, the variance was so large that statistical significance was not achieved. Overall, there was no statistically significant change in PM levels before the renovation and afterwards (either in the short or long term). However, if the top 25th percentile of Panel 1 (who also participated in Panel 3) is isolated, there is a statistically significant decrease in both $PM_{2.5}$ and PM_{10} in the long term (paired t-test, N=13 out of 53: $t=2.167$, $p<0.05$ and $t=2.219$, $p<0.05$, respectively).

One of the largest factors connected to elevated indoor PM concentrations was smoking. This is shown specifically for each panel in Table 3.4. Mean and median $PM_{2.5}$ concentrations and indoor/outdoor ratios are given.

Table 3.4

Means and medians for $PM_{2.5}$ concentrations and indoor/outdoor ratios for all three panels, separated by smoking units and non-smoking units: Panel 1 (N=16, N=56) from 2010, Panel 2 (N=9, N=44) from 2011, and Panel 3 (N=11, N=42) from 2012.

	Smoking $PM_{2.5}$			Non-smoking $PM_{2.5}$		
	Indoor concentrations ($\mu g/m^3$)	Outdoor concentrations ($\mu g/m^3$)	Indoor/Outdoor Ratio	Indoor concentrations ($\mu g/m^3$)	Outdoor concentrations ($\mu g/m^3$)	Indoor/Outdoor Ratio
Panel 1 Mean	209 ± 232	24 ± 18	8.5	20 ± 38	19 ± 22	1.4
Panel 1 Median	99	20	4.6	12	12	1
Panel 2 Mean	361 ± 430	28 ± 20	12	22 ± 14	15 ± 11	2.2
Panel 2 Median	257	51	5	19	12	1.6
Panel 3 Mean	82 ± 173	13 ± 6	4.3	25 ± 41	10 ± 5	2.5
Panel 3 Median	25	10	2.5	16	10	1.9

Statistical analysis using various covariates was used to see if resident demographics or habits had an impact. In the short term, the resident's length of stay, whether the resident smoked, and use of odor-masking products were covariates that had statistical impact.

In the short term (between Panels 1 and 2), both $PM_{2.5}$ and PM_{10} concentrations increased as the length of time residents lived at SSM increased ($PM_{2.5}$ $t = 3.063$, $p = 0.003$; PM_{10} $t = 3.041$, $p < 0.003$). However, the indoor/outdoor ratios decreased with length of time living there (I/O $PM_{2.5}$ $t = 3.721$, $p < 0.001$; I/O PM_{10} $t = 3.732$, $p < 0.001$); no coherent or consistent explanation could be found for this association. The units of those residents who used odor-masking products showed increased levels of $PM_{2.5}$ and PM_{10} in the short term ($PM_{2.5}$ $t = 1.963$, $p = 0.052$; PM_{10} $t = 1.972$, $p = 0.051$), but there was no similar change of indoor/outdoor PM ratios. Not surprisingly, PM concentrations and I/O ratios were significantly higher in homes of those residents who smoked than in the units of non-smokers ($PM_{2.5}$ $t = 3.717$, $p < 0.001$, PM_{10} $t = 3.960$, $p < 0.001$; I/O $PM_{2.5}$

t=6.592, p <0.001, I/O PM_{10} t=6.957, p < 0.001). However, there was no significant change in the short term when smoking was added as a covariate.

In the long term (between Panels 1 and 3), the resident's length of stay, resident's age, and whether the resident smoked were statistically significant covariates. Contrasting to the short term changes, as a resident's length of stay increased a decrease in long term $PM_{2.5}$ and PM_{10} concentrations was identified ($PM_{2.5}$ t =-1.865, p = 0.065; PM_{10} t = -1.897, p =0.061). This change was not reflected in the indoor/outdoor ratios. When compared to the increasing age of a resident, both long term PM concentrations and indoor/outdoor ratios decreased ($PM_{2.5}$ t = -2.214, p = 0.029; PM_{10} t = -2.151, p = 0.034 and I/O $PM_{2.5}$ t = -2.151, p = 0.034; I/O PM_{10} t = -1.929, p = 0.057, respectively). Finally, units occupied by residents who smoke had higher PM levels than units with nonsmoking residents ($PM_{2.5}$ t = 6.186, p <0.001; PM_{10} t = 6.161, p <0.001). The higher PM concentrations measured in units with smokers has a significant decrease compared to non-smokers ($PM_{2.5}$ t = -3.078, p < 0.001; PM_{10} t = -3.059, p <0.003).

Carbonyl measurements. Table 3.5 summarizes acetone, acetaldehyde, and formaldehyde concentrations and indoor/outdoor ratios for each panel. We also illustrate the cumulative frequencies of the formaldehyde and acetaldehyde data in Figures 3.3 and 3.4. Figure 3.3 also includes reference lines for the most recent California 8-h REL, the Health Canada 8-h REL, and the California acute REL.

Table 3.5

Mean and median concentrations of acetone, acetaldehyde, and formaldehyde for each Panel.

		Acetone		Acetaldehyde		Formaldehyde	
		Indoor concentrations ± standard deviation (ppb)	Indoor/Outdoor Ratio	Indoor concentrations ± standard deviation (ppb)	Indoor/Outdoor Ratio	Indoor concentrations ± standard deviation (ppb)	Indoor/Outdoor Ratio
N=72	Panel 1 Mean	41 ± 41	8.7	20 ± 9	11	39 ± 11	8.7
	Panel 1 Median	28	8.1	18	9.8	38	7.7
N=54	Panel 2 Mean	91 ± 45	14	34 ± 17	13	42 ± 13	9.5
	Panel 2 Median	90	11	33	10	43	7.1
N=53	Panel 3 Mean	52 ± 42	11	20 ± 7	10	27 ± 7	7.1
	Panel 3 Median	39	9.7	20	9.1	26	6.8

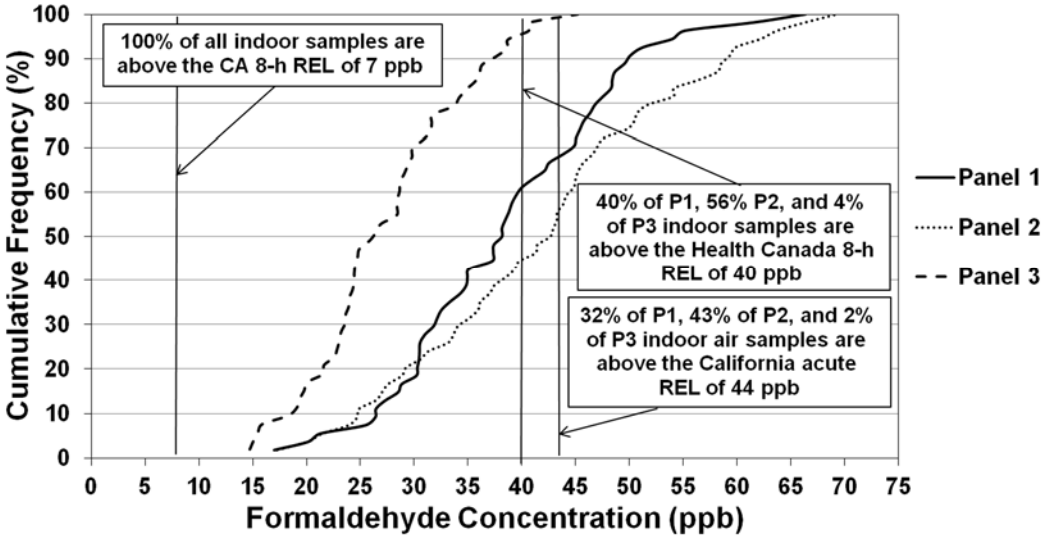

Figure 3.3. Cumulative frequency plot of formaldehyde from Panel 1(solid), Panel 2 (dot), and Panel 3 (dash).

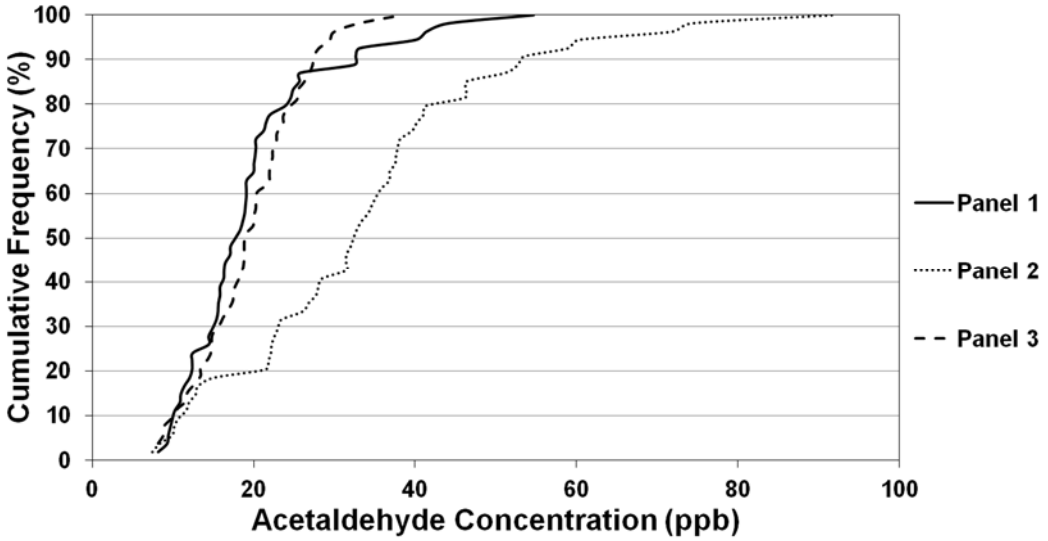

Figure 3.4. Cumulative frequency plot of acetaldehyde from Panel 1(solid), Panel 2 (dot), and Panel 3 (dash).

As seen in Figure 3.3, 100% of samples in all three panels, with levels ranging from 17 to 69 ppb, exceeded the California EPA 8-hour reference exposure level (REL) of 7 ppb. When compared to the CA acute REL standard of 44 ppb, 32% of Panel 1 and 43% of Panel 2 units were above the standard. Additionally, 40% of Panel 1 samples and 56% of Panel 2 samples exceeded the Health Canada REL of 40 ppb. However, no unit exceeded the WHO guideline of 80 ppb. These formaldehyde levels are comparable or higher than those reported for US buildings and homes. Offermann (2009) determined a median of 29 ppb formaldehyde in new homes, and Hodgson and Levin (2003) reported a median formaldehyde level of 17 ppb, with a 95 %-ile of 61 ppb. Similar residential formaldehyde levels have been reported in other countries, with a mean of 18 ppb in the UK (n=833, 1997-1999), 19 ppb in Germany (n=586, 2003-2006), 33 ppb in Finland, 20 ppb in Austria (n=160), 25 ppb in Japan (n=1181, 2005), and a median of 16 ppb in France (n=554, 2003-2005) and 24 ppb in Canada (n=96, 2005) (WHO, 2010). By

contrast, very high levels have been reported in recently remodeled Chinese homes, with a mean of 190 ppb (n~6000, 1999-2006) (WHO, 2010), and in trailers supplied by the US Federal Emergency Management Agency (FEMA) to shelter evacuees from Hurricanes Katrina and Rita in 2005, with a mean formaldehyde concentration of 77 ppb (n=519) (Murphy et al., 2013).

All measured acetaldehyde levels, reported in Figure 3.4, were below the health-based exposure levels recommended by the California EPA (8-h REL = 160 ppb and 1-h REL = 260 ppb). Acetone levels measured in this study do not pose any health hazards, as the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 250 ppm as a time-weighted average for up to 10 hour work shift over a 40 hour work week (NIOSH, 1994). Acetone levels are included in this report, even though levels are far below health guidelines, to illustrate the behavior of a common indoor VOC generated by sources predominantly related to human activities.

As can be seen in table 3.3, long term changes were notably different from those of the short term for formaldehyde. While there was no change in the short term, there is a significant decrease in the long term ($t= -6.376$, $p<0.001$). This decrease held after controlling for most of the mediating building characteristics (orientation, wing, floor) and other covariates. While older residents had higher formaldehyde concentrations in their apartments, there was no change between Panels 1 and 3.

Interestingly, acetaldehyde and acetone did not follow the same trends as formaldehyde. In contrast, both acetone and acetaldehyde had a statistically significant increase in the short term ($t=5.928$, $p<0.001$ and $t=4.924$, $p<0.001$, respectively), even after controlling for mediating factors. Additionally, residents who have lived longer at

the residence or began using odor masking products had a higher increase in acetaldehyde concentrations in their homes ($t=2.180$, $p=0.031$ and $t=1.934$, $p=0.056$, respectively) while those who stopped using indoor insecticide saw a decrease ($t= -2.483$, $p=0.015$). In the long term, neither chemical experienced a change from panel 1, although acetaldehyde concentrations were higher in units where residents indicated they smoked ($t=-5.290$, $p<0.001$)

Correspondence between improvements in air quality and reported health. Given the relatively brief scope of this study and lack of a control group, we did not expect to find definite changes in health conditions after the retrofit, particularly among the more serious medical and health diagnoses. Nonetheless, we did examine whether the significant decrease in formaldehyde levels in the long term measurements also resulted in improved health conditions. For example, an index of respiratory conditions, an index of quality of life/health, emotional distress, and number of hours sleeping during the night are conditions that may be responsive to improved indoor air quality.

As shown in Table 3.6, differences between individual unit formaldehyde concentrations are associated with self-reported health conditions, particularly in the short term. Using fixed effects regression of data between Panels 1 and 2, changes in formaldehyde concentrations were correlated with residents' reported quality of life/health and reduction in emotional distress. That is, as the formaldehyde levels in one's apartment improved (i.e. declined in concentration levels), residents expressed greater satisfaction with their quality of life/health and less emotional distress. Between Panels 1 and 3, formaldehyde change correlated with to reduced emotional distress scores, but only at marginal statistical significance possibly because all formaldehyde

concentrations showed a significant decrease in Panel 3. These findings between formaldehyde reductions and emotional distress improvements are suggestive only. The larger study (Ahrentzen et al., 2013) noted correspondence between emotional improvements and other environmental improvements (e.g. temperature) and physiological factors (e.g. functional limitations). Multivariate modeling to examine interrelationships between these variables was not conducted because of the small sample size. However, given the prominent improvement in emotional distress in the larger study, future research with larger sample sizes should examine the role of multiple environmental factors in improving mental health of older adults. There were no significant correlations between formaldehyde changes and sleep or respiratory conditions.

Table 3.6

Fixed Effects Regression of Formaldehyde Change in Unit and Resident Reported Emotional Distress and Life/Health Quality, Both Short Term and Long Term

	Short Term				Long Term			
	Quality of Health/Life		Emotional Distress		Quality of Health/Life		Emotional Distress	
	t	p value	t	p value	t	p value	t	p value
Formaldehyde Level in Unit	2.624	< 0.01	-3.912	< 0.001	1.257	n.s.	-1.781	< 0.08

Conclusions

The research presented here reports key indoor air quality parameters, including PM levels and carbonyl concentrations, for a low-income senior apartment complex before and after an energy efficiency retrofit. The air quality sampling was combined with a detailed health questionnaire and educational material on “green” and healthy homes. The questionnaire was used to garner information on the personal habits and

general health of residents. The educational booklet was designed specifically for the residents at Sunnyslope Manor and was distributed prior to the Panel 3 data collection (Ahrentzen et al., 2013).

Although it was expected to have a short term increase in PM concentrations after the retrofit, this was only statistically apparent with two covariates: length of stay for the occupant and the use of odor-masking products. In general, smokers had higher PM concentrations in all three panels, but no short term change and a slight decrease in the long term. In the long term, a decrease in PM concentrations occurred in units with residents who had lived longer at the apartment complex.

The Panel 1 and Panel 2 formaldehyde levels measured in this study were comparable or higher than other US buildings and homes, as described in the literature. Panel 3 concentrations, however, showed a significant decrease with only 4% of units exceeding the Health Canada 8-hour REL of 40 ppb and virtually none exceeding the California acute REL of 44 ppb. The units tested here are much smaller than the reported literature studies, so increased surface-to-volume ratios could be a factor in the elevated concentrations. The significant decrease in formaldehyde levels in Panel 3 is most likely a result of the replacement of building materials and furnishings during the retrofit. This is supported by the fact that only formaldehyde, but not acetaldehyde and acetone (which are measured simultaneously with the same method), showed a significant reduction in concentration. Changes in ventilation would have affected all three carbonyls similarly. Other factors, such as variations in the use of insecticide, were also not correlated with long term changes in carbonyl levels.

While both acetone and acetaldehyde concentrations experienced an increase in the short term, long term concentrations were unchanged and well below any defined risk levels.

CHAPTER 4

GLYOXAL AND METHYLGLYOXAL IN THE INDOOR ENVIRONMENT

Introduction

As discussed in Chapter 1, carbonyls are a subset of organic compounds in which a carbon has a double-bonded oxygen attached. A dicarbonyl, such as glyoxal or methylglyoxal, has two separate carbons double bonded to oxygen atoms. Carbonyls are ubiquitous in our atmosphere and their presence is important for two reasons: health impacts of exposure to extreme concentrations and the propensity to form secondary organic aerosols (Schwier et al., 2010). Glyoxal ($C_2H_2O_2$), also known as ethanedial, is the smallest dicarbonyl. Methylglyoxal ($C_3H_4O_2$), also known as pyruvaldehyde or 2-oxopropanal, is the second smallest dicarbonyl (Figure 4.1).

Figure 4.1 Molecular structures for glyoxal (left) and methylglyoxal (right).

Glyoxal and methylglyoxal are highly reactive, volatile, and polar molecules. One of the reaction pathways of dicarbonyls is the formation of secondary organic aerosols (SOA) via uptake into the aqueous phase of an aerosol particle or cloud droplet (Schwier et al., 2010). SOA formation is of great concern due to the impacts on climate change, visibility, and adverse health effects and both glyoxal and methylglyoxal have been identified as precursors (Liggio et al., 2005; Carlton et al., 2007; Schwier et al., 2010;

Tan et al., 2010). Additionally, glyoxal and methylglyoxal are toxic at high concentrations, have exhibited carcinogenic and mutagenic properties (Ueno et al., 1991; Ankrah and Appiah-Opong, 1999; Murata-Kamiya and Kamiya, 2001; O'Brian et al., 2005; Thronally, 2008; Desai et al., 2010), and are linked to dermatitis in workers who are regularly exposed (Elsner et al., 1990; Uter et al., 2001; Aalto-Korte et al., 2005).

Sources of carbonyls differ for each species and can be either biogenic or anthropogenic. In the atmosphere, carbonyls are often generated from the oxidation of hydrocarbons, and thus secondary reaction products. Sources of formaldehyde, acetaldehyde, and acetone were discussed in Chapters 2 and 3. Well determined production pathways of glyoxal and methylglyoxal include oxidation or photochemical reactions of 1-3 butadiene, acrolein, isoprene, and aromatic hydrocarbons such as xylene or toluene (Nojima et al., 1974; Grosjean, 1990a; Grosjean et al., 1993; Grosjean et al., 1994; Liu et al., 1999; Destaillats et al., 2002; Nishino et al., 2010). 1-3 butadiene is an anthropogenic hydrocarbon, most commonly found in tobacco smoke, automobile exhaust, and gasoline (Liu et al., 1999). Isoprene is one of the most abundant biogenic hydrocarbons, accounting for up to 80% of hydrocarbons emitted from forests (Grosjean et al., 1993). Gas phase glyoxal and methylglyoxal have been reported in chamber studies (Nojima et al., 1974; Grosjean et al., 1993; Grosjean et al., 1994; Liu et al., 1999; Fan et al., 2003; Nishino et al., 2010; Rossignol et al., 2013), outdoor smog chamber studies (Liu et al., 1999), outdoor urban environments in Brazil (Grosjean et al., 1990b), California (Kean et al., 2001; Destaillats et al., 2002; Liu et al., 2006), Texas, and New Jersey (Liu et al., 2006), outdoor rural environments in Virginia (Munger et al., 1995)

and Portugal (Cerqueira et al., 2003), and outdoor suburban environments in Japan (Ortiz et al., 2006; Ortiz et al., 2013).

The sources of dicarbonyls in an indoor environment are less well-studied. While reaction pathways are similar to those observed in the outdoor environment, the importance of the respective pathways might be substantially different. Rossignol and co-workers suggested that the ozonolysis of limonene, emitted from lemon-smelling cleaning products, is one indoor formation pathway for methylglyoxal (Rossignol et al., 2013). Other sources of indoor dicarbonyls include off gassing from building materials, air fresheners, cleaning products, and human combustion activities (e.g. cooking, smoking, and burning incense) (Crump and Gardiner, 1989; Liu et al., 2006; Rossignol et al., 2013). Indoor gas phase glyoxal and methylglyoxal has been reported in the United Kingdom (Crump and Gardiner, 1989), Paris (Rossignol et al., 2013), and the United States (Liu et al., 2006).

Common analytical tools to detect and quantify glyoxal and methylglyoxal include electron capture detector-gas chromatography (ECD-GC) (Nojima et al., 1974), gas chromatography mass spectrometry (GC-MS) of (O-(2,3,4,5,6-pentafuorobenzyl)-hydroxylamine (PFBHA) derivatives (Liu et al., 1999; Destaillats et al., 2002; Ortiz et al., 2006; Nishino et al., 2010; Rossignol et al., 2013; Ortiz et al., 2013), high performance liquid chromatography ultraviolet absorption (HPLC-UV) of hydrazone derivatives (Crump and Gardiner, 1989; Grosjean et al., 1990b; Grosjean et al., 1993; Grosjean et al., 1994; Munger et al., 1995; Kean et al., 2001; Cerqueira et al., 2003; Fan et al., 2003), and HPLC-fluorescence of dansylhydrazine derivatives (Zhang et al., 2000; Liu et al., 2006).

In this study, liquid chromatography ultraviolet absorption is utilized to detect glyoxal and methylglyoxal in their hydrazine derivative forms. In order to detect the dicarbonyls, they must first be reacted with 2,4-dinitrophenylhydrazine (DNPH) in an acid solution to form a hydrazone derivative. The resulting hydrazone absorbs at 430nm and increases the molecular weight of glyoxal and methylglyoxal to 418 and 432 g/mol, respectively (Figure 4.2).

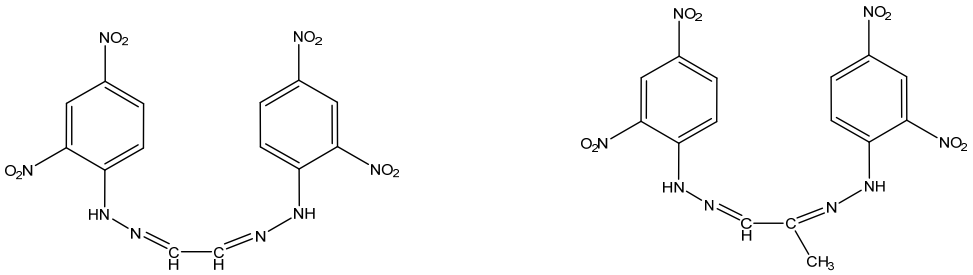

Figure 4.2 Molecular structures for DNPH-derivatized glyoxal (left) and methylglyoxal (right).

This chapter investigates the occurrence of glyoxal and methylglyoxal in the indoor environment of an apartment complex for low-income seniors in Phoenix, AZ and compares those levels to simultaneous outdoor measurements to consider overall concentrations and the impacts of possible infiltration.

Materials and Methods

Collection and analysis of samples are similar to the procedures described in Chapters 2 and 3. Samples of indoor and outdoor glyoxal and methylglyoxal were collected using commercial solid phase collection cartridges containing dinitrophenyl hydrazine (DNPH)-coated silica gel (Sep-Pak XPoSure Aldehyde Sampler, #WAT047205, Waters Corp., Milford, MA). The cartridges were preceded by an ozone scrubber (Sep-Pak Ozone Scrubber, # WAT054420, Waters Corp., Milford, MA) to

eliminate ozone from the incoming air and prevent oxidation of sorbed carbonyls and resulting negative artifacts. Air was drawn through the cartridges by means of pumps operating at ~2 L min^{-1}. Samples were collected over 1-hour periods using portable gas pumps (Universal XR Pump, Model PCXR4, SKC Inc., Eighty Four, PA). The sampling flow of each pump was calibrated in the laboratory before and after the sampling period using a bubble flow meter and a primary air flow calibrator (Gilibrator-2 Sensidyne, St. Petersburg, FL).

Three samples were collected simultaneously in the living room, kitchen, and balcony of each unit and all units had 619 ft^2 of livable space and are identical in interior (Figure 4.3).

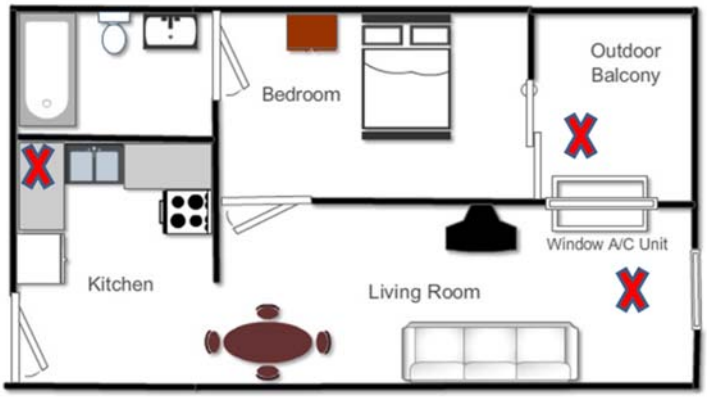

Figure 4.3 Sample pumps were deployed simultaneous in the kitchen, living room, and outdoor balcony, as marked by the red "X"

After collection, each DNPH cartridge was capped, labeled and stored at 4 ^oC until it was extracted and analyzed. The extractions took place at Lawrence Berkeley National Laboratory by collaborators, as described in Chapters 2 and 3, and the extracts were sent to Arizona State University for dicarbonyl analysis. The acetonitrile (ACN) extracts were analyzed by liquid chromatography with UV detection (LC-UV) at 430 nm

using a gradient elution (ACN and water) and 20μL injections. Specific instrument parameters are listed in Appendix A. Retention times for glyoxal and methylglyoxal were 29.2 and 30.3 minutes, respectively. Example chromatograms are shown in Figure 4.4. The concentration value reported in each case corresponded to a time-integrated average over the sampling period. Calibration curves for quantification were determined with authentic standards of the dinitrophenylhydrazones of glyoxal and methylglyoxal (AmChemteq, Inc, Port Matilda, PA).

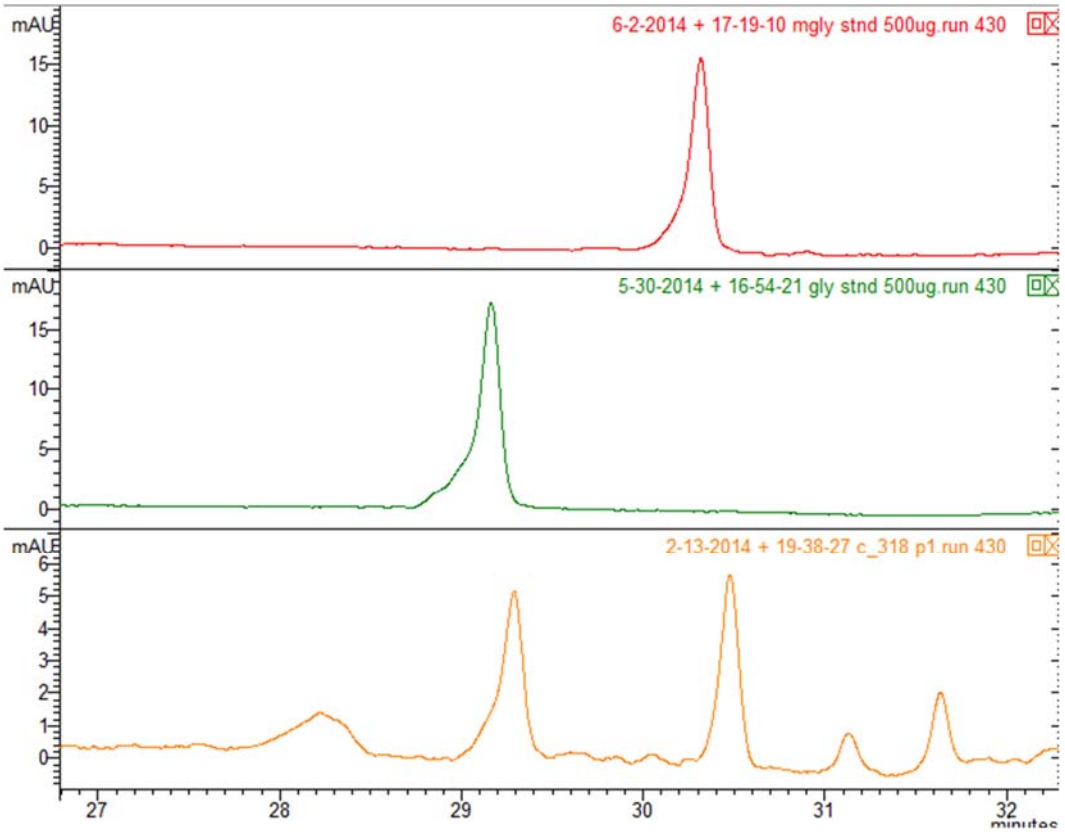

Figure 4.4. Examples of typical chromatograms, showing methylglyoxal standard (top, red), glyoxal standard (middle, green), and an outdoor sample (bottom, orange).

Results and Discussion

A total of 26 units in 2010 (Panel 1) and 10 units in 2012 (Panel 3) were evaluated for the presence of glyoxal and methylglyoxal. Table 4.1 shows the mean and median concentrations for each location and panel. 100% of the units had detectable levels of both compounds. A table of all values can be found in Appendix A.

Table 4.1

Concentrations of glyoxal and methylglyoxal in the living room, kitchen and outdoor (balcony). N=26 for Panel 1; N=10 for Panel 3.

		Living Room Conc. Mean[Median] $\mu g/m^3$	Kitchen Conc. Mean[Median] $\mu g/m^3$	Outdoor Balcony Conc. Mean[Median] $\mu g/m^3$
Glyoxal	Panel 1	7.3 [7.2] (σ=2.1)	6.6 [6.5] (σ=1.5)	2.7 [2.6] (σ=1.8)
	Panel 3	6.9 [7.0] (σ=1.7)	6.7 [6.4] (σ=1.8)	1.2 [1.2] (σ=0.8)
Methylglyoxal	Panel 1	8.6 [8.6] (σ=2.3)	8.9 [8.5] (σ=2.2)	5.0 [4.7] (σ=2.7)
	Panel 3	6.3 [5.7] (σ=2.8)	7.0 [6.4] (σ=3.5)	4.1 [4.7] (σ=1.9)

The kitchen and living room are close in proximity to each other with no walls separating the spaces, so while concentrations were not equal, differences were not statistically significant for either glyoxal (t-test: Panel 1 $t=2.22$, $p<0.04$; Panel 3 $t=0.9$, $p<0.4$) or methylglyoxal (t-test: Panel 1 $t=-0.9$, $p<0.4$; $t=0.7$, $p<0.5$). Figures 4.4 and 4.5 compare the concentrations of glyoxal and methylglyoxal between the two indoor samples, with a black line indicating a 1 to 1 ratio. Data above this line had greater concentrations in the living room while data below this line had greater concentrations in the kitchen.

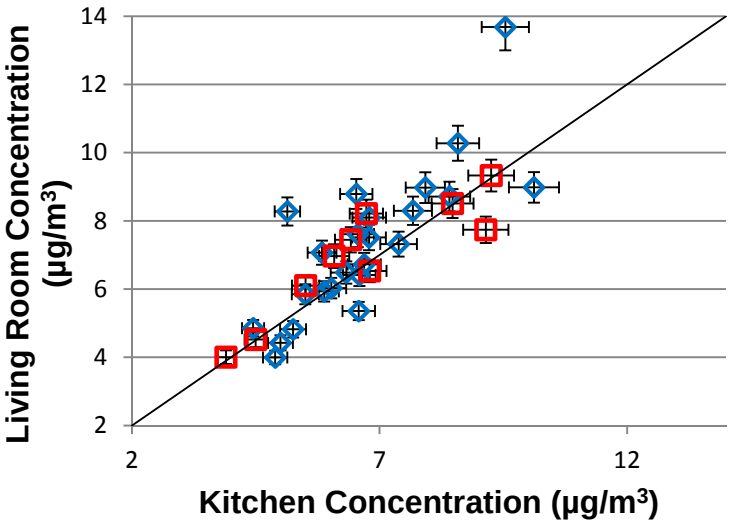

Figure 4.5. Indoor concentrations of glyoxal. Blue diamonds indicate samples collected in Panel 1 (2010) and red squares indicate samples collected in Panel 3 (2012). The black line shows the 1 to 1 ratio. Data above this line had greater concentrations in the living room while data below this line had greater concentrations in the kitchen.

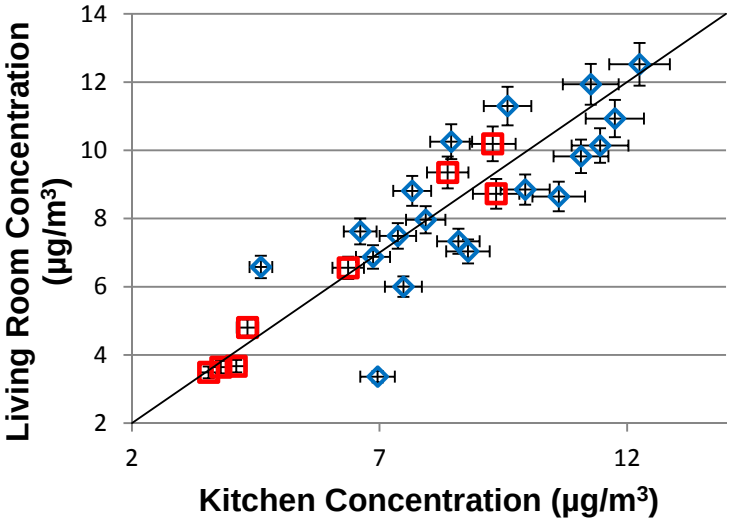

Figure 4.6. Indoor concentrations of methylglyoxal. Blue diamonds indicate samples collected in Panel 1 (2010) and red squares indicate samples collected in Panel 3 (2012). The black line shows the 1 to 1 ratio. Data above this line had greater concentrations in the living room while data below this line had greater concentrations in the kitchen.

Of the 26 units tested in Panel 1, 5 belonged to smokers. Of the 10 units tested in Panel 3, 3 were smokers. While the maximum concentrations of glyoxal and methylglyoxal in each panel were from smoking units, there was no statistically significant difference in the means between smoking and nonsmoking units. This is an unexpected result, as acrolein is a common species found in cigarette smoke and is a known precursor of glyoxal (Grosjean, 1990a; Grosjean et al., 1994; Destaillats et al., 2002). It is possible that the reaction time for the conversion of acrolein to glyoxal is slower than the timescale in which we collected data.

Similarly, 17 residents in Panel 1 and 7 residents in Panel 3 reported using air fresheners at least once a week in their homes, however there was no statistically significant difference in the means for both glyoxal and methylglyoxal in either panel. This is an unexpected result considering that the presence of indoor methylglyoxal has been correlated to cleaning products, such as scented air fresheners (Crump and Gardiner, 1989; Liu et al., 2006; Rossignol et al., 2013).

Figures 4.6 and 4.7 show a comparison between average indoor concentration and the corresponding indoor/outdoor (I/O) ratio. The vertical line indicates where I/O concentrations are equal. Data points to the left of this line indicates that outdoor concentrations exceeded indoor concentrations. For glyoxal, only one unit had an I/O ratio equal to 1 and no units with greater outdoor concentrations. Similarly, methylglyoxal I/O ratios had only 1 unit with a greater outdoor concentration. Average indoor concentrations are significantly higher than outdoor concentrations for glyoxal (t-test: Panel 1 $t=10.423$, $p<0.001$; Panel 3 $t=8.554$, $p<0.001$) and for Panel 1 methylglyoxal (t-test: Panel 1 $t=10.807$, $p<0.001$; Panel 3 $t=2.167$, $p<0.073$). This could imply that

indoor sources are more prevalent than outdoor sources, as was the case for Liu, et al. (2006), which found median indoor/outdoor concentrations to be 2.53/1.81 and 2.75/2.05 μg/m^3 for glyoxal and methylglyoxal, respectively.

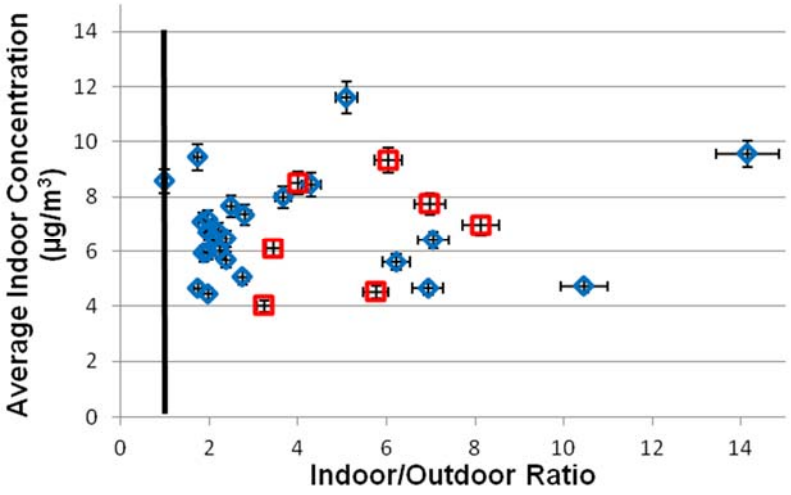

Figure 4.7. Average indoor concentrations vs. indoor/outdoor ratios of glyoxal. Blue diamonds indicate samples collected in Panel 1 (2010) and red squares indicate samples collected in Panel 3 (2012). The vertical black line shows I/O= 1 Data to the left of the line had greater outdoor concentrations; data to the right of the line had greater indoor concentrations.

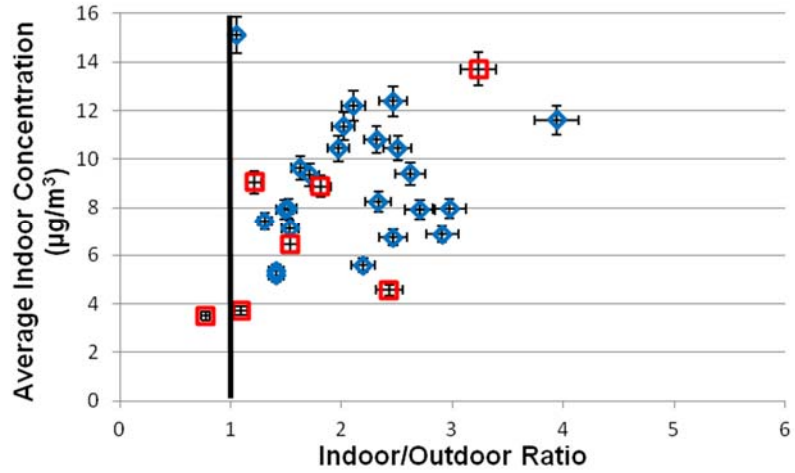

Figure 4.8. Average indoor concentrations vs. indoor/outdoor ratios of methylglyoxal. Blue diamonds indicate samples collected in Panel 1 (2010) and red squares indicate samples collected in Panel 3 (2012). The vertical black line shows the 1 to 1 ratio. Data to the left of the line had greater outdoor concentrations; data to the right of the line had greater indoor concentrations.

When observing changes over time, there was no statistically significant change from Panel 1 to 3 for either indoor or outdoor concentrations, as well as I/O ratios for glyoxal (t-test: Indoor $t=1.4$, $p<0.2$; Outdoor $t=1.2$, $p<0.3$; I/O $t=0.31$; $p<0.81$) or methylglyoxal (t-test: Indoor $t=7.94$, $p<0.08$; Outdoor $t=0.8$, $p<0.5$; I/O $t=1.05$, $p<0.40$).

The median indoor glyoxal concentrations of 7.0 and 7.2 $\mu g/m^3$ and median indoor methylglyoxal concentrations of 8.6 and 5.7 $\mu g/m^3$ observed in this study are more than twice as large as previously reported literature values. Rossignol, et al. (2013) measured indoor concentrations after the use of cleaning products in a home to be 2.3 ± 0.5 and 2.0 ± 0.5 $\mu g/m^3$ for glyoxal and methylglyoxal, respectively. Elevated concentrations should be linked to increased use of potential sources, however we were unable to statistically link resident behaviors such as smoking and cleaning product use to higher glyoxal and methylglyoxal concentrations. This could be the result of either an insufficient amount of data points, or an unknown source dominating the reaction pathways. While previous researchers were able to directly correlate limonene concentrations to methylglyoxal production in a controlled environment, we did not simultaneously observe precursor concentrations and had to rely on self-reported resident behaviors, which is a limitation of this study.

The median outdoor glyoxal concentrations of 2.6 and 1.2 $\mu g/m^3$ and median outdoor methylglyoxal concentrations of 4.7 $\mu g/m^3$ are generally larger than literature values. In rural Portugal, outdoor maxima of glyoxal and methylglyoxal were 0.14 and 4.82 $\mu g/m^3$ (Cerqueira et al., 2003). Ortiz, et al. (2013) found roadside average concentrations in suburban Japan to be 0.032 and 0.084 $\mu g/m^3$, respectively. In an urban

outdoor environment, methylglyoxal was measured in the range of 0.039 to 0.101 $\mu g/m^3$ (Destaillats et al., 2002), which is much lower than the rural maxima previously mentioned. The present study measured dicarbonyl concentrations in a residential setting where the environment is more closely related to an urban environment. Thus our elevated median outdoor concentrations of methylglyoxal of 4.7 $\mu g/m^3$ in both 2011 and 2012, which are close to the maximum values for rural Portugal, are unexpected results. Our median outdoor concentrations of glyoxal are greater than all previous studies, regardless of the environment.

As both indoor and outdoor concentrations exceeded literature values, with an exception for outdoor methylglyoxal in Portugal, it is likely that multiple reaction pathways are responsible for the formation of these compounds in Arizona. More research is needed to determine if factors unique to this desert environment, including elevated temperatures and low humidity, are influencing concentrations of glyoxal and methylglyoxal, as well as other aldehydes, and increasing the number of available reaction pathways.

Figure 4.8 compares the concentrations of glyoxal to methylglyoxal for both panels, with a black line indicating a 1 to 1 ratio. Data above this line had greater concentrations of glyoxal, while data below this line had greater concentrations of methylglyoxal. Methylglyoxal is statistically greater than glyoxal in both the living room and kitchen in Panel 1 (t-test: Living Room $t=-3.373$, $p<0.003$; Kitchen $t=-4.614$, $p<0.001$). However, there was no significant difference between glyoxal and methylglyoxal in Panel 3 (t-test: Living Room $t=0.4$, $p<0.7$; Kitchen $t=-0.2$, $p<0.8$).

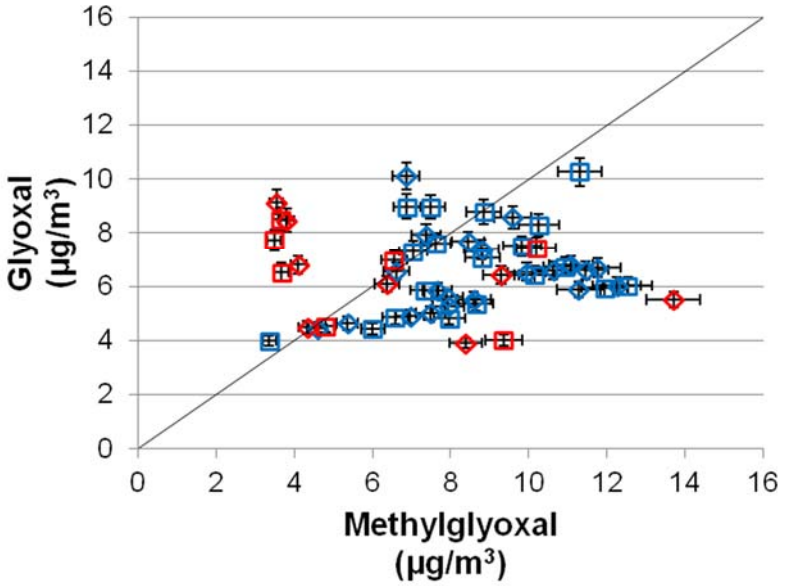

Figure 4.9. Indoor concentrations of glyoxal vs. methylglyoxal. Data points for Panel 1-Kitchen (blue diamonds), Panel 1-Living Room (blue squares), Panel 3-Kitchen (red diamonds), and Panel 3-Living Room (red squares) are shown. The black line shows the 1 to 1 ratio. Data above this line had greater concentrations of glyoxal, while data below this line had greater concentrations of methylglyoxal.

The ratios of the median concentrations of glyoxal and methylglyoxal can be compared with the available literature values, as seen in Table 4.2.

Table 4.2

Ratio of glyoxal to methylglyoxal in this study (median values) and comparable literature values, indoor and outdoor.

	Indoor Ratio of Glyoxal/Methylglyoxal	Outdoor Ratio of Glyoxal/Methylglyoxal
Panel 1 – Living Room	0.8	0.6
Panel 3 – Living room	1.2	0.3
Panel 1 – Kitchen	0.8	0.6
Panel 3 – Kitchen	1.0	0.3
Liu, et al. 2006	0.9	0.9
Ortiz, et al. 2013	--	0.4
Rossignol, et al. 2013	1.2	--

The indoor ratio of glyoxal to methlygloxal is for Panel 1 is closest to Liu, et al. (2006) while the Panel 3 values are closer to Rossignol, et al. (2013). Outdoor ratios in Panel 3 are close to Ortiz, et al. (2013), however Panel 1 ratios are between the available literature values. While the median values presented here exceed literature values, the ratios between glyoxal and methlygloxal are comparable to previously reported data.

Conclusions

The present chapter reports the occurrence and concentrations of glyoxal and methylglyoxal before and one year after an energy efficiency retrofit at a Phoenix, AZ apartment complex (described in Chapter 3). Median concentrations were found to exceed previously reported values for both indoor and outdoor environments. Indoor sources of glyoxal and methylglyoxal are predominant, as the majority of units had I/O ratios exceeding 1. Methylglyoxal was more abundant than glyoxal pre-retrofit, but no difference was observed post-retrofit, in Panel 3.

Some observations were unexpected, especially having no statistically significant differences for smoking units or users of air fresheners, as was observed for PM and acetaldehyde discussed in Chapter 3. This, however, could be related to the limited sample size, which was smaller than for PM and aldehydes because some samples were destroyed in a freezer malfunction.

The higher indoor concentrations, compared to outdoor concentrations, suggest that important indoor sources, leading to either primary or secondary emissions, have yet to be determined. Additional research into the sources and reaction pathways of both glyoxal and methylglyoxal in the indoor environment is necessary. Further investigations, including additional sampling in the same and different seasons, would be advantageous

in order find patterns or identify correlations between human activity and increased dicarbonyl concentrations.

CHAPTER 5

TOBACCO SPECIFIC NITROSAMINES IN THE INDOOR ENVIRONMENT

Introduction

Tobacco specific nitrosamines (TSNAs) are of great importance because they are carcinogenic and affect both smokers and nonsmokers. TSNAs are found in mainstream, side stream, and third hand (residual toxins after extinguishing) cigarette smoke and in smokeless tobacco (Hecht et al., 1974; Hecht et al., 1978a; Hoffmann et al., 1979; Brunnemann et al., 1996; Sleiman et al., 2010; Matt et al., 2011).

In this study we focus on three nitrosamines: N'-nitrosonornicotine (NNN), 4-(methyl-nitrosamino)-4-(3-pyridyl)-butanal (NNA) and 4-(methylnitrosoamino)-1-(3-pyridyl)-1-butanone (NNK), whose structures are shown in Figure 5.1. These compounds are most commonly formed by the nitrosation of nicotine ($C_{10}H_{14}N_2$), which can occur at ambient temperatures in a pH range of 2 to 7 (Brunneman et al., 1996).

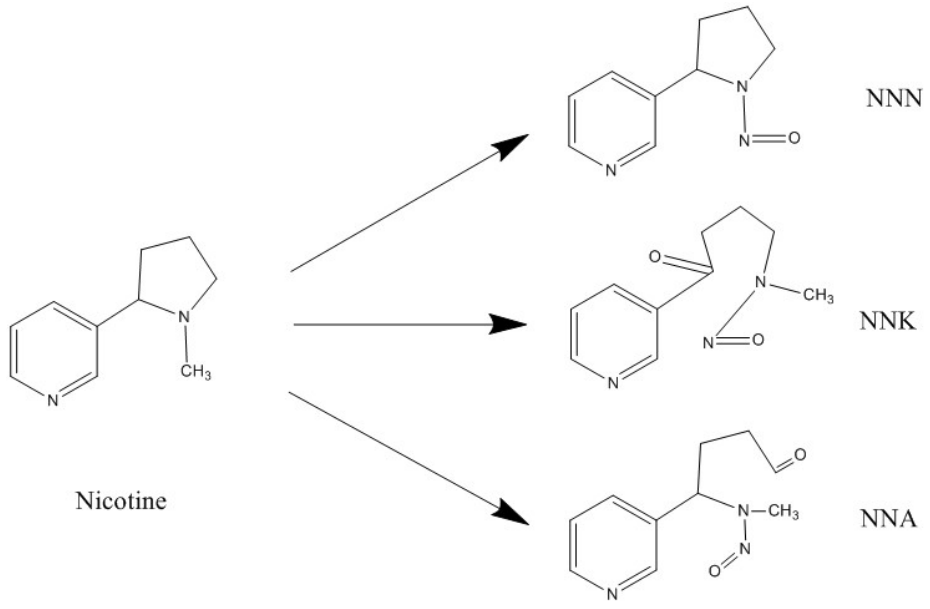

Figure 5.1. Molecular structures of nicotine, NNN, NNK, and NNA. These nitrosamines are commonly formed by the nitrosation of nicotine.

Common analytical tools to detect and quantify TSNAs include gas chromatography with thermal energy analyzer (GC-TEA) (Brunnemann et al., 1977; Klus et al., 1992; Brunnemann et al., 1996), high performance liquid chromatography with UV absorption detection (HPLC-UV) (Hecht et al., 1978b; Caldwell et al., 1991), GC-mass spectrometry (GC-MS) (Hoffmann et al., 1974; Munson and Abdine, 1977; Hecht et al., 1978a; Caldwell et al., 1991; Sleiman et al., 2010), and liquid chromatography tandem mass spectrometry (LC-MS/MS) (Wu et al., 2003; Sleiman et al., 2010; Gordon et al., 2011; Intorp et al., 2012). TSNAs have been studied and quantified in a variety of ways, including liquid-extraction from processed tobacco (Hoffmann et al., 1974; Brunnemann et al., 1996), reactions of tobacco with human saliva (Prokopczyk et al., 1992), as biomarkers for environmental tobacco smoke (ETS) (Hecht et al., 1978a; Hoffmann et al., 1987; Anderson et al., 2001), laboratory controlled cigarette smoke collection (Brunnemann et al., 1977; Wu et al., 2003; Gordon et al., 2011; Intorp et al., 2012), aqueous reactions with nicotine (Hecht et al., 1978a), indoor air analysis from bars, offices, and homes (Klus et al., 1992), controlled chamber studies (Sleiman et al., 2010), and collection of particle-bound TSNA surface samples (Sleimann et al., 2010).

$$\text{Rate}=k[\text{nicotine}][\text{nitrite}] \qquad \text{Equation (5.1)}$$

The kinetics of the nitrosation of nicotine have been studied in the aqueous phase, and while the nitrosation of tertiary amines is slow, the rate constant for the formation of NNA is an order of magnitude larger than NNN and NNK at ambient temperatures (Hecht et al., 1978a; Caldwell et al., 1991; Brunnemann et al., 1996). According to the

rate law, Equation (5.1), rate constants were observed at pH 3.7 and 37˚C to be $k_{NNN}=5.2x10^5$, $k_{NNK}=6.8x10^5$, and $k_{NNA}=50x10^5$ $Lmol^{-1}min^{-1}$ (Caldwell et al., 1991). However, under extreme conditions (excess nitrite and temperatures upwards of 90˚C), NNA was no longer observed and yields increased for NNK and NNN (Hecht et al., 1978a). This instability at high temperatures could explain why NNA is not detected in mainstream smoke, but is predominant in secondary reactions (Hecht, 2004).

Both NNN and NNK have been determined to be highly toxic and carcinogenic (Hecht, 2004; WHO, 2008; NPT, 2011). NNK has been found to be the only tobacco smoke carcinogen that induces lung tumors in all three rodent models: rats, hamsters, and mice (Hecht, 1998; Hecht, 2004). In a 2001 study, it was found that women highly exposed to environmental tobacco smoke (ETS) absorb up to five times more NNK than women living in non-smoking households (Anderson et al., 2001). This research provides a biochemical link between second-hand smoke and lung cancer, using NNK as a biochemical marker (Hecht, 2004). Due to the health risks associated with TSNAs, the World Health Organization has listed NNK and NNN as toxins recommended for mandatory lowering in tobacco products and suggest levels of 0.072 NNK per mg of nicotine and 0.114 μg NNN per mg of nicotine for international brands of tobacco products (WHO, 2008).

Detecting the presence of these TSNAs in our indoor environments is the initial process required to researching the effect of carcinogenic exposure on human health. Brunnemann, et al. (1992) and Klus, et al. (1992) investigated NNN and NNK in both mainstream and side-stream smoke, utilizing field collection of air samples. Mean concentrations (range in parentheses) of NNK and NNN were determined to be 2.8 (n.d.-

6.0) and 4.9 (n.d.-13.5) ng/m^3, respectively in a poorly ventilated office (Klus et al., 1992). In a separate study, 10 different locations, including bars, trains, offices, and a smoker's home, revealed concentrations of NNN and NNK that ranged from n.d.-22.8 and 1.4-29.3 µg/m^3, respectively (Brunnemann et al., 1996). Concentrations of these compounds have also been shown to vary between mainstream and side-stream smoke, due to reaction times and availability of reactants. Mainstream smoke yielded concentrations ranging from 40-278 and 17-156 ng per cigarette smoked for NNN and NNK, respectively. Sidestream smoke had elevated values, compared to mainstream smoke: concentrations for NNN and NNK ranged from 170-330 and 240-468 ng per cigarette smoked, respectively (Brunnemann et al., 1996). Apart from air sampling, it has been found that particle-bound TSNAs are also abundant in environments with regular exposure to ETS. These particles are the result of third-hand smoke. Surface studies of NNA and NNK were carried out by Sleiman et al. in 2010, with ranges from 3-256 ng/m² for NNA and 0.44-36.5 ng/m² for NNK on household surfaces.

The present work investigates the presence of NNN, NNK, and NNA in the indoor air of both smoking and non-smoking environments. Air samples were collected in three field campaigns, undertaken in Phoenix, AZ. The first in a multiunit housing complex during Panel 3 of the large-scale project discussed in Chapters 2 and 3, the second in the living room and balcony of a heavy smoker, and the third in the car of a heavy smoker.

Materials and Methods

Sampling sites. The first round of air sampling was conducted at an apartment complex, Sunnyslope Manor, in Phoenix, AZ, described in detail in Chapters 2 and 3.

Originally built in the early 1970's, this three-story, 116-unit structure underwent renovations and energy efficiency improvements in the fall of 2010. Air samples were collected in the summer of 2012 in 52 apartment units as part of Panel 3. All units have 619 ft^2 of livable space and are identical in interior layout and are all-electric homes (i.e. no fireplaces, gas stoves, etc.) with individual window air conditioning units. Performing the air quality measurements and questionnaire simultaneously ensured that resident activities (i.e. cooking, smoking) did not bias the data and would not be present during sampling. Portable air pumps (SKC, Universal XR Pump Model PCXR4) equipped with Supelclean Coconut Charcoal SPE cartridges (Sigma-Aldrich, 57144-U, 2g) were deployed in the living room of each unit. Air was drawn through the sampler at ~1.2 or 3.4 L min^{-1}. Samples were collected for approximately 1 hour each.

The second campaign was conducted in the apartment of a self-reported heavy smoker (approximately 30 cigarettes, or 1.5 packs per day) in Scottsdale, AZ. Portable air pumps (SKC, Universal XR Pump Model PCXR4) equipped with Supelclean Coconut Charcoal SPE filters (Sigma-Aldrich, 57144-U, 2g) were placed on the outdoor balcony and in the living room (about 12 feet away from the exterior sliding glass door). Air was drawn through the sampler at approximately 1.2 or 2.2 L min^{-1}. Samples were collected for approximately 1 hour each. The first hour of sampling occurred during active smoking, when 8 cigarettes were consumed within the hour on the balcony, with the door to the living room open. The second and third hours of sampling occurred with no active smoking and the sliding glass door remaining closed. Sampling took place in February in Arizona, so no mechanical ventilation (i.e. air conditioning or heating) was present.

The third campaign was conducted inside the parked car of a self-reported heavy smoker with the windows closed and during the evening hours, after sunset. Three portable air pumps (SKC, Universal XR Pump Model PCXR4) equipped with Supelclean Coconut Charcoal SPE filters (Sigma-Aldrich, 57144-U, 2g) were run simultaneously in the driver's seat for 87 minutes with flow rates ranging from 1.2 to 2.2 L min^{-1}. The last smoking event in the vehicle occurred approximately 20 minutes before testing began, with the windows open. During sampling, the windows were closed, the engine was off, and no ventilation was occurring.

Sample storage and analysis. The SPE cartridges were stored at 4 ºC until they were extracted and analyzed. The samples were extracted by first adding 200µL of an internal standard 500ppb NDMA-d6 (Cambridge Isotope Laboratories, Inc., Andover, MA). After the SPE cartridge was dried with 30 mL of air, 30 mL of dichloromethane (DCM, Fisher Scientific, Fair Park, NJ) was used as an eluent, followed by 30 mL of air to remove all eluent from the column. The eluate was dried using anhydrous sodium sulfate (Sigma-Aldrich, St. Louis, MO) and concentrated under a gentle flow of ultra-high purity nitrogen (UHP N_2) and under protection from light to prevent photochemical degradation. When the solution had evaporated to <5 mL, the extract was transferred to a 5 mL evaporation vial and dried down further to a final volume of 200 µL then transferred into a GC vial with a 200 µL insert.

Extracts were analyzed using gas chromatography chemical ionization mass spectrometry (GC-CI-MS) (Agilent 6890N/5973) in select ion mode, using ammonia as the reagent gas (Charrois, et al. 2004; Hutchings, et al. 2010). The GC-CI-MS separation and analysis was performed with the parameters, equipment, and settings listed in

Appendix B (Table B1). In brief, the chromatographic column used was an Agilent DB-1701P (30 m x 0.250 mm x 0.25 µm) and followed a pulsed splitless injection (10 psi) set at 250°C with a reduced diameter solid-phase-microextraction (SPME) inlet liner (Sigma Aldrich, St. Louis, MO). The oven temperature was initially 40°C for 3 minutes followed by an increase to 110°C at 4°C min^{-1}, and a final temperature increase to 220°C at 15°C min^{-1}, for a total run time of 53 minutes. The mass selective detector was set to analyze for mass-to-charge ratios of 98 (NDMA-d6 + NH_4^+), 178 (NNN + NH_4^+), and 208 (NNK + NH_4^+ and NNA + NH_4^+). The GC-MS was calibrated with a series of authentic standards (Sigma-Aldrich, St. Louis, MO) and quantification was performed against the NDMA-d6 internal standard. NNN, NNK, and NNA eluted at 35.9, 38.2, and 45.3 minutes, respectively, as can be seen in Figure 5.2.

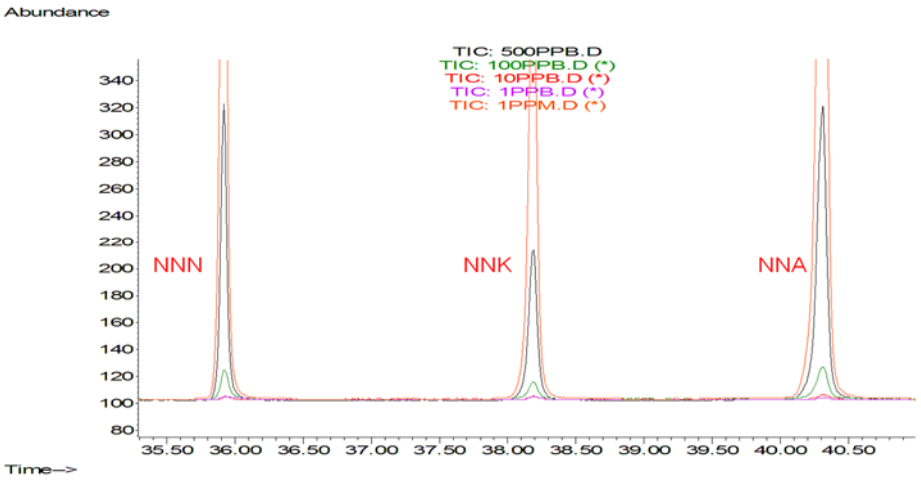

Figure 5.2. GC-MS chromatogram featuring the peaks and retention times for NNN, NNK, and NNA at 35.9, 38.2, and 45.3 minutes, respectively. Each colored chromatogram represents a different standard concentration. Orange is 1 ppm, black is 500 ppb, green is 100 ppb, red is 10 ppb, and purple is 1 ppb, but is below the quantification limit.

Results and Discussion

Sunnyslope Manor. Samples from 35 units at Sunnyslope Manor were collected, extracted, and analyzed using GC-MS. All three nitrosamines were detected in at least one unit, however, all but 4 units had concentrations below our quantification limits (BQL) which is <10 ppb extract concentration or 9-25 ng/m^3 air concentration (depending on flow rate and sampling duration for each individual sample). Table 5.1 shows the results for all units and detailed results are reported in a table in Appendix B (Table B2).

Table 5.1

Concentrations of NNN, NNK, and NNA by unit

Unit ID	NNN (ng/m^3)	NNK (ng/m^3)	NNA (ng/m^3)	Smoker?
x000f	<9	nd	18	n
xf043	nd	nd	14	n
xdc06	nd	nd	347	n
x047a	nd	nd	nd	n
xc7dc	< 24	nd	nd	y
yf2db	nd	nd	nd	y
x5938	nd	nd	nd	n
x6449	nd	nd	9	n
xdf9b	nd	nd	nd	y
x102f	< 25	nd	< 25	y
xefe8	nd	nd	nd	n
x98f4	nd	nd	nd	n
x5f2c	nd	nd	nd	n
x0a51	nd	< 10	nd	n
xd041	< 24	nd	nd	n
x3dc3	nd	nd	< 10	n
x56ce	nd	nd	nd	n
x88a9	nd	nd	nd	n
xfe26	nd	< 2	nd	n
xe7df	nd	nd	nd	y
x37aa	nd	nd	nd	n
x658b	nd	nd	nd	n
x57db	nd	nd	nd	n
x9ag2	nd	nd	nd	n
x82cd	< 24	nd	nd	y
x9d7c	nd	nd	nd	n
xbcc0	< 10	nd	nd	n
xmy23	< 24	nd	nd	n
x0dc2	< 26	nd	nd	n
x6dee	nd	nd	nd	n
xef99	< 27	nd	nd	y
xeb12	< 27	nd	nd	n
x97fc	nd	nd	nd	n
xk52d	nd	nd	nd	n
x5dbf	nd	nd	< 9	n

Seven units belonged to residents who reported smoking in their homes and 28 units were nonsmoking. NNN, NNK, or NNA were detected in 86% of the smoking units and 46% of the nonsmoking units. NNN was detected in 8 units, NNK in 2 and NNA in 7. Only NNA was quantified, in 4 of the 7 units. Surprisingly, these 4 units belonged to nonsmokers, suggesting that secondhand smoke must be infiltrating into these apartments. However, it is expected that smoking units would also have NNA and at larger concentrations.

Comparisons between average concentrations of NNN, NNK, and NNA in smoking and nonsmoking units, along with the average formaldehyde and PM_{10} concentrations are shown in Figure 5.3. For units where nitrosamines could not be quantified, but were detected, a maximum value was calculated assuming a 10 ppb extract concentration, which was the smallest standard that could be quantified using our method. For units in which a compound was not detected, the value zero was used.

As discussed in Chapters 2 and 3, smoking has the largest impact on indoor PM concentrations. Along with the knowledge that TSNAs are the products of nicotine reactions, it was expected that higher PM_{10} concentrations would be associated with TSNA concentrations; however there is no apparent correlation. NNN and NNK were expected to have the greatest concentrations, due to previous studies reporting mainstream and sidestream smoke ranging from 40-330 and 17-468 ng per cigarette smoked, respectively (Brunnemann et al., 1996), but NNK was not detected in any smoking units and BQL in two nonsmoking units. Additionally, no connection between formaldehyde and TSNA concentrations was observed in this study.

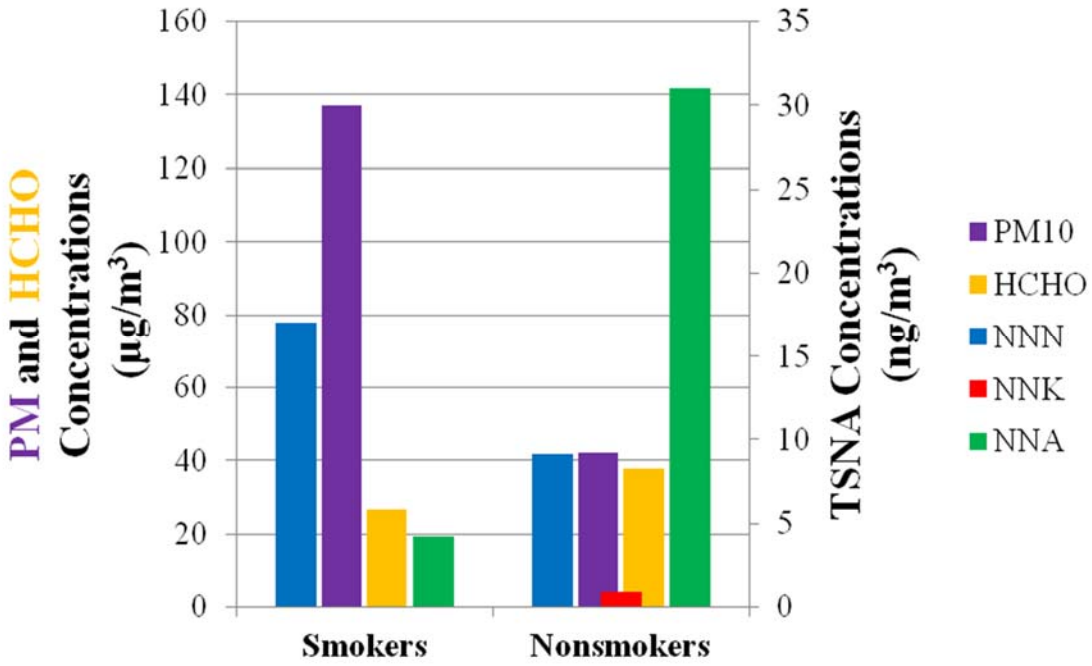

Figure 5.3. Average concentrations of NNN, NNK, NNA, PM_{10}, and formaldehyde in the units that had at least one nitrosamine detected, separated by smokers (N=7) and non-smokers (N=12). For units BQL, a maximum value was calculated assuming a 10 ppb extract concentration. NNK was not detected in any smoking units.

A comparison between average values from this study to literature values is shown in Figure 5.4. The greatest concentrations observed in this study were of NNA, which is not consistent with the literature values. NNA has been detected in surface studies (Sleiman et al., 2010), but there are no reported concentrations of NNA measured in air studies. It was also expected that all three nitrosamines would be more abundant in the units belonging to smokers. While this was true for NNN, both NNK and NNA had greater abundance in nonsmoking units. The average concentration of NNN in nonsmoking units is within the range observed in bars, but exceeds the concentrations detected in a car, trains, and a poorly ventilated office (Brunnemann et al., 1992; Klus et al., 1992). NNK values are below the range of the other studies presented, which is most

likely related to the experimental conditions of the collection. In fact, our air samples were taken when no active smoking was occurring, while the previous studies collected air samples during active smoking and over a longer periods of time, averaging 3 to 12 cigarettes per hour. NNK has also been observed to have twice the concentration in sidestream smoke compared to mainstream and up to 10 times greater sidestream to mainstream ratio compared to NNN (Adams et al., 1987). Our results indicate that thirdhand, or residual cigarette smoke may favor NNA and NNN, compared to NNK, which agrees with the results of thirdhand smoke surface studies (Sleiman et al., 2010).

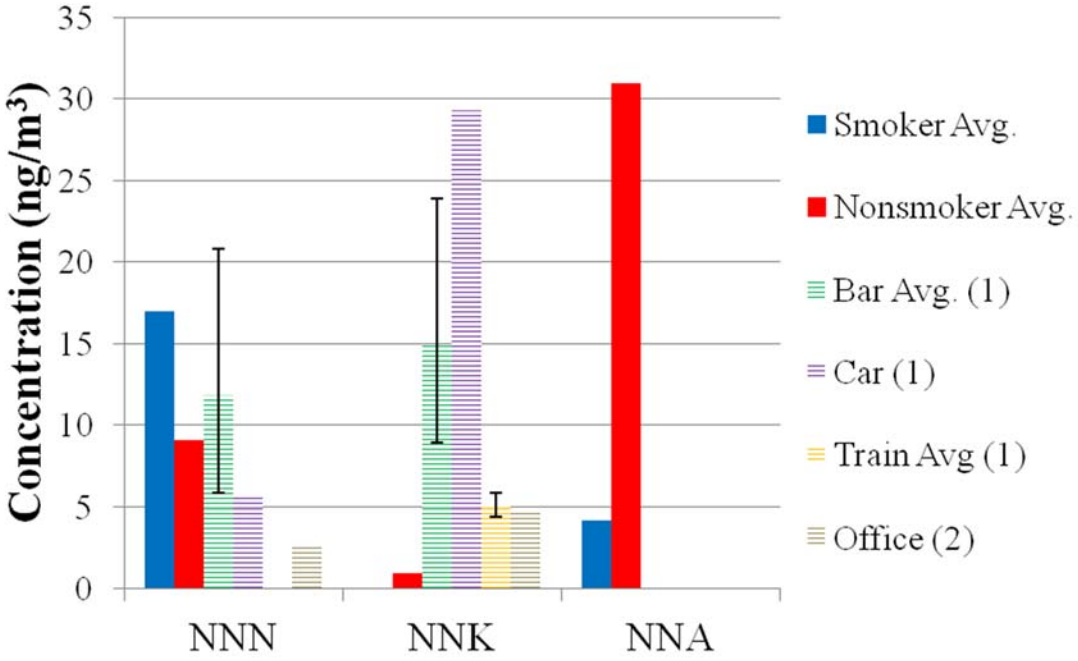

Figure 5.4. Average concentrations of NNN, NNK, and NNA from this study (solid colors) compared to reported literature values (textured colors). Ref 1 is from Brunnemann, et al. 1992 and Ref 2 is from Klus, et al. 1992.

Sampling during and after active smoking in a Scottsdale, AZ apartment. Air samples were collected in an 1130 ft^2 apartment in Scottsdale, AZ as described in the methods section. In the first hour of sampling, during active smoking, traces (BQL) of

NNN and NNK were found on the balcony and nothing was detected in the indoor samples. This is consistent with the literature, where NNA is more likely to be found in second and third hand smoke and NNN and NNK are detectable immediately after pyrolysis of the cigarette (Hecht, 2004).

In the second hour of sampling, with no active smoking, traces (BQL) of NNN and NNK were still present outdoors, but none of the three TSNAs were detected in the living room. In the third hour of sampling, with no active smoking, trace amounts of NNN and NNK were found in the living room, however no traces were found on the balcony. This could be due to the initial nicotine compounds adsorbing onto the indoor surfaces followed by partitioning of NNN and NNK into the gas phase overtime or as human activity persisted in the home. Figure 5.5 visually summarizes the timeline and findings of this sampling campaign.

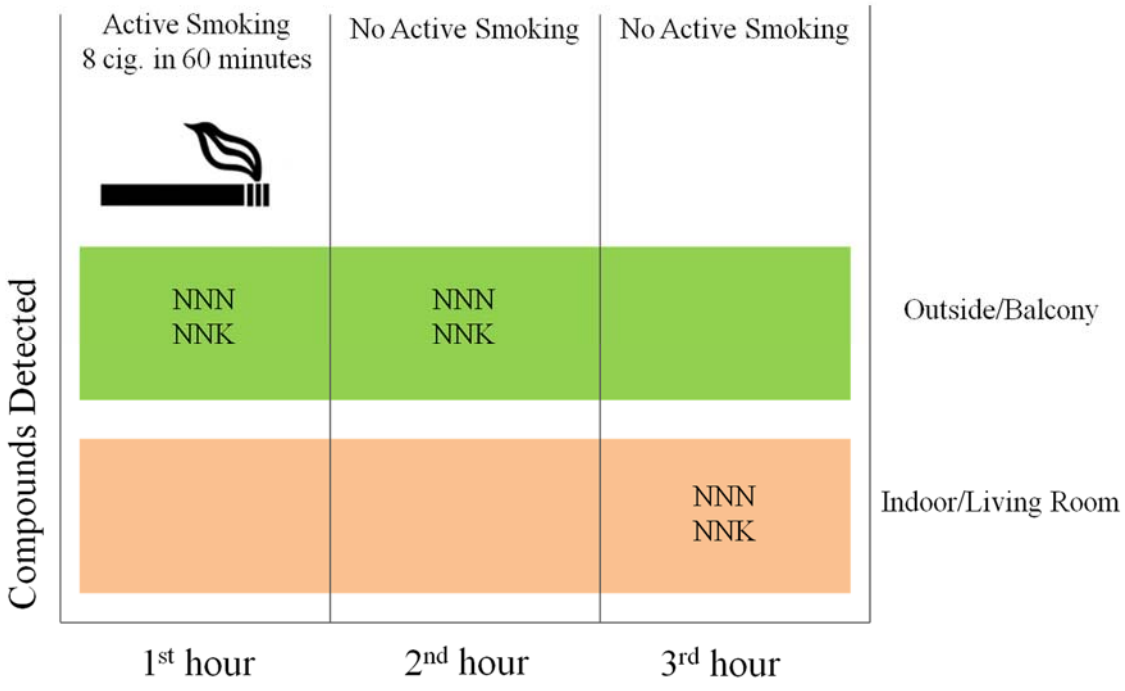

Figure 5.5. Cartoon of air sampling during and after an active smoking event. NNN and NNK were detected outside in the first and second hour and inside during the third hour.

The sampling was completed in February in Arizona, when it is not typical to run air conditioning or heating. With no forced ventilation, only natural ventilation occurred. The smoking event was performed on a balcony with the door to the living room open. During the second and third hour of sampling, the door was closed, but a complete seal is unlikely. While the residents typically smoke outside, they often keep the door open or partially open, therefore their indoor environment is exposed to all three types of smoke (mainstream, secondhand, and thirdhand). The time it took for NNN and NNK to be detected inside could be a function of either air exchange or reaction mechanisms. It has been reported that NNK is more predominate in secondhand smoke, compared to NNN (Brunnemann et al., 1996). This apartment would be a great candidate for future studies involving thirdhand smoke (i.e. surface samples) where NNA concentrations have been estimated upwards of 256 ng/m^2 (Sleiman et al., 2010).

Sampling in a vehicle. The third campaign was conducted inside the vehicle of a self-reported heavy smoker with the windows closed, in the evening hours. The last smoking event in the vehicle occurred approximately 20 minutes before testing began, with the windows open while driving. The car was parked, turned off and the windows closed. Although the car had an odor from years of smoking and a smoking event occurred 20 minutes prior to testing, no detectable amounts of NNN, NNK, or NNA were observed.

There have been limited studies attempting to detect TSNAs in vehicles. Brunneman, et al. (1992) observed NNN and NNK at 5.7 and 29.3 ng/m^3 (Figure 5.4), which is below the quantification limit of this study. More recently, concentrations of nicotine in air, dust and on surfaces in used cars were quantified. It was reported that cars

of smokers who smoked in their vehicles showed significantly elevated levels of nicotine in dust, on surfaces, and in the air compared with nonsmoker cars (Matt et al., 2008; Fortmann et al., 2010; Matt et al., 2011). Mean concentrations for nicotine in the air were 740 and 20 ng/m^3 for smokers and nonsmokers, respectively (Matt et al., 2008). The volatile components of cigarette smoke (such as nicotine) and particulates are able to absorb into surfaces within minutes and are highly reactive in the presence of light, extreme temperatures, and minimal ventilation (Matt et al., 2008).

While NNN and NNK are readily detected in air during active smoking, the compounds could be quickly reacting or depositing on surfaces. As previously mentioned, surface studies of NNA, NNK, and NNN in a truck were carried out by Sleiman et al. in 2010. Concentrations of NNN were too low to be quantified, and NNA and NNK were detected in the range of 1-5 ng/cm^2. When exposed to HONO for three hours, these concentrations increased 10-fold, highlighting the importance of nitric acid to propel the reaction. Estimating that 0.35% and 0.05% of nicotine concentrations convert to NNA and NNK, respectively, concentrations on household surfaces were calculated to range from 3-256 ng/m² for NNA and 0.44-36.5 ng/m² for NNK on household surfaces (Sleiman et al., 2010). The research presented here could be greatly enhanced in the future with an improved ability to detect lower concentrations as well as simultaneous collection of surface samples.

Conclusions

The present chapter reports on the detection and quantification of the TSNAs NNN, NNK, and NNA in three different sampling campaigns. Overall, NNN, NNK, or NNA was detected in 86% of the smoking units and 46% of the nonsmoking units. NNN

was detected in 8 units, NNK in 2 and NNA in 7. Only NNA was above quantification limits (10ppb) in 4 of the 7 units. It was unexpected that the highest detectable concentrations of NNA were observed in nonsmoking units; therefore cross-contamination could be a larger issue than previously thought. NNA had not been previously observed using gas phase collection methods, but is predominant in solid phase samples. While the observation of NNA and the lack of NNK presented here do not align with published studies, this is likely due to the lack of active smoking during acquisition at Sunnyslope Manor.

Samples were also collected in 2014 in the car and home of a heavy smoker. During active smoking and in the first hour afterwards, NNN and NNK were observed on the balcony where smoking took place. In the 2nd hour after the smoking event ended, concentrations of NNN and NNK were observed indoors in the living room, but not on the balcony.

Additional sampling of PM and surface collection of TSNAs during and after smoking events would help explain the current observations. In the future, with lower quantification limits and larger sample sizes, a greater understanding of TNSAs in the indoor environment can be realized.

CHAPTER 6

SUMMARY

The present work explores the indoor air quality (IAQ) as it relates to particulate matter (PM), specific carbonyls (formaldehyde, acetaldehyde, acetone, glyoxal, and methylglyoxal), and tobacco-specific nitrosamines (TSNAs). Most of the sampling occurred at Sunnyslope Manor, a low-income senior living center in Phoenix, AZ before and after an energy-efficiency retrofit. Samples were collected over a period of three years, during the summer months of 2010, 2011, and 2012. Additional samples for TSNA analysis were collected in February of 2014 in an apartment and car of a self-reported heavy smoker.

Chapter 2 described the first field campaign which occurred before any construction began, in order to obtain baseline IAQ. Particulate matter, formaldehyde, and acetaldehyde concentrations were analyzed. It was observed that smoking was the dominating source of indoor PM, as mean values of living room PM_{10} were 213 ± 58 $\mu g/m^3$ for smokers versus 24 ± 5 $\mu g/m^3$ for non-smokers (N= 56). Formaldehyde levels were found to be elevated compared to regulations, with 36% of living room samples and 44% of kitchen samples exceeding the Health Canada REL for chronic exposure to formaldehyde of 40 ppb. Although this study allowed us to sample many units, one hour sampling lead to some research limitations, such as large variance. In addition, the inability to monitor cross-contamination between different units could impact the evaluation of resident habits and measured IAQ.

As described in Chapter 3, the second and third campaigns were conducted immediately after energy efficiency retrofit construction was completed, from late April

through September 2011, and one year later, from June through early August 2012, respectively. Although it was expected to have a short term increase in PM concentrations after the retrofit, this was only statistically apparent with two covariates: length of stay for the occupant and the use of odor-masking products. In general, smokers had higher PM concentrations in all three panels, but no short term change and a slight decrease in the long term. A decrease in PM concentrations occurred in units with residents who had lived longer at the apartment complex in the long term. A significant decrease in formaldehyde levels in Panel 3 was observed and is most likely a result of the replacement of building materials and furnishings during the retrofit. This is supported by the fact that only formaldehyde, but not acetaldehyde and acetone (which are measured simultaneously with the same method), showed a significant reduction in concentration. While both acetone and acetaldehyde concentrations experienced an increase in the short term, long term concentrations were unchanged and well below any defined risk levels.

Using samples from the first and third panels (2010 and 2012), additional analysis of carbonyls was used to quantify glyoxal and methylglyoxal in the indoor and outdoor environments. Chapter 4 described the concentrations and I/O ratios of glyoxal and methylglyoxal. Panel 1 concentrations ranged from 4.4-11.6 and 5.2-12.4 $\mu g/m^3$ for glyoxal and methylglyoxal, respectively. Panel 3 concentrations ranged from 4.0-9.3 and 3.5-13.7 $\mu g/m^3$, respectively. These values were higher than previously reported in indoor environments. Additionally, it was expected that elevated concentrations would be correlated with smoking or use of air fresheners, but no statistical significance was observed. Methylglyoxal was more abundant than glyoxal pre-retrofit, but no difference

was observed post-retrofit, in Panel 3. Future experiments would benefit from larger sample sizes for these species.

During the third panel in 2012, additional collection techniques were utilized to investigate the presence of TSNAs in the indoor environments of both smokers and non-smokers. Observations of NNN, NNK, and NNA were reported in Chapter 5. Measuring the presence of NNN and NNK in indoor air hasn't been reported since the 1990s and we report the first air measurements of NNA. More recent studies have shown NNK and NNA are abundant on surfaces in the presence of nitric acid. It was unexpected that the highest detectable concentrations of NNA were observed in nonsmoking units; therefore cross-contamination could be a larger issue than previously thought. Air samples were also collected in 2014 in the car and home of a heavy smoker. During active smoking and in the first hour afterwards, NNN and NNK were observed on the balcony where smoking took place. In the 2nd hour after the smoking event ended, concentrations of NNN and NNK were observed indoors in the living room, but not on the balcony. Additional sampling of PM and surface collection of TSNAs during and after smoking events would illuminate the current observations.

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APPENDIX A

CHROMATOGRAPHIC PARAMETERS FOR THE LC-UV-MS

Table A1 LC-UV-MS Setup for analysis for carbonyl compounds.

Instrument	
LCMS System	Varian 1200L LCMS (Varian, Palo Alto, CA)
Pumps	Varian Prostar 210
Auto Injector	Varian Prostar 410 Variable Volume
Absorbance Spectrophotometer	Varian 335 Diode Array
Mass Spectrometer	Varian 1200L Triple Quadrupole MS

Solvents	
A	Water (>18MΩ, Millipore, Billerica, MA)
B	Acetonitrile (Fisher Scientific, Optima grade, Waltham, MA)

Solvent Program	
Time (min)	Composition (A:B)
0:00	60:40
14:00	60:40
26:00	5:95
35:00	5:95
38:00	60:40
Seven minute post-run equilibration	

Instrumental Parameters	
Injection volume (□L)	20
Solvent Flow (mL min^{-1})	0.5
Column Model	Supelcosil-LC-18, 25cm ^{x} 3mm ^{x} 5µm
Column Temperature (□C)	25
Diode Array Wavelengths (nm)	360, 430

Mass Spectrometer Parameters	
Ion Source	Electrospray Ionization (ESI)
Ionization Mode	Negative
Detection Mode	Selected Ion Monitoring (SIM)
Detector Voltage (V)	– 1000
Needle Voltage (V)	– 2600
Shield Voltage (V)	– 600
ESI Housing Temperature (□C)	50
Drying Gas Temperature (□C)	200
Drying Gas Pressure (psi)	18
Drying Gas Type	Ultra High Purity N_2
Nebulizing Gas Pressure (psi)	55
Nebulizing Gas Type	Ultra Zero Air

APPENDIX B

CHROMATOGRAPHIC PARAMETERS FOR THE GCMS AND COMPLETE DATA TABLE OF NITROSAMINES

Table B1. GCMS Parameters for analysis for Tobacco Specific Nitrosamines

Instrument	Agilent 6890N/5973
Injection	
Injection mode	Pulsed Splitless, He gas
Injection pressure	10 psi
Injection port temperature	250 ˚C
Column	Supelco SPB-1
Column flow rate ($mLmin^{-1}$)	1.3
Oven Program	40 ˚C for 3 min
	4 ˚$Cmin^{-1}$ to 110˚C
	15 ˚$Cmin^{-1}$ to 220˚C
	220 ˚C for 20 min
Total run time	53 minutes
Mass spectrometer	
Transfer line temperature	275 ˚C
Ionization mode	Chemical ionization (Ammonia gas)
	Single ion monitoring (SIM)
Analyte	Corresponding m/z
NDMA-d6	98
NNN	178
NNK	208
NNA	208

Table B2. Detection of NNN, NNK, and NNA in each unit.

Unit ID	NNN (ppb)	NNK (ppb)	NNA (ppb)	Total Vol (m^3)	NNN (ng/m^3)	NNK (ng/m^3)	NNA (ng/m^3)	Smoker?
X000f	<10ppb	nd	19	0.211	<9	nd	18	n
Xf043	nd	nd	14	0.201	nd	nd	14	n
Xdc06	nd	nd	354	0.204	nd	nd	347	n
X047a	nd	nd	nd	0.083	nd	nd	nd	n
Xc7dc	<10ppb	nd	nd	0.082	< 24	nd	nd	y
Yf2db	nd	nd	nd	0.204	nd	nd	nd	y
X5938	nd	nd	nd	0.088	nd	nd	nd	n
X6449	nd	nd	10	0.218	nd	nd	9	n
Xdf9b	nd	nd	nd	0.084	nd	nd	nd	y
X102f	<10ppb	nd	<10ppb	0.080	< 25	nd	< 25	y
Xefe8	nd	nd	nd	0.085	nd	nd	nd	n
X98f4	nd	nd	nd	0.082	nd	nd	nd	n
X5f2c	nd	nd	nd	0.078	nd	nd	nd	n
X0a51	nd	<10ppb	nd	0.204	nd	< 10	nd	n
Xd041	<10ppb	nd	nd	0.083	< 24	nd	nd	n
X3dc3	nd	nd	<10ppb	0.204	nd	nd	< 10	n
X56ce	nd	nd	nd	0.207	nd	nd	nd	n
X88a9	nd	nd	nd	0.245	nd	nd	nd	n
Xfe26	nd	<10ppb	nd	1.095	nd	< 2	nd	n
Xe7df	nd	nd	nd	0.204	nd	nd	nd	y
X37aa	nd	nd	nd	0.190	nd	nd	nd	n
X658b	nd	nd	nd	0.214	nd	nd	nd	n
X57db	nd	nd	nd	0.201	nd	nd	nd	n
X9ag2	nd	nd	nd	0.207	nd	nd	nd	n
X82cd	<10ppb	nd	nd	0.084	< 24	nd	nd	y
X9d7c	nd	nd	nd	0.197	nd	nd	nd	n
Xbcc0	<10ppb	nd	nd	0.204	< 10	nd	nd	n
Xmy23	<10ppb	nd	nd	0.083	< 24	nd	nd	n
X0dc2	<10ppb	nd	nd	0.077	< 26	nd	nd	n
X6dee	nd	nd	nd	0.204	nd	nd	nd	n
Xef99	<10ppb	nd	nd	0.073	< 27	nd	nd	y
Xeb12	<10ppb	nd	nd	0.078	< 27	nd	nd	n
X97fc	nd	nd	nd	0.170	nd	nd	nd	n
Xk52d	nd	nd	nd	0.228	nd	nd	nd	n
Y5dbf	nd	nd	<10ppb	0.235	nd	nd	< 9	n

APPENDIX C

STATEMENT OF PERMISSION FROM CO-AUTHORS

Co-authors on the previously published articles “Characterization of Indoor Air Quality and Resident Health in an Arizona Senior Housing Apartment Building” and “The Effects of an Energy Efficiency Retrofit on Indoor Air Quality” have granted their permission for use of the articles in this dissertation. This list of co-authors includes: Destaillats, H., Cohn, S., Ahrentzen, S., and Fraser, M.P.