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Assessing and Controlling
Concentrations of Volatile Organic Compounds
in the Retail Environment

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Assessing and Controlling Concentrations of Volatile Organic Compounds in the Retail Environment

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Dedication

To my mother, father, and sister,

for keeping me grounded and yet pushing me to live to the fullest.

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Assessing and controlling concentrations of volatile organic compounds in the retail environment

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Retail buildings have potential for both short-term (customer) and long-term (occupational) exposure to indoor pollutants. A multitude of sources of volatile organic compounds (VOCs) are common to the retail environment. Volatile organic compounds can be odorous, irritating or carcinogenic. Through a field investigation and modeling study, this dissertation investigates exposure to, and control of, VOCs in retail buildings.

Fourteen U.S. retail stores were tested one to four times each over a period of a year, for a total of twenty-four test visits. Over a hundred parameters were investigated to characterize each of the buildings, including ventilation system parameters, and airborne pollutants both indoors and outdoors. Concentrations of VOCs were simultaneously measured using five different methods: Summa canisters, sorbent tubes, 2,4-dinitrophenylhydrazine (DNPH) tubes, a photoionization detector (PID), and a colorimetric real-time formaldehyde monitor (FMM). The resulting dataset was analyzed to evaluate underlying trends in the concentrations and speciation of VOCs, identify influencing factors, and determine contaminants of concern. A parametric framework based on a time-averaged mass balance was then developed to compare strategies to reduce formaldehyde concentrations in retail stores. Mitigation of exposure to formaldehyde through air cleaning (filtration), emission control (humidity control), and targeted dilution (local ventilation) were assessed.

Results of the field study suggested that formaldehyde was the most important contaminant of concern in the retail stores investigated, as all 14 stores exceeded the most conservative health guideline for formaldehyde (OEHHA TWA REL = 7.3 ppb) during at least one sampling event. Formaldehyde monitors were strongly correlated with DNPH tube results. The FMM showed promising characteristics, supporting further consideration as real-time indicators to control ventilation and/or environmental parameters. The vast majority of the remaining VOCs were present at low concentrations, but episodic activities such as cooking and cleaning led to relatively high indoor concentrations for ethanol, acetaldehyde, and terpenoids.

Results of the modeling effort demonstrated that local ventilation caused the most uniform improvements to indoor formaldehyde concentrations across building characteristics, but humidity control appeared to have a very limited impact. Filtration used under specific conditions could lead to larger decreases in formaldehyde concentrations than all other strategies investigated, and was the least energy-intensive.

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1. Introduction

1.1. PROBLEM STATEMENT

Energy efficiency has become one of the most important control parameters for building design and operation. According to the U.S. Energy Information Administration, in 2012 the building sector consumed 39.5% of the energy produced in the U.S., and was responsible for 37.5% of U.S. CO_2 emissions [1]. A recent shift in interest from solely energy-efficient to healthy buildings strives to refocus building design and operation to include the health, comfort and productivity of occupants [2]. Indoor air quality is a decisive component of healthful environments [3]. Volatile organic compounds (VOCs), defined as organic chemicals with boiling points below 250 °C [4], are a broad class of chemicals ubiquitous in the indoor environment. While exposure to most VOCs at typical indoor concentrations has not been shown to negatively impact human health, specific compounds have been associated with a variety of adverse health effects. Such outcomes may include mucosal irritations, lower respiratory symptoms, central nervous system symptoms, and cancers [5-7]. Indoor air quality can be improved by controlling the sources of pollutants or removing, actively or passively, the contaminants released. The most common strategy for removal of pollutants of indoor origin is ventilation [8-10].

The retail sector is a compelling environment to investigate the associations between ventilation and indoor air quality. With 443,000 buildings occupying up to 401 million m^2 of floorspace [11, 12], the retail sector is a major component of the U.S. building stock. According to the last commercial building energy consumption survey, retail space cooling, heating, and ventilation alone used 148 trillion BTUs, which amounted to 46% of the total energy consumed by U.S. retail buildings [13]. Reducing ventilation in retail buildings could therefore lead to considerable energy savings. In addition to energy concerns, the retail sector has a significant potential for both short-term and occupational exposure to indoor pollutants. Typical VOC sources found in retail stores include merchandise, displays, building materials, as well as cooking and cleaning activities [14-16]. As of December 2013, more than 15 million employees worked in retail stores [17]. Moreover, every day 36% of the U.S. civilian population engages in consumer goods purchases, and these consumers spend approximately one hour on average in retail environments [18]. These shopping activities are highly lucrative; during the last quarter of 2013 (adjusted for seasonal variation), U.S. retail sales exceeded $380 billion monthly [19]. Not only would changes in indoor air quality have an impact on the health of retail workers and customers, but it could also influence the customer shopping experience [20, 21], leading to a potentially significant economic benefit for the store. However, little has been published on the subject of indoor air quality in retail stores, and no comprehensive framework has been developed to specifically assess the trade-off between energy and exposure to harmful VOCs in the retail environment.

1.2. OBJECTIVES

The general objective of this dissertation is to characterize concentrations of VOCs in retail store and to investigate appropriate strategies to control VOCs of concern.

Specific objectives are to:

- Identify VOCs of concern and their possible sources.
- Evaluate the effects of ventilation and ozone chemistry on VOC concentrations.
- Assess the impact of measurement techniques on decision-making.
- Evaluate the validity of real-time VOC sampling methods.
- Model reductions in formaldehyde concentrations by use of alternative removal strategies.
- Evaluate the energy consequences of reducing concentrations of formaldehyde in retail stores.

1.3. SCOPE AND INTEGRATION

The research presented in this dissertation is organized in four phases that are summarized in Figure 1. The main thread throughout the work is the development and refinement of techniques and models for measuring and controlling VOCs in retail buildings.

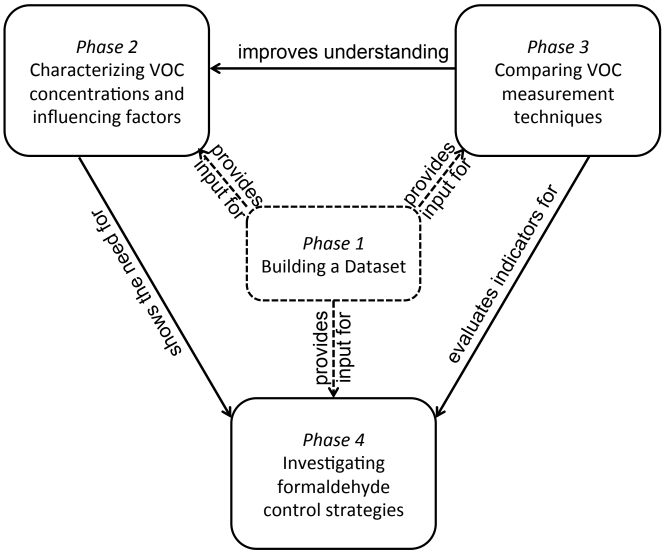

Figure 1: Illustration of the connections between the four phases of this work.

The first phase of the research consists of field studies in Texas and Pennsylvania. We sampled fourteen retail stores one to four times each over a period of a year, for a total of twenty-four test visits. Sampled retail types included general merchandise (four stores), home improvement (two stores), furniture (two stores), mid-size grocery (two stores), small grocery (two stores), electronics (one store), and office supply (one store). Over a hundred parameters were investigated in order to characterize the building, its ventilation system, and airborne pollutants indoors and outdoors. Specifically, we measured VOC concentrations using five methods: Summa canisters, sorbent tubes, DNPH tubes, a photoionization detector (PID), and a colorimetric real-time formaldehyde monitor (FMM). Total (outdoor-to-indoor) air exchange rates were obtained with the SF_6 decay method. Indoor and outdoor concentrations of ozone were monitored over three to five days.

Phase 2 of the research addresses the lack of information on indoor air quality and ventilation in retail environments, and the data collected is used as inputs in the modeling effort of Phase 4. Phase 2 consists of an exploration of the dataset obtained in Phase 1. Two hundred and eighty eight VOCs were collected in the retail stores. We develop fourteen VOC categories to facilitate the analysis of the influencing factors. Influencing factors investigated include (1) store type, (2) seasons, (3) outdoor concentrations, and (4) ozone concentrations. Non-parametric regressions are conducted to uncover correlations between speciated VOC concentrations and air exchange rates.

In phase 3, we examine VOC measurement techniques and the variation in their output to investigate what method, if any, would be more appropriate to serve as an indicator to control ventilation in retail stores. This phase consists of a comparison of the sampling techniques used to collect and analyze VOCs in Phase 1. For Summa canister and sorbent tube results, we analyze the differences in VOC identification and quantification by compound. Four-hour averaged TVOC (and formaldehyde) concentrations monitored by PID (and FMM) are correlated with simultaneous integrated measurements by Summa canisters (and DNPH tubes).

Based on the results of phases 2 and 3, formaldehyde was identified as a pollutant critical to control. In phase 4, we propose solutions to save energy by demonstrating the most energy-efficient control strategy for formaldehyde. Phase 4 consists of the development of a parametric framework to compare formaldehyde control strategies in retail stores that is based on a time-averaged mass balance. The parameters investigated in a sensitivity analysis include: ventilation rates, filtration efficiency, and relative humidity in the space. In addition, we estimate the cost due of the implementation of each measure.

The overall focus of this research is to investigate contaminants of concern in retail stores, which is important in order to balance the need for an acceptable indoor air quality and the prospects of energy savings. The completion of this research should add substantially to the body of knowledge regarding exposure to, and control of, volatile organic compounds in retail buildings.

1.4. ORGANIZATION

This dissertation consists of two major parts. An executive summary briefly presents the motivation, methodology, and key results for every research phase. The full texts of journal papers that describe every research phase in more details can be found in Appendices A-C:

- Appendix A: Nirlo E.L., Crain N., Corsi R.L., Siegel J.A. Volatile Organic Compounds in Fourteen U.S. Retail Stores. Accepted for publication in Indoor Air in January 2014.
- Appendix B: Nirlo E.L., Crain N., Corsi R.L., Siegel J.A. Field Evaluation of Five VOC Measurement Techniques: Implications for Green Building Decision-Making. Submitted to HVAC&R Research.
- Appendix C: Nirlo E.L., Siegel J.A., Corsi R.L. Formaldehyde control strategies for U.S. retail buildings. To be submitted to Building and Environment.

2. Background

2.1. VOLATILE ORGANIC COMPOUNDS IN RETAIL STORES

Health impacts associated with VOCs vary significantly between compounds. Many VOCs are not considered a threat to human health at the concentrations typically observed in the indoor environment [22], but can be respiratory, or eye, nose and throat irritants at elevated concentrations. For example, acute exposure to formaldehyde is believed to cause nausea, headaches, and irritation of the skin, eyes, and mucous membranes [23]. Chronic exposure to formaldehyde at typical indoor concentrations has been suspected to cause non-negligible respiratory effects in sensitive individuals, particularly children [23, 24]. Moreover, based on extensive evidence in rats, formaldehyde is classified as a probable human carcinogen by the U.S. Environmental Protection Agency [25]. The International Agency for Research on Cancer further considers that there is sufficient evidence of formaldehyde causing nasopharyngeal cancer and leukemia, and limited evidence of sinonasal cancer in humans to classify formaldehyde as a human carcinogen [26].

Previous researchers have identified VOCs of potential concern in the retail environment, but little is known about the impact of store type or ventilation parameters on VOC concentrations. Previous research has focused on benzene, toluene, ethylbenzene, xylene (BTEX), and to a lesser extent styrene (BTEXS). Identified BTEXS sources include motor vehicle exhaust [27, 28], newspaper ink [29, 30], as well as building materials [31, 32]. Reported concentrations of other VOCs in retail stores are surprisingly sparse. Halogenated compounds were found in a shopping mall in South China [31], mainly due to the use of chlorinated cleaning agents. Limonene, likely emitted by household cleaning products and scented consumer products, had the highest concentrations of all VOCs measured in two supermarkets studied by Bruno et al. [32]. Pressed wood products [33, 34], and carpet [35] were identified as major sources of formaldehyde in retail stores.

At least four studies have explored the variation in VOC concentrations between types of retail stores [31, 34, 36, 37]. Tang et al. [31] and Eklund et al. [36] observed spatial variability in BTEX concentrations within shopping malls in China and New Jersey, and evidence of cross-contamination amongst contiguous stores. In the Boston Exposure Assessment in Microenvironments (BEAM) study, toluene was the dominant VOC in multipurpose stores, formaldehyde in houseware and furniture stores, and acetaldehyde in grocery stores [34]. Similar trends have been reported by Chan et al. [37] in two grocery stores and three furniture stores. Only three research teams have investigated the relationship between concentrations and ventilation rates. In a general merchandise store, Hotchi et al. [33] observed increases in VOC concentrations ranging from 15% to 170% when decreasing ventilation rates by 30%. Grimsrud et al. [38] investigated three general merchandise stores and suggested that ventilation rates could be lowered, while maintaining total volatile organic compound (TVOC as toluene measured using passive organic badges) and formaldehyde concentrations under reference levels recommended by ASHRAE Standard 62.1 [8]. However, Chan et al. [37] found formaldehyde, acetaldehyde and acrolein concentrations exceeding their respective health guidelines in stores where air exchange rates complied with ASHRAE Standard 62.1. In phase 2 of this research, a finer analysis is conducted on a larger sample of stores to investigate the impact of ventilation rates on VOC concentrations. A more detailed analysis of the current state of knowledge on VOCs in retail stores is presented in Appendix D.

2.2. SAMPLING TECHNIQUES

Assessing exposure to VOCs requires information about the compounds present in the air and their concentrations at a specific location and time. This section will first introduce challenges inherent to VOC measurements, then present some common techniques and their limitations, and finally summarize the few previous studies comparing measurement techniques. In phase 3 of the research described in this dissertation, we investigate how the selection of a

VOC sampling method impacts decision-making in retail environments, especially regarding ventilation control.

2.2.1. The challenges of measuring VOCs

Although the U.S. Environmental Protection Agency and the American Society for Testing and Materials publish standardized methods and protocols for measuring indoor air pollutants [39-42], VOC measurements are not widely practiced. These measurement techniques are compound-specific, requiring the need to know what VOCs are suspected to be present in the space prior to sampling in order to select the appropriate collection and analysis technique. Multiple guides [43, 44] warn facility managers, operators, technicians and consultants about the price associated with sampling, the necessity of selecting an appropriate technique and representative time, duration and location of sampling, as well as the complexity of interpreting the results. Therefore, direct measurements are only advised as a last resort [43], and simpler techniques are commonly used as proxies to evaluate indoor air quality [2]. Indoor air quality investigations triggered by a complaint are typically limited to a site assessment and/or a perception survey, and can be accompanied with measurements of ventilation rates and environmental parameters (e.g., temperature, relative humidity, CO2 concentrations) [43]. Information obtained through these indirect methods is not always sufficient to design and operate a VOC removal strategy that may be needed to create and maintain a healthy environment. If information on indoor air quality is required during the modeling phase of the removal system, the designer is encouraged to compare the space studied to similar existing environments [8]. However, cross-study comparisons of VOC concentrations are problematic as studies differ in sampling method, time and duration. In addition, it can difficult to determine what “similar environments” are. For instance, in the case of retail buildings, stores investigated in the literature also differ in merchandise carried and layout (Appendix D).

2.2.2. Presentation of selected techniques

Many collection and analysis techniques exist to measure VOCs, and each method is associated with advantages and limitations. Summa canisters (CAN) are a whole-air sampling technique commonly used in field measurements. The sampling and analytical procedures are documented in EPA compendium method TO-15 [45]. Canisters are simple to use, highly reproducible and have the advantage of allowing for multiple analysis from the same sample [46]. However, some limitations have been described in the literature, especially regarding the stability and recovery of polar compounds such as aldehydes and terpenes [46, 47]. Wang et al. [48] pointed out the additional issues of cleaning and condensation.

The procedure of active sampling through tubes packed with sorbents (SOR), followed by thermal desorption and gas chromatography/mass spectrometry, is documented in EPA compendium method TO-17 [49]. This method is popular, although subject to mass breakthrough, decomposition and desorption issues [46].

Both CAN and SOR samples can be sent to certified laboratories for analysis for approximately \$300 USD/sample and \$200 USD/sample, plus shipping, respectively. Identification and quantification of VOCs on a mass spectrum is based on the fragmentation pattern of ions of individual peaks. If the speciation of the air sampled is already known, customized target lists can be created for both CAN and SOR analysis to improve identification and quantification of the selected compounds. Compounds that are not on the target list are identified using a library compound search (LCS), and compared to the nearest internal standard for quantification. Both the identification and quantification of LCS compounds is associated with a greater uncertainty than that of targeted compounds.

A variant of sorbent tube sampling used to collect light aldehydes requires the use of adsorbent cartridges coated with 2,4-dinitrophenylhydrazine (2,4-DNPH), followed by the separation and analysis of the hydrazone derivative by high performance liquid chromatography with ultraviolet (UV) detection (EPA compendium method TO-11A [50]). DNPH tubes are a reliable but field-intensive sampling technique. The cost of analysis by a certified laboratory in the United States is approximately $100 USD/sample.

Photoionization detectors (PID) use high-energy UV light to ionize molecules in the sampled airstream. The instrument measures the current produced by the electrically charged gas and converts the signal to the concentration, providing rapid onsite screening for total volatile organic compounds (TVOC) [51]. Photoionization detectors are easy to use and light, therefore adapted for personal monitoring. However, PIDs are limited by the non-specificity of the response [52], as they cannot identify individual compounds. In addition to the initial price of the instrument (above $5,000 USD), additional costs are associated with the use of consumables needed for the instrument calibration before and after sampling.

A formaldehyde multimode monitor (FMM) is an easy-to-use, self-calibrating device. The instrument couples a chemical sensor element with spectrophotometric analysis to provide 30-minute averaged concentrations of formaldehyde. The main limitation of this instrument concerns its use for concentrations under 20 ppb, commonly found in indoor environments, that has not been verified by the manufacturer. However, tests conducted in a controlled environment by Carter et al. [53] indicated a good performance of the FMM at 5 and 10 ppb. The authors also reported a decreased accuracy at high concentrations, and some inconsistency amongst sensor batches.

2.2.3. Comparison of methods

While many studies have compared the output of two analytical procedures used simultaneously in a controlled environment with gas mixtures of known concentrations [54], few studies have used field data to compare sampling methodologies [52, 55-59]. Such studies were specific to a targeted subset of compounds, mainly BTEXS, and to the environment sampled (cokery [57]; newly-built apartments [58]; construction sites with painting jobs [52]). None of these studies were conducted in retail stores, and less than twenty compounds were investigated.

Most of the published investigations compared passive to active collection techniques (canister vs. organic vapor monitor (OVM) [55, 59]; sorbent vs. OVM [56, 57]). No study was found that compared more than two techniques used simultaneously in a non-controlled environment. In phase 3 of this work, simultaneous measurements of VOCs by Summa canister, sorbent tubes, and PID in retail stores are compared.

2.3. FORMALDEHYDE CONTROL STRATEGIES

As mentioned in Section 2.1, previous studies have found formaldehyde to be a contaminant of concern in retail stores. In this section, the current status of strategies available to control or remove indoor formaldehyde is summarized. In phase 4 of this research, we use methods and parameters of viable removal solutions presented here as inputs for a modeling effort to compare formaldehyde control strategies in retail stores.

2.3.1. Formaldehyde removal

This section is a summary of the various technologies that have been investigated to remove formaldehyde from an airstream. We indicate whether these solutions could be used as a control device for removal of formaldehyde under typical indoor conditions.

Photocatalytic oxidation. Many studies have investigated the photodegradation of formaldehyde by TiO_2 (or titania) [60-63]. This process requires contact between the photocatalyst and the pollutant, and the presence of light (or UV). The titania can be placed on a glass plate reactor [64, 65] to simulate coated windows, on lighted textile [66], on meso-porous materials [67], or in paints [68]. Reported downsides include the price and low efficiency of the photocatalytic oxidation process, issues with deactivation and competitive conversion in gas mixtures [69, 70], and the formation of by-products [71]. No study reported clean air delivery rates (CADR = flow times efficiency).

Adsorption. Formaldehyde can be captured by activated carbon (AC) filters if the AC is chemically enhanced with metal oxides (copper [72], manganese [73, 74]). Other options include silica materials functionalized with amino-propyl groups [75], scallop shell nanoparticles [76], or the addition of nano-size carbon colloids onto a filter [77]. Strommen and Gesser [78] tested coating air filters with polymeric amines and glycerol to capture aldehydes, and reported initial single pass efficiencies of 40% for acetaldehyde. Only one study [72] reported removal efficiencies and clean air delivery rates for a copper-enhanced AC filter, although the CADRs (0.098-0.154 m^3/h) were extremely low.

Combined technologies. A common combination is that of AC filters, generally in a honeycomb rotor, and photocatalytic reactors [79-81]. Sekine et al. [82] developed an air cleaner that combines a photocatalyst filter, an AC filter, and a MnO2 filter, recommended for formaldehyde and toluene. The reported CADR ranged from 20 to 35 m^3/h for an input formaldehyde concentration of 10 mg/m^3.

None of the technologies presented here can be considered mature or widely accepted for removal of formaldehyde. Control technologies marketed for formaldehyde removal are limited, and commercially available products provide no guarantee of efficiency; technical specifications are not readily available for any products.

2.3.2. Formaldehyde control using relative humidity

If sources of formaldehyde cannot be simply removed, the rate at which sources emit formaldehyde might be controlled, notably by changing the temperature or relative humidity (RH) in the space. Many studies have investigated the impact of temperature and RH on formaldehyde emissions [83-88]. The impact of RH can be modeled following the rationale for classical adsorption isotherms and transport coefficients [87, 89]. Chamber experiments have been conducted on formaldehyde emissions from wallboard, carpet [87], pressed-wood products [83-86], and other building materials [88]. A recent test of benchseats and cabinetry extracted from temporary housing units suggested that increasing RH from 50% to 85% leads to a 1.8 to

2.6-fold increase in formaldehyde [90]. However, the changes in release rates reported in these chamber studies are specific to the material tested and the levels of RH selected.

2.3.3. Modeling formaldehyde removal strategies

Previous modeling studies have investigated the use of ventilation as a solution to improve indoor air quality in residences [91] and in commercial buildings [92-94]. The U.S. EPA [92] conducted an extensive modeling effort to evaluate the energy costs associated with various ventilation scenarios. The study simulated the impacts on thermal comfort, but not on pollutant concentrations. The authors guided building designers and operators towards “indoor air quality-compatible” measures to reduce HVAC energy. Ng et al. [94] investigated the impact of reducing or doubling ventilation rates on formaldehyde concentration and energy consumption in a model stand-alone retail building, and concluded on the importance of first reducing emissions. Apte et al. [93] modeled the influence of ventilation and other removal strategies on the concentrations of 36 contaminants of concern. The authors suggested that reduced ventilation rates combined with air cleaning and local ventilation could lead to significant decreases in formaldehyde concentrations and energy use. However, the simulation was conducted on a model “big box” retail store, and was limited to Californian cities. Phase 4 of this research spans retail buildings of various characteristics, in three cities representing typical climates in the U.S.: hot and humid, cold and dry, as well as hot and dry.

3. Methods

3.1. EXPERIMENTAL METHODS

3.1.1. Description of the sample

Phase 1 of the research was performed at fourteen retail stores in Pennsylvania and Texas, with six stores sampled two to four times over the course of a year, resulting in 24 test visits (Table 1). Stores varied in retail type, size and location. More details on the sample of buildings selected can be found in Appendix A.

Table 1: Summary information about the retail stores sampled.

Store code[a]	Num. of Test Visits[b]	Type	Location	Months Tested	Volume [m^3]
HaP	2	Home improvement	PA	May, Nov	93 400
HaT	1	Home improvement	TX	Jun	91 800
MbP	4	General merchandise	PA	Sep, Jan, May, Jul	99 500
MbT	4	General merchandise	TX	Jul, Oct, Feb, Apr	61 200
MiP	1[c]	General merchandise	PA	Apr	66 800
MiT	1[c]	General merchandise	TX	Apr	55 200
EgP	2	Electronics	PA	Feb, Jun	20 300
OhT	1	Office supply	TX	May	20 700
FfP	1	Furniture	PA	Mar	8170
FfT	2	Furniture	TX	Oct, Feb	19 800
GeP	1	Grocery (mid-size)	PA	Jul	25 300
GeT	2	Grocery (mid-size)	TX	Sep, Jan	14 900
ScP	1	Grocery (small)	PA	Aug	3340
SdT	1	Grocery (small)	TX	Aug	5390

[a] Three-character code that identifies a unique store. The first letter identifies the store type (H for home improvement, M for general merchandise, E for electronics, O for office supply, F for furniture, G for grocery (mid-size) and S for small grocery); the second letter differentiates the brand of the store; and the third letter the location of the store (P for Pennsylvania and T for Texas).

[b] At stores where multiple visits occurred, sampling events are identified with a four-character code composed of the store code and a number (1-4) referring to the test visit considered.

[c] Stores MiP and MiT were selected for additional testing. Two sampling events occurred at each store; the first sampling event was conducted at artificially elevated ventilation conditions (results excluded from summary data), and the second sampling event was conducted at normal ventilation conditions.

3.1.2. VOC measurements

Sampling was conducted at each site over the course of a week. A permanent indoor sampling location was selected in each store where instruments were set-up for continuous monitoring. The choice of this permanent location was dictated by access to power plugs, sufficient shielding from customers, and limited impact on the daily operations of the store. Therefore, fixed sampling often occurred from non-central locations (corners of the store, top of refrigerated cases) that may not be fully representative of average conditions in the store, but can give us relevant information regarding temporal variations. In an attempt to capture a spatial average of the conditions in the store, some instruments were placed into a shopping cart (or basket) that was continuously pushed (carried) through the retail floor to conduct a "mobile sampling" of indoor air for four hours, usually in the middle of a day.

Five methods were used to measure VOC, aldehyde, and TVOC concentrations: Summa canisters (CAN), sorbent tubes (SOR), photoionization detectors (PID), DNPH tubes (DNPH), and formaldehyde multimode monitors (FMM). The instruments used for each type of measurement, along with the manufacturer/laboratory reported uncertainty, detection limit, and resolution are summarized in Table 2.

Table 2: Instrumentation used for VOC sampling in the present investigation.

Concentrations Measured	**Time Resolution**	**Instrument**	**Detection Principle**	**Uncertainty**	**Detection Limit**	**Resolution**
Speciated VOCs	Integrated 4 hrs	Summa canisters, analyzed by CL1[a], CL2[a]	Gas chromatography, mass spectrometry	±30% (TC)[b] ±100% (LSC)[c]	0.5 ppb	
	Integrated 4 hrs	Tenax-GR sorbent tubes, analyzed in-house	Thermal desorption, gas chromatography, mass spectrometry	±100%	2 ng	1 ng
TVOC	Continuous 5 min	RAE Systems ppbRAE Plus PGM-7240	UV absorption	Greater of ± 20 ppb and 10% of the reading	1 ppb	1 ppb
Formaldehyde	Integrated 4 hrs	DNPH tubes, analyzed by CL1, CL3[a]	High-performance liquid chromatography	±30% (CL1) ±12.4%[d] (CL3)	100 ng	
	Continuous 30 min	Shinyei Formaldehyde Multimode Monitor	UV absorption	±10% at 40, 80, 160 ppb[e]	20 ppb[e]	1 ppb

[a] Commercial laboratories.

[b] Targeted compounds.

[c] Library search compounds.

[d] While most laboratories (CL1, CL2, in-house) reported VOC concentrations with the uncertainty prescribed in the EPA compendium corresponding to the collection and analysis

technique used, CL3 also maintained an ongoing uncertainty calculation based on the performance of continuing calibrations standards. For the time period in which the samples for this project were processed, the uncertainty for DNPH analysis was ±12.4% for formaldehyde. If the uncertainty associated with the flowmeter (±1%) and the pumps used (±5%) were added in quadrature, the calculated uncertainty on the formaldehyde concentrations would increase by a percentage point. In the rest of the analysis, concentrations are reported with the laboratory reported uncertainty only.

[e] Manufacturer only calibrates device to 20 ppb. Readings below 20 ppb were made using special software provided by the manufacturer for this investigation. The uncertainty associated with these readings is also assumed to be ± 10% [53].

Indoor Summa canister samples were successfully collected at all sampling events. Five sets of duplicate samples were also collected. Sorbent tube samples were collected using a modified version of the U.S. EPA compendium method TO-17 [49] and analyzed in-house. Thirty-one indoor sorbent tube samples were collected, including eight sets of duplicates. The sorbent tube sampling system was successfully collocated in the shopping cart or basket with the Summa canister for twenty-three sampling events.

Photoionization detectors were used for each test to measure 5-minute averages of the total volatile organic compound (TVOC) concentration. The PID was successfully collocated in the shopping cart or basket with the Summa canister for twenty-seven mobile sampling events.

DNPH tubes were successfully collected during all sampling events, including 13 sets of duplicates. Concurrently, formaldehyde multimode monitors (FMM) were used at fourteen test visits to measure 30-minute averages of the formaldehyde concentration. The quality assurance and quality control procedures for all VOC measurements are documented in Appendix B.

3.1.3. Other selected measurements

During a site visit, several other indoor air quality and ventilation parameters were investigated. All measurement methods are described in more detail in Siegel et al. [95]. During the mobile sampling period, a sulfur hexafluoride (SF_6) decay test was performed to determine the air exchange rate in the space. Ozone concentrations were monitored from the fixed sampling location using a Model 202 Ozone Monitor manufactured by 2B Technologies, with an uncertainty defined as the greater of ±2% or ±1.5 ppb. Analysis of the ozone results is presented in Appendix E. The store employees' perception of indoor air quality was probed with surveys at most sites. More details on the surveys administered and results are discussed in Appendix F.

3.2. DATA ANALYSIS

3.2.1. Time-integrated measurements

Across all sampling events, 288 VOCs were identified and quantified. To facilitate the analysis, VOCs were grouped into fourteen categories based on similarities in chemical structure and/or potential exposure characteristics (Table 3). Indoor VOC concentrations were averaged when replicate samples were collected.

Table 3: VOC categories and their occurrence on the sales floor across test visits.

Category	n[a]	Indoor Occurrence	Category	n[a]	Indoor Occurrence
1 - Formaldehyde	1	24/24[b]	8 - Isopropyl alcohol	1	23/24[c], 4/20[d]
2 - Acetaldehyde	1	17/24[b]	9 - C4-C10 carbonyls	55	22/24[c], 19/20[d]
3 - Ethanol	1	22/24[c], 7/20[d]	10 - BTEXS	5	24/24[c], 20/20[d]
4 - Non-halogenated alkanes	73	23/24[c], 20/20[d]	11 - Halogenated alkanes	13	23/24[c], 0/20[d]
5 - Acetone	1	24/24[c], 2/20[d]	12 - Non-BTEXS aromatics	17	8/24[c], 16/20[d]
6 - Total terpenoids	15	20/24[c], 11/20[d]	13 - C4-or-greater alcohols	28	5/24[c], 18/20[d]
7 - Acetonitrile	1	17/24[c], 0/20[d]	14 - Other	40	15/24[c], 20/20[d]

[a] Number of compounds in categories found across all sampling events, sampling techniques and locations.
[b] DNPH tube samples.
[c] Summa canister samples.
[d] Sorbent tube samples.

3.2.2. Time-resolved measurements

For every test, data points where the concentration was not within three standard deviations of the overall mean were flagged as potential outliers, and removed from the time series data after a visual check (Appendix B). As a way to compare results obtained from the different techniques, time-resolved concentrations were averaged over the four-hour mobile sampling period where real-time monitoring (PID, FMM) was concurrent with time-integrated measurements (CAN, SOR, and DNPH).

PID results are compared to a TVOC concentration calculated by summing the individual concentrations obtained by the Summa canisters (C_{CAN}^{TVOC}). Further comparisons are conducted using PID TVOC concentrations adjusted to the specific air mixture sampled. Mixture correction factors are calculated for each sample using mole fractions determined by Summa canisters. Detailed calculations are available in Appendix B.

3.3. MODELING

This section briefly describes the modeling effort conducted to investigate the impact of removal strategies on formaldehyde concentrations and their associated energy penalty in retail stores. Mitigation of exposure to formaldehyde through air cleaning (filtration), emission control (humidity control), and targeted dilution (local ventilation) are considered in this analysis. More details are presented in Appendix C.

3.3.1. Indoor formaldehyde concentrations

The main processes influencing the fate of formaldehyde in a single-zone retail store are illustrated in Figure 2.

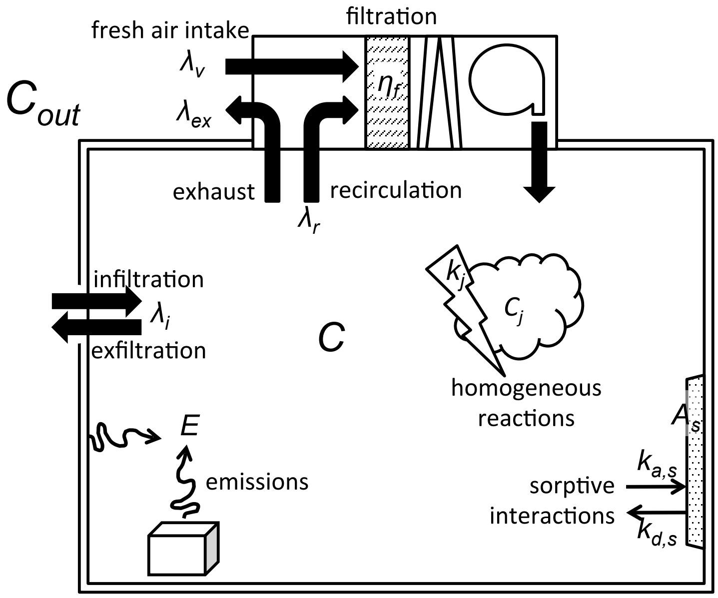

Figure 2: Schematic for modeling of indoor formaldehyde concentration in retail stores in a single-zone model. Block arrows represent airflows.

Indoor formaldehyde concentrations in a single well-mixed environment can be determined by incorporating all gain and loss processes shown in Figure 2 into a mass balance, as presented in Equation 2.

$$\frac{dC}{dt} = E\frac{A}{V} + \left(1-\eta_f\right)\left(\lambda_v C_{out} + \lambda_r C\right) + \lambda_i C_{out} + \sum_s k_{d,s}\frac{A_s}{V}M_s - \left(\lambda_{ex} + \lambda_r\right)C - \lambda_i C - \sum_s k_{a,s}\frac{A_s}{V}C \pm \sum_j k_j C_j C \qquad \text{(Eq. 2)}$$

Where V is the volume of the store (m^3), A is the floor area of the retail space (m^2), C is the indoor formaldehyde concentration ($\mu g/m^3$), C_{out} is the ambient formaldehyde concentration ($\mu g/m^3$), E is the formaldehyde emission rate ($\mu g/m^2.h$), λ_v is the make-up ventilation rate at which outdoor air is introduced into the space by the HVAC system (h^{-1}), λ_{ex} is the air exhaust rate (h^{-1}), λ_r is the air recirculation rate (h^{-1}), λ_i is the infiltration rate at which air enters and exits the space through the building envelope (h^{-1}), η_f is the efficiency of a filter designed to remove formaldehyde (-), k_j is the rate at which formaldehyde reacts with a compound j found at a concentration C_j ($\mu g/m^3$), $k_{a,s}$ is the adsorption rate coefficient (m/h) and $k_{d,s}$ the desorption rate coefficient (h^{-1}). The latter two parameters represent sorptive interactions between formaldehyde and indoor materials with surface area A_s (m^2) containing a mass of formaldehyde per unit area of surface M_s ($\mu g/m^2$).

Equation 2 can be time-averaged to obtain hourly concentrations of indoor formaldehyde by assuming that all parameters are constant over a 1-hour period [96]. These parameters are varied in a parametric analysis to explore their relative influence on hourly concentrations of indoor formaldehyde.

For simplicity, the effects of sorptive interactions [97, 98] are neglected in the rest of this study, and rates of removal and formation for reasonable indoor reactant concentrations are deemed negligible compared to losses by ventilation and gains through emissions [99, 100].

The impact of filtration on indoor formaldehyde concentrations is modeled through varying η_f (assuming $\alpha_{RH}=1$) in Equation 3. The RH impact factor α_{RH} is calculated following the Berge equation [101] to represent the effect of RH on formaldehyde emission rates. Equation 3 is also used to model the impact of humidity control on indoor formaldehyde concentrations through varying α_{RH} (assuming $\eta_f=0$).

$$C_{operating} = \frac{\frac{\alpha_{RH} \cdot E \cdot A}{V} + (1-\eta_f)\lambda_v C_{out} + \lambda_i C_{out}}{\eta_f \lambda_r + \lambda_v + \lambda_i} \qquad \text{(Eq. 3)}$$

Where $C_{operating}$ is the indoor formaldehyde concentration in the store during operating hours ($\mu g/m^3$), and all other variables are as defined previously. We assume that the HVAC system operates on reduced airflows when the store is closed, and the indoor formaldehyde concentration C_{closed} can be calculated by setting λ_v and λ_i to their lowest modeled value in Equation 3.

In order to reduce the amount of fresh air required to dilute indoor formaldehyde, we investigate the potential to partition the store into two zones, providing increased ventilation locally to the zone containing the formaldehyde sources. The majority of formaldehyde-emitting products (e.g. the furniture section) are grouped in a small part of the store (Zone 1) and kept separate from the rest of the store (Zone 2) by an air curtain or a physical partition. Airflows at the scale of the entire store are balanced, but Zone 1 is assumed to be negatively-pressurized and Zone 2 positively-pressurized to avoid contamination from Zone 1 to Zone 2. The introduction of air from Zone 2 to Zone 1 would likely create some backflow from Zone 1 to Zone 2 around the partition, and locally challenge the well-mixed assumption for both zones. Considering the scope of this analysis, I neglect these effects. The parameter controlling this strategy is the exhaust airflow in Zone 1, $\lambda_{ex,1}$. Two mass balances similar to Equation 2 must be simultaneously solved to calculate the impact of local ventilation on formaldehyde concentrations in the two zones of the partitioned store. During closed hours, we investigate the influence of having HVAC system servicing Zone 2 operating under reduced airflows, and the Zone 1-HVAC remains unchanged. Parameters and equations defining the local ventilation strategy are detailed in Appendix C.

3.3.2. Energy implications

The energy implications of implementing measures to reduce formaldehyde concentrations is characterized in this study as one or a combination of the following: (1) heating, (2) cooling, (3) fan use, (4) humidification, or (5) dehumidification. Heating is assumed to be provided by a gas furnace following the recommendations of the U.S. EPA Exposure Factor Handbook for commercial buildings [102]. For the calculation of cooling and dehumidification energy, air handling units are assumed to be equipped with a cooling coil operating under the minimum requirement for electrically operated unitary AC units of ASHRAE Standard 90.1 [103]. Humidification is provided by a gas-fired steam humidifier operating with an efficiency of 90% based on engineering judgement. For simplicity, we further assume that units are equipped with fans with speed control that could maintain a constant airflow, although fans without speed control may be more commonly used by actual retail stores [95, 104]. Parameters and equations used to calculate the energy penalty associated with each removal strategy are detailed in Appendix C.

3.3.3. Framework

The model described above is used to investigate the impact of filtration (F), humidity control (HC), and local ventilation (LV) on indoor formaldehyde concentrations on a broad scale. Each removal strategy is associated with a defining parameter, as introduced in the previous section. Filtration is defined for three filter efficiencies: 20%, 60%, and 100%. Humidity control is defined for four levels of RH_{in}: 30%, 40%, 50%, and 60%. Local ventilation is defined for four levels of Zone 1-exhaust flowrate: 0.75 h^{-1}, 1.5 h^{-1}, 3 h^{-1}, and 6 h^{-1}. Parameters defining the modeled buildings and ambient conditions are also varied in three levels. A scenario is defined as a unique combination of parameters. Parameters selected for modeling of indoor formaldehyde concentrations are summarized in Table 4.

Table 4: Summary of varied parameters. Base case values for each parameter are shown in bold.

Parameters	Strategy[a]	Cases	References
E [$\mu g/m^2.h$]	NR, F, HC, LV	24.7, **61.0**, 91.0	calculated [35, 38]
C_{out} [$\mu g/m^3$]	NR, F, HC, LV	0, **2.1**, 4.2	measured [105]
T_{out} [°C]	NR, F, HC, LV	0, **15**, 35	assumed
RH_{out} [-]	NR, F, HC, LV	30%, **50%**, 75%	assumed
HVAC Operation	NR, F, HC, LV(2)	**continuous**, reduced@night	assumed
	LV(1)	**continuous**	
V [m^3]	NR, F, HC, LV	510, **3310**, 6116	[102]
Airflows (λ_v, λ_r, λ_i)	NR, F, HC, LV(2)	40RA low, 40RA med, 40RA high, 65RA low, **65RA med**, 65RA high, 90RA low, 90RA med, 90RA high[b]	measured and [106]
	LV(1)	$\lambda_{ex,1}$ [h^{-1}]: 0.75, **1.5**, 3, 6; $\lambda_{i,1}$[h^{-1}]: **0.3**	assumed
RH_{in} [-][c]	NR, F, LV	**50%**	[101, 107]
	HC	30%, 40%, **50%**, 60%	
η_f [-]	F	20%, **60%**, 100%	assumed
	NR, LV, HC	**0%**	

[a] NR refers to the no-removal (reference) case, F to filtration, HC to humidity control. LV(1) refers to Zone 1 of the partitioned store modeled when investigating local ventilation, LV(2) refers to Zone 2.

[b] "40RA" stands for 40% recirculated air, "65RA" for 65% recirculated air, and "90RA" for 90% recirculated air; while "low", "med" and "high" qualify the overall level of flowrates. See Appendix C for exact definition of corresponding sets of λ_v, λ_r, λ_i.

[c] See Appendix C for calculation of corresponding α_{RH}.

Every combination of parameters was modeled, which amounted to 4,374 scenarios for the no removal case (NR), 13,122 scenarios for the filtration strategy (F), 17,486 scenarios for the humidity control strategy (HC), and 17,496 scenarios for the local ventilation strategy (LV). Results obtained with this model are compared to the three strictest health guidelines for formaldehyde: the California Office of Environmental Health Hazard Assessment chronic and 8-hour exposure reference exposure levels (OEHHA chREL = 9 $\mu g/m^3$), the National Institute for Occupational Safety and Health guideline for 8-hour exposures (NIOSH REL = 19.6 $\mu g/m^3$), and the minimum standard recommended in a compliance alternative path of the Leadership in Energy & Environmental Design rating system (LEED EQpc68 = 33 $\mu g/ m^3$).

The additional energy required to implement the three removal strategies is modeled following the same framework across all parameters shown in Table 4. Changes in energy consumption are calculated over a fictional month during which all parameters are assumed to remain constant. All quantities used for energy calculations are summarized in Appendix C.

A sensitivity analysis on modeled indoor formaldehyde concentrations was completed by varying the parameters presented in Table 4 from their base values (in bold) to their low and high values. In this part of the analysis only flowrates are un-coupled, and low and high values for $\lambda_{i,}$ $\lambda_{v,}$ and λ_r are defined separately (0.08 h^{-1} and 0.3 h^{-1}; 0.18 h^{-1} and 0.75 h^{-1}; 0.29 h^{-1} and 3.87 h^{-1}; respectively). Baselines are defined for every removal strategy. The filtration baseline consists of a filter efficiency of 60%. The humidity control baseline consists of a relative humidity of 50%. The local ventilation baseline consists of $\lambda_{ex,1}$ set at 1.5 h^{-1}.

3.3.4. Case study

To help in the comparison of filtration, humidity control, and local ventilation as removal strategies, the analysis is restricted to a case study. Filtration is modeled for a 60% efficient filter. Humidity control is modeled for an indoor relative humidity of 30%. Local ventilation is modeled with a Zone 1-exhaust flowrate of 6 h^{-1}. A traditional ventilation strategy (whole-building ventilation) where the make-up ventilation flowrate for the whole building is raised to 6 h^{-1} is also considered as a basis for comparison. Concentrations, energy, and energy costs are estimated in three buildings of low, medium and high volume. Each building is simulated in three cities: Austin, TX (hot and humid climate); Seattle, WA (cold and humid climate); and Phoenix, AZ (hot and dry climate). Calculations are run over a year using TMY3 hourly weather data files [108]. Outputs are first generated for a reference case with no removal, then for each of the removal strategies with parameters defined in Appendix C.

4. Results and discussion

4.1. FIELD CHARACTERIZATION OF VOLATILE ORGANIC COMPOUNDS IN FOURTEEN RETAIL STORES

4.1.1. Indoor concentrations and potential indoor sources

Formaldehyde was detected indoors during every sampling event at concentrations that ranged from 4.6 ± 0.3 ppb at HaP1 to 67 ± 8.3 ppb at OhT (Figure 3). Office and furniture stores OhT and FfT exhibited the highest formaldehyde concentrations; it is likely that much of the formaldehyde originated from the pressed-wood furniture, displays, and carpet used in these stores. Acetaldehyde was detected during 17 of the 24 test visits (Figure 3), including in all grocery stores, at concentrations ranging from 3.1 ± 1.2 ppb at FfP to 92 ± 13 ppb at grocery store GeT1. The highest concentrations were measured in stores where bread baking was observed during the sampling event. Higher than average concentrations of acetaldehyde were also observed during test visits to one home improvement store (HaP2) and one general merchandise store (MbP1), where acetaldehyde was probably emitted by building materials and consumer products (e.g. adhesives, coatings, lubricants, and inks) that are commonly found in home improvement and general merchandise stores [109, 110].

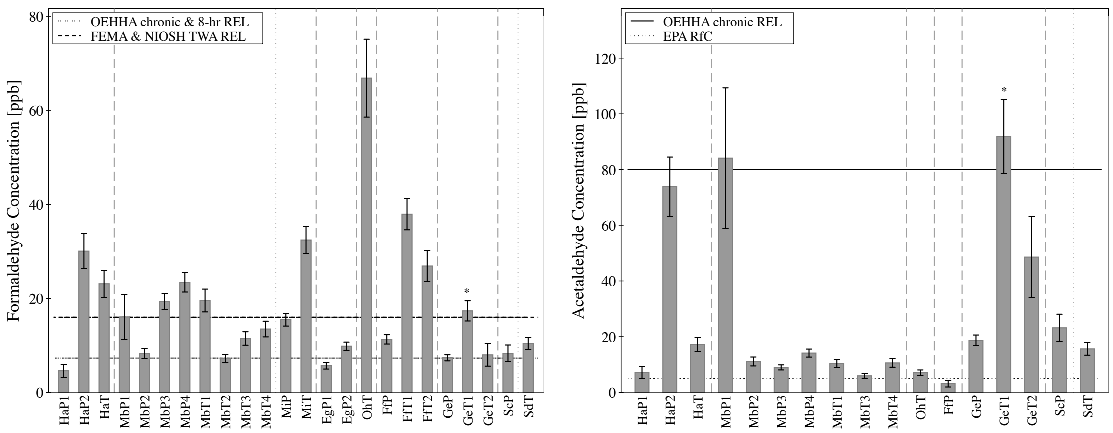

Figure 3: Formaldehyde and acetaldehyde concentrations (dashed lines separate test visits by retail type; dotted lines separate stores of a same retail type by brand). The error bars represent the uncertainty reported by the laboratory that analyzed the DNPH tubes. The star indicates that the laboratory reported an incidence of breakthrough in the DNPH tube collected at GeT1, which means that these concentrations should be interpreted as a lower bound on the actual concentrations.

Ninety-five compounds from VOC Categories 3 through 14 (Table 3) were detected indoors using Summa canister sampling. Indoor concentrations of categorized VOCs measured using Summa canisters are presented in Appendix A. Within each VOC category, concentrations vary by up to three orders of magnitude between stores, indicating that retail spaces are not easily generalized.

The most common VOC categories detected using Summa canisters were acetone and BTEXS. Acetone is a light solvent commonly used in consumer products and building materials [111, 112]. BTEX are common petroleum derivatives, whose ubiquity might be partially explained by the proximity of all sampling sites to parking lots, idling delivery trucks and major roadways. Styrene is a by-product of combustion, and also present in packaging and carpets [113, 114].

Home improvement stores had higher than average concentrations of terpenoids, non-halogenated alkanes, and “other” compounds. Terpenoids are commonly associated with fragrances and are found in cleaning products [115]. At HaP, α-pinene was the dominant terpenoid, making up 74 to 86% of total terpenoids. Pinene also naturally occurs in solid wood products [116]. Non-halogenated alkanes are common components of gasoline, sealants, greases and floor waxes [111, 117, 118].

High levels of ethanol were observed in mid-size grocery stores, with concentrations up to 2.6 ppm, and to a lesser extent in some general merchandise stores that had grocery sections. In the grocery stores investigated, baking and cooking took place before and/or during the sampling event. Ethanol was likely emitted by the preparation of dough and baking, and to a lesser extent from soaps and detergents, and ripening fruits [119-122].

The specific activity occurring in the store, such as baking or cleaning, seems to have a larger impact on VOC speciation, than retail store type. The variability in VOC concentrations at individual stores over the course of a year was investigated in Appendix A.

4.1.2. Contribution of outdoor sources

Sorbent tube samples were simultaneously collected indoors and outdoors at a subset of fourteen test visits to investigate VOCs from Categories 3 through 14 (Table 2). A total of 181 compounds were detected. Ninety-three compounds were detected exclusively indoors, suggesting those compounds originated from indoor sources. Related compounds include mainly non-halogenated alkanes, as well as benzene derivatives. Only thirty-two compounds were detected exclusively outdoors, suggesting those compounds originated from outdoor sources. Their concentrations were below 1 ppb 84% of the time. The relative importance of indoor and outdoor sources with respect to indoor concentrations was more intricate for the remaining fifty-six compounds. Overall, results detailed in Appendix A suggested that indoor sources were the main contributors to indoor concentrations for not all, but a majority of contaminants encountered in the retail stores studied.

4.1.3. Temporal profiles of total volatile organic compound (TVOC)

The temporal profiles of TVOC for three selected stores are displayed in Figure 4. During the three-day period presented here, the monitors remained at a fixed location in the stores.

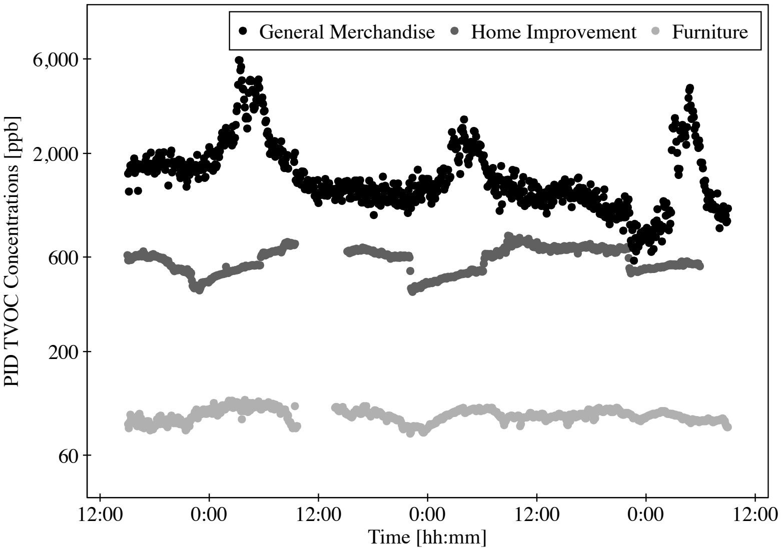

Figure 4: Temporal variations of TVOC concentrations monitored by the PID for selected stores over the course of three non-concurrent days. On the abscissa, 12:00 refers to noon and 0:00 to midnight. Note that the concentrations are displayed on a logarithmic scale. Data acquisition was momentarily interrupted by a power outage in the home improvement store, and a logging error in the furniture store.

TVOC concentrations at the furniture store (FfT2) remained relatively low and constant over time, ranging from 77 ppb to 114 ppb, with a coefficient of variation of 7% (Figure 5). This finding may be explained by the absence of VOC-generating activities in the store, such as cleaning and cooking, and an absence of fragranced products. At the home improvement store (HaP2), TVOC concentrations ranged from 400 ppb to 769 ppb, with a mean (SD) of 581 (83) ppb. The highest concentrations were obtained in the middle of the day. The highest TVOC concentrations and the widest temporal variations were observed at a general merchandise store (MbP4). The temporal profile shows a cyclical pattern over the three days displayed. The regularity of the pattern suggests either a constant source or a change in ventilation operation or a combination of these two factors. This store conducted their cleaning activities overnight, which may be a contributor to increased VOC concentrations and generally reduced their ventilation air flow rate during unoccupied periods. These factors suggest the potential for occupational exposure during overnight cleaning and stocking activities.

Although the PID provides relevant information on the daily variation of the TVOC concentration, caution should be used because the instrument did not provide accurate results when compared to Summa canister (CAN) results. A linear regression indicates that the PID TVOC concentration is significantly but poorly correlated ($p=0.0021$, $R^2=0.39$, coefficient=0.2) with the CAN TVOC concentration. 34% of PID results are within ±50% of CAN results, but all PID results lay within ±100% of CAN results. A possible explanation for this dispersion is the choice of isobutylene as the calibration gas. The molecular structure of isobutylene is very different compared to the observed compounds that had the highest concentrations, such as ethanol or isopropanol. Using a dissimilar calibration gas may have generated a calibration curve that under-estimated the concentrations of these compounds. In order to account for that difference, mixture correction factors can be applied to the PID value. Corrected PID TVOC concentrations are 1.2 to 8.8 times higher after correction to the air mixture compared to Summa canister results. The correlation between corrected-to-CAN PID TVOC concentrations and CAN TVOC concentrations is still significant, but poorer ($p=0.0039$, $R^2=0.35$). Consistent with higher corrected PID TVOC concentrations, a linear regression gives a coefficient higher than one. A minority of high concentrations (>1.5 ppm by either technique) found at one brand of grocery stores and one brand of general merchandise stores strongly influence this fit. Limitations associated with the calculation of mixture correction factors are detailed in Appendix B.

Based on our small sample, it does not appear that generic mixture correction factor could be used to adjust PID TVOC concentrations measured in these retail stores. Therefore, quantitative results from a PID may only be accurate if the characterization of the air mixture sampled is either known a priori to calibrate the instrument accordingly, or estimated simultaneously by speciated VOC techniques to correct the PID results.

4.1.4. Comparison with other indoor environments

Categorized VOC concentrations observed in this investigation were compared to those observed in the Relationships of Indoor, Outdoor, and Personal Air (RIOPA) study that surveyed 100 residences in each of three American cities [105], and the Building Assessment Survey and Evaluation (BASE) study that surveyed 100 office buildings across the U.S. [123]. Overall, categorized VOC concentrations observed in this investigation were similar to, or slightly lower than, concentrations typically observed in offices and residences for the BASE and the RIOPA studies, respectively. Average formaldehyde concentrations across all test visits in the current investigation (18.1 ± 13.8 ppb) were significantly higher (t-test, $p=0.05$) than concentrations observed in offices (13 ± 7 ppb in the BASE study), but not significantly different ($p=0.83$) from concentrations in residences (21 ± 11 ppb in the RIOPA study).

The data suggest that the vast majority of VOCs did not represent a serious health concern in the stores sampled. The main VOC sources identified were the merchandise sold (e.g., furniture) and store-based activities (e.g., food preparation, cleaning), each of which should be considered when improvements in indoor air quality are desired for a particular retail store.

4.2. DETERMINATION OF CONTAMINANTS OF CONCERN

To determine what contaminants may be of concern to exposed populations, measurements of volatile organic compounds are to be compared with concentration guidelines. This section summarizes an exploration of the impact of the selection of a VOC sampling method on such a decision in retail environments. The analysis is presented in more detail in Appendix B.

4.2.1. Time-integrated measurements of VOCs

Two hundred and thirty-nine distinct compounds were identified in the 23 paired Summa canister (CAN) and sorbent tube (SOR) samples. The resulting 1,112 concentrations are shown in Figure 5, where all CAN and SOR VOC concentrations are organized by the molecular weight (MW) of the corresponding compound.

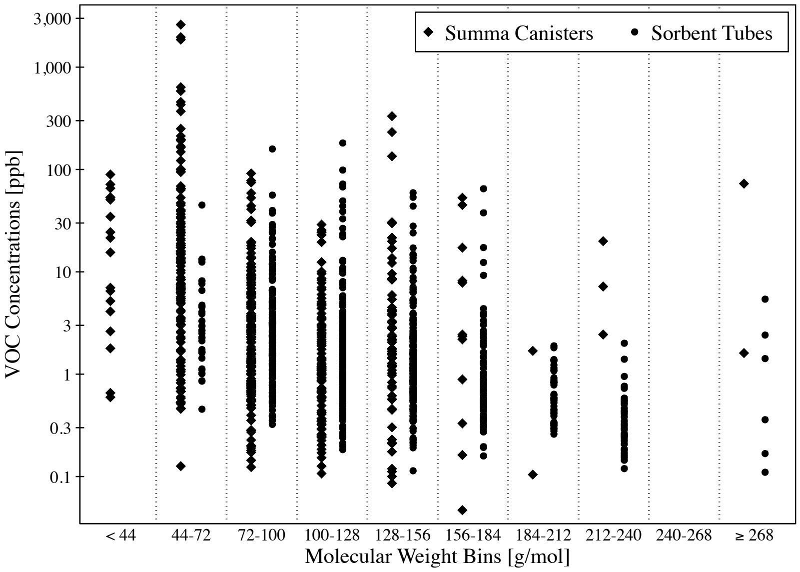

Figure 5: Comparison of all VOC concentrations measured simultaneously by Summa canisters and sorbent tubes across all test visits, displayed by molecular weight.

Summa canisters appear to prevail amongst low molecular weight compounds (< 72 g/mol). The first bin consisted of a single compound, acetonitrile (41 g/mol), which was only observed in CAN samples. The second bin (44≤MW<72 g/mol) was also dominated by Summa canisters, in terms of instances quantified (151 measurements vs. 35 for sorbent tubes), diversity of VOCs identified (15 compounds vs. 5 for sorbent tubes), and range of concentrations measured (4 orders of magnitude covered vs. 2 for sorbent tubes). The highest VOC concentration observed was for ethanol, which was measured at 2.6 ppm in the Summa canister sample, but was found to be only 8.1 ppb in the sorbent tube sample. These findings are consistent with the physical properties of the sorbent used in this investigation. Tenax GR is a relatively low surface area sorbent and is not adapted to collect compounds with fewer than four carbon atoms and relatively high vapor pressures [124]. The following three bins ($72 \leq MW < 156$ g/mol) hold the most measurements and compounds, for both techniques. Sorbent tubes introduced more diversity as 149 individual VOCs were identified in SOR samples vs. 69 in CAN samples, and SOR concentrations appeared generally higher than CAN concentrations. Sorbent tubes dominated over the remaining five bins ($MW \geq 156$ g/mol), with the exception of one bin ($240 \leq MW < 268$ g/mol) that contained no compound. Three to 10 times as many compounds were identified per bin in SOR samples as were in CAN samples, for a total of 160 measurements for SOR samples vs. 19 for CAN samples. Sorbent tubes may be more suitable to sample for high molecular weight compounds since they allow for the deposition of particles onto which low vapor pressure compounds may have sorbed, whereas a filter prevents such particles from entering Summa canisters. Low vapor pressure compounds may also adhere to the walls of the canisters and are not thermally desorbed since canisters are not heated for analysis [125]. A more detailed analysis on speciated compounds can be found in Appendix B.

This comparison is influenced by the fact that all compounds in SOR samples were identified through a library search, while CAN analysis targeted 70 compounds and was complemented by a limited library search to identify up to the 20 largest non-target concentration peaks per sample. Therefore it is possible that other compounds were captured by the Summa canisters but did not appear in the analysis report. It should further be noted that there are compounds for which none of these sampling techniques are appropriate. For instance, neither CAN nor SOR samples captured acetaldehyde, which was found at concentrations exceeding the chronic OEHHA limit of 78 ppb in up to three DNPH samples (Figure 2).

These differences in compound identification and quantification amongst measurement techniques directly influence whether a VOC may be considered of concern in the space sampled.

Out of all compounds from VOC Categories 2 to 14 identified in the retail stores sampled, there were fifteen exceedances of either LEED EQpc68 or ASHRAE 62.1 guidelines (Table 5), four of which were observed in Summa canister (CAN) samples and fourteen in sorbent (SOR) samples (including four in both measurements). All compounds other than naphthalene were part of the CAN target list.

Table 5: Exceedances of VOC concentration limits referenced by LEED EQpc68 and ASHRAE 62.1 in SOR and CAN samples.

Compound	**C_{SOR} [ppb]**	**C_{CAN} [ppb]**	**LEED EQpc68**			**ASHRAE 62.1**		
			C_{ref} [ppb]	**Exc. in SOR**	**Exc. in CAN**	**C_{ref} [ppb]**	**Exc. in SOR**	**Exc. in CAN**
Benzene	8.3 ± 8.3	0.8 ± 0.2	18.8			3^a	X	
Toluene	158.5 ± 158.5	18 ± 5.4	79.6	X		79.6^b	X	
Xylenes	181.4 ± 140	22.9 ± 5.6	161.2	X		50^a	X	
Tetrachloroethene	64.8 ± 64.8	45 ± 13.5	5.2	X	X	5.2^b	X	X
Tetrachloroethene	4.4 ± 4.4	7.8 ± 2.3	5.2		X	5.2^b		X
Tetrachloroethene	17.3 ± 17.3	ND	5.2	X		5.2^b	X	
Naphthalene	1.1 ± 1.1	ND	1.7			0.7^a	X	
Naphthalene	2.2 ± 1.6	ND	1.7	X		0.7^a	X	
Naphthalene	2.3 ± 2.3	0.7 ± 0.2	1.7	X		0.7^a	X	X
Naphthalene	1.5 ± 1.5	ND	1.7			0.7^a	X	
Naphthalene	1.3 ± 1	ND	1.7			0.7^a	X	
Naphthalene	1.3 ± 0.9	ND	1.7			0.7^a	X	
Naphthalene	0.8 ± 0.2	0.2 ± 0.1	1.7			0.7^a	X	
Naphthalene	0.7 ± 0.7	ND	1.7			0.7^a	X	
Naphthalene	1.9 ± 1.9	1.6 ± 0.5	1.7	X		0.7^a	X	X

[a] ATSDR MRL Chronic.

[b] CA OEHHA REL Chronic.

Sorbent tubes samples were the only testing technique where benzene, toluene, and xylenes were measured at concentrations exceeding their exposure limit. There were three exceedances of both guidelines for tetrachloroethylene (PCE): one detected by both sampling techniques, one observed in a CAN sample only, and one in a SOR sample only. Naphthalene concentrations were measured above the LEED EQpc68 guideline by sorbent tubes alone three times. Out of the nine exceedances of the ASHRAE 62.1 guideline for naphthalene, the two sampling approaches agreed twice. The remaining seven exceedances were observed in SOR samples only. This finding may be partially explained by the fact that naphthalene was the only compound with concentrations measured above health guidelines in this investigation that was not part of the CAN target list. Therefore, naphthalene may have been captured by Summa canisters but not been reported because napthtalene concentrations were lower compared to the 20 largest peaks identified by a library search in these samples. There were no other exceedances of the OEHHA chronic RELs by VOCs in Categories 2 to 14 (Table 3).

Overall, more exceedances were observed in sorbent tube samples. Depending on the sampling technique chosen, the number of spaces with unacceptable levels of VOCs (excluding formaldehyde) varied from 3 to 10. This analysis illustrates the need to identify potential contaminants of concern in advance to select the appropriate sorbent to be used in SOR sampling [49, 124], and to create customized target lists for both CAN and SOR analysis. This would reduce the uncertainty on the identification and quantification of compounds for a more accurate comparison with health guidelines and therefore a more definitive determination of compounds of concern.

4.2.2. Formaldehyde: time-integrated vs. time-resolved

Parametric (paired t-test) and non-parametric (Wilcoxon signed rank sum test) tests performed on formaldehyde concentrations obtained by DNPH tubes and the FMM indicate that results from both techniques were not significantly different from each other ($p=0.108$ and $p=0.084$, respectively). Based on these findings, it appears that both methods could lead to similar assessments of indoor air quality in retail stores if FMM readings below 20 ppb are made available to all, depending on the reference concentration chosen.

This analysis, because it is based on average FMM results, fails to take advantage of the information given by the FMM on temporal and spatial variations of formaldehyde concentrations (Figure 6). For instance, formaldehyde concentrations shown in Figure 6 for the furniture store (FfT2) were consistently above the OEHHA chronic and occupational REL (7.3 ppb) and the NIOSH and FEMA chronic REL (16 ppb), as were the average FMM and the DNPH tube concentrations during the mobile sampling period. However, three FMM measurements also exceeded the acute (1-hour average) OEHHA REL (44.8 ppb). This exceedance was missed by the DNPH tubes because of the time of sampling selected. Conversely, for the general merchandise store (MbT4) in Figure 6, the DNPH sampling occurred during the time of maximum concentrations. DNPH and FMM formaldehyde concentrations exceeded the CA OEHHA chronic and 8-hour average during mobile sampling. However, continuous measurements of formaldehyde by the FMM indicate that the store was only in non-attainment 22% of the three days of sampling. This suggests both the importance of selecting sampling time and possible opportunities to adjust ventilation strategies when considering this contaminant.

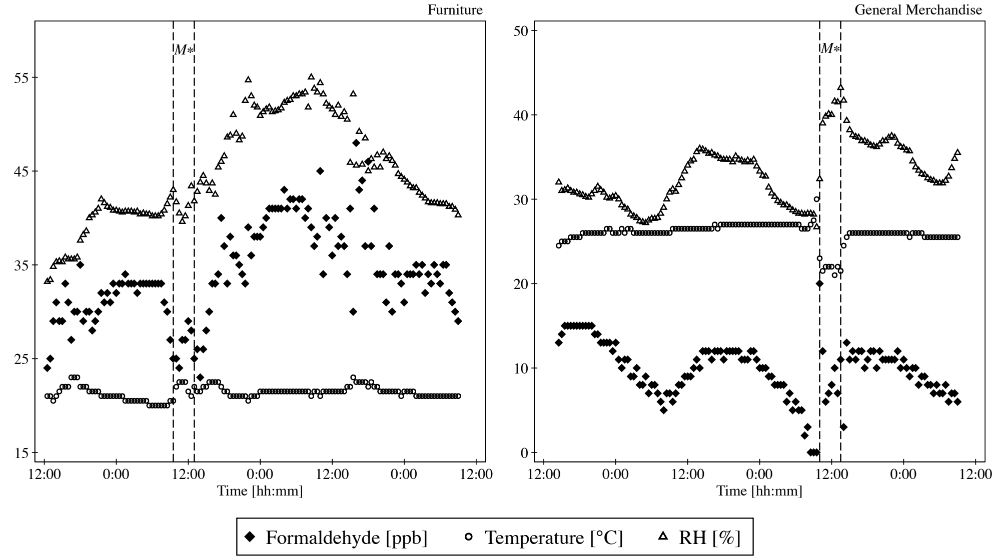

Figure 6: Temporal variations of formaldehyde concentrations, temperature and relative humidity (RH) monitored by the formaldehyde multimode monitors (FMM) for selected stores over the course of three days. On the abscissa, 12:00 refers to noon and 0:00 to midnight. Note that most of the monitoring occurred from a specific location on the sales floor (fixed sampling), but that the monitors were continuously moved through the sales floor for up to four hours (mobile sampling M*).

Variations of temperature and relative humidity measured by the FMM are also shown on Figure 6. At the furniture store, the temperature was relatively constant, ranging from 20ºC to 23ºC with a mean (SD) of 21.4 (0.7)ºC. However, the relative humidity (RH) varied widely, from 33% to 55%, in a pattern similar to the formaldehyde profile. The formaldehyde concentration at the general merchandise also followed RH variations closely. Since the instrument has been shown to operate consistently under RH conditions ranging from 40 to 80% [53, 129, 139], it is unlikely that water vapor acted as an artifact on the formaldehyde sensor. To prevent humidity from affecting the sensor, the FMM is manufactured with two light sources operating at different wavelengths. The similarity between formaldehyde concentration and RH trends observed in Figure 6 may rather be explained by the fact that pressed-wood products were likely the main sources of formaldehyde at both stores. Previous studies have shown that changes in temperature and relative humidity have significant impacts on formaldehyde emissions from various pressed-wood products [47-51]. At the furniture store, displays and building materials were made out of pressed wood, while the general merchandise store had a section offering pressed-wood furniture.

4.3. REDUCING FORMALDEHYDE CONCENTRATIONS IN RETAIL STORES

As evidenced in previous sections, formaldehyde is a ubiquitous contaminant that was repeatedly found at concentrations exceeding selected health guidelines in the retail stores sampled. Similarly, other studies [126] have found formaldehyde to be a major contaminant in the retail environment. When formaldehyde originates from merchandise offered by the store, removal of the source is not an option. This section summarizes the results of a screening evaluation of strategies to remove formaldehyde in retail buildings. Detailed results are presented in Appendix C.

4.3.1. Field investigation of the influence of ventilation

In the stores sampled in this investigation, there was no significant association between formaldehyde and air exchange rate across all sampling events. This finding does not suggest that ventilation has no impact on formaldehyde, but rather indicates that variation in building characteristics or source strength between stores must be also taken into account. To that intent, two sets of measurements were conducted at two stores, MiP and MiT, where ventilation rates were increased by 54% and 53%, respectively. The reduction in indoor formaldehyde (38% and 22% for MiP and MiT, respectively) was not directly proportional to the increase in air exchange rate. This may have been due to a counter-active effect of increasing the airflow or changes in environmental conditions, leading to higher formaldehyde emissions, as noted in residences by other researchers [127, 128]. These general findings support the use of ventilation as a removal strategy in retail stores. However, indoor concentrations of speciated VOCs and other contaminants should be checked while doing so, since indoor concentrations of outdoor contaminants are expected to increase with air exchange rate. Moreover, increased ventilation would likely be accompanied with significant increases in energy.

4.3.2. Modeled alternative control strategies

Exposure to formaldehyde may be mitigated through air cleaning (filtration), emission control (humidity control), and targeted dilution (local ventilation). All three options were considered in this modeling effort. Indoor formaldehyde concentrations varied widely across parameters, as represented by the box plots in Figure 7. The bottom of the box indicates the 25th percentile; the horizontal line indicates the median and the top of the box the 75th percentile of model simulations. The whiskers indicate the data ranging within 1.5 times the interquartile range of the 25th and 75th percentile. Filled circles are outliers. Concentrations are presented for various values of all parameters defining the removal strategies investigated. In the case of local ventilation, the output consists of two boxes that represent the formaldehyde concentrations in Zone 1 (light gray) and Zone 2 (dark gray).

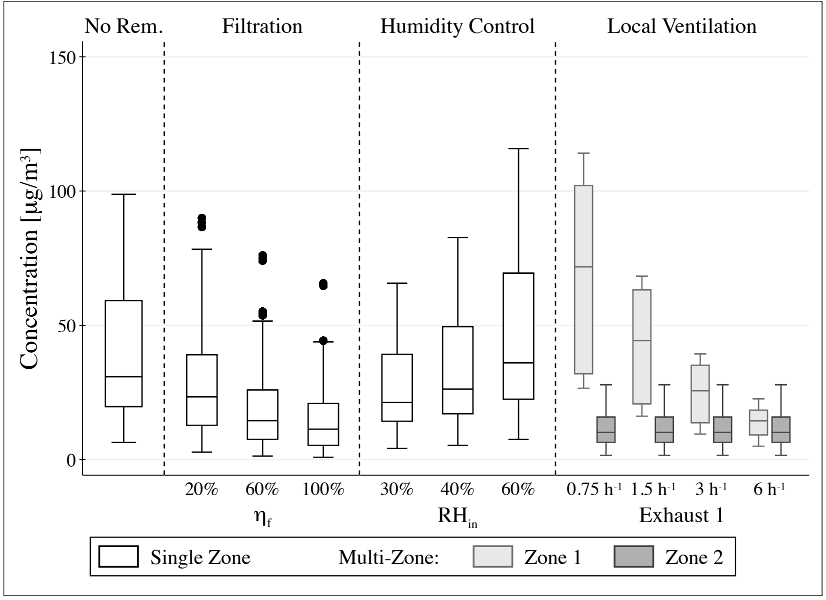

Figure 7: Impact of removal strategies and their defining parameters on modeled indoor formaldehyde concentrations. Parameter codes are defined in Table 5. “No Rem.” indicates formaldehyde concentrations modeled without any removal strategy.

The first (leftmost) box summarizes indoor concentrations when no removal (NR) is intended and all other parameters varying as a basis for comparison. NR concentrations ranged from 6.4 to 99 μg/m^3, with a median of 31 μg/m^3. These results are consistent with measured concentrations of formaldehyde sampled for an earlier phase of this work in fourteen U.S. retail stores, that ranged from 5.6 to 82 μg/m^3 (Figure 3), which confirms that the input parameters selected in this modeling study are representative of actual retail buildings. When filtration was introduced, the overall range of concentrations remained similar to the no removal case (0.9 – 90 μg/m^3), but the median was halved to 16 μg/m^3. A significant decrease in median concentration was observed with increasing filter efficiency, from 23 μg/m^3 for a low efficiency filter, to 15 μg/m^3 for a 60% efficient filter, and 11 μg/m^3 for a perfect (100% efficient) filter. The effectiveness of filtration is limited not only by single-pass removal efficiency, but also by the fraction of time that air recirculated through the filter (cycling frequency).

The humidity control (HC) case investigates the impact of relative humidity on indoor concentrations. When set to its high value (RH_{in}=60%), HC does not act as a removal strategy, but induces an increase in emission rate. For this reason, the maximum concentration obtained in this strategy was higher than concentrations obtained in the no removal scenario, reaching as high as 116 μg/m^3. Decreasing indoor RH below the base value (50%) led to slight decreases in median concentrations to 26 μg/m^3 (RH=40%) and 21 μg/m^3 (RH=30%).

Indoor concentrations obtained when modeling the use of local ventilation (LV) were overall the lowest for Zone 2. Concentrations in Zone 1 ranged from 5.0 to 114 μg/m^3, with a median of 28 μg/m^3, while concentrations in Zone 2 were relatively low in comparison, ranging from 1.6 to 27.9 μg/m^3, with a median of 10.2 μg/m^3. Increasing exhaust rates in Zone 1 led to consistent decreases on Zone 1 concentrations, but had no impact on Zone 2 concentrations. Although the median Zone 1 concentration was higher than the NR median concentration for low (72 μg/m^3) and base (44 μg/m^3) values of $\lambda_{ex,1}$, high and very high values of $\lambda_{ex,1}$ resulted in median concentrations lower in Zone 1 than in the NR case (26 μg/m^3 and 14 μg/m^3, respectively, vs. 31 μg/m^3).

The percentages of scenarios that generated concentrations lower than specific health guidelines for each level of every parameter are detailed in Appendix C. When filtration was introduced, formaldehyde concentrations under the LEED reference limit were guaranteed for all scenarios if the recirculation rate was set to its maximum (90RA) for all filter efficiencies. Partitioning the store ensured that formaldehyde never was a contaminant of concern in the major part of a store (Zone 2) according to the LEED limit, but only a very high $\lambda_{ex,1}$ guaranteed that stores would achieve the LEED level over all parameters.

Overall, local ventilation resulted in the most uniform improvements to indoor formaldehyde concentrations across building characteristics, while filtration used under specific conditions could lead to larger improvements. In comparison, the impact of humidity control appeared limited. To further investigate and separate the impact of individual parameters, a sensitivity analysis was conducted in Appendix C. It should be noted that if European health guidelines had been considered, formaldehyde control strategies would have been unnecessary in all scenarios considered here.

4.3.3. Energy and cost comparison

The monthly energy penalty due to the implementation of filtration, humidity control, and local ventilation was modeled across all parameters. Implementing filtration as a measure to reduce formaldehyde concentrations led to increases in monthly energy consumption ranging from 0.5 kWh to 3990 kWh, with a median of 53 kWh in all scenarios modeled. For the humidity control strategy, changes in relative humidity, indoors or outdoors, had a relatively small influence on the energy consumed. However, notable changes were observed for variations of outdoor temperature. The energy consumed was significantly higher at high T_{out} (4890 kWh) than at low (2563 kWh) or medium (1711 kWh) T_{out} because of the need for dehumidification and subsequent re-heating. Local ventilation resulted to the minimum and the maximum energy consumed, and was the only removal strategy considered in this study to have the potential to decrease the amount of energy used monthly. Detailed results can be found in Appendix C.

Since the model used to obtain these results is strongly influenced by the assumptions made when defining the removal strategies, these findings serve mostly to illustrate trends and to highlight promising strategies to remove formaldehyde in retail buildings. Moreover, the energy results should be considered as an upper bound on what actual energy consumption might be. The energy consumption could be decreased if, for instance, stores were equipped with more efficient equipment (humidifiers, dehumidifiers, fans [130]), or if heat from the exhaust airflows was recovered [131]. For the humidity control strategy, energy calculations also don't take into account the heat added to the airstream by the fan, although it has been shown to alter humidity control [132]. In the local ventilation removal strategy, we further neglected the energy penalty associated with the operation of an air curtain [133].

To illustrate the tradeoffs of formaldehyde removal, energy consumption and energy costs for each removal strategy in a more realistic setting, three buildings (low, medium and high volume) were modeled over a year for three cities: Austin, TX; Seattle, WA; and Phoenix, AZ. Key results for the medium-sized building are presented here.

Table 6 shows the decreases in concentrations (ΔC) and increases in annual energy consumption (ΔE) and cost (ΔEC) relative to the base case following the implementation of filtration, humidity control, and local ventilation for the medium-sized store in the three cities. A simple increase in air exchange rate for the entire store, referred to as "whole-building ventilation" here, was also modeled as a basis to assess the performance of the three removal strategies investigated in this study.

Table 6: Predicted performance, annual energy consumption and cost following the implementation of three alternative formaldehyde removal strategies in a medium retail building in three U.S. cities, as compared to the use of whole-building ventilation (in italics).

Removal Strategy	**ΔC**	**Austin**			**Seattle**			**Phoenix**		
	[µg/m^3]	**ΔE [kWh/year]**	**ΔEC [\$/year]**	**R [\$/(µg/m^3)/year]**	**ΔE [kWh/year]**	**ΔEC [\$/year]**	**R [\$/(µg/m^3)/year]**	**ΔE [kWh/year]**	**ΔEC [\$/year]**	**R [\$/(µg/m^3)/year]**
Filtration	32[a]	2501	250	7.8	2501	250	7.8	2501	250	7.8
Humidity control	13	78 990	2199	166	51 895	1224	92	44 436	1072	81
Local ventilation	26[a]	41 819	923	36	46 389	1391	54	103 580	1006	39
Whole-building ventilation	*18*	*172 519*	*4961*	*282*	*192 808*	*7401*	*421*	*435 565*	*4333*	*247*

[a] The formaldehyde concentration reached met the NIOSH REL.

Whole-building ventilation is the removal strategy most commonly recommended to reduce exposure to indoor pollutants such as formaldehyde [8]. In the case study modeled here, whole-building ventilation led to a decrease in formaldehyde concentration close to half that caused by the use of filtration, but was seventeen to thirty times as expensive in terms of annual energy cost. Not only was whole-building ventilation the most expensive and energy-intensive removal strategy across cities, it was amongst the most cost-intensive solutions with humidity control. Both strategies had annual costs per unit of formaldehyde removed one order of magnitude higher than filtration or local ventilation.

Local ventilation and filtration caused formaldehyde concentrations to drop under the NIOSH exposure limit. In Phoenix, local ventilation was associated with a larger energy penalty than humidity control and filtration. However, local ventilation was the second least cost-intensive solution in all cities. Filtration was the strategy with the cheapest yearly operational energy costs ($250 USD across cities), and was the most cost-effective strategy with a mere \$7.8/(µg/m^3)/year. However, electricity costs were modeled here as a fixed rate, when part of the price of electricity for most commercial buildings is based off peak demand. Since local ventilation was amongst the most energy-intensive strategies in this case study, and the energy associated with local ventilation in this investigation is solely due to additional conditioning, the energy cost of local ventilation may actually be higher than predicted here in a climate that would require mostly cooling or dehumidifying in the middle of the day. Additional limitations associated with this analysis are detailed in Appendix C.

In addition, it should be noted that the metric used in this analysis only takes into consideration energy costs, and different conclusions may have been reached if capital costs were included. In the local ventilation strategy, potentially significant costs could be associated with the purchase and use of an appropriate air curtain to separate the two zones in the store. The filtration strategy would likely appear considerably more cost-intensive if filter acquisition and maintenance costs were included in the analysis. Little to no information is available regarding the price and frequency of replacement of formaldehyde filters. Considering the reluctance of retail stores to upgrade from MERV 8 filters to reduce $PM_{2.5}$ contamination [104], it seems likely that such costs would restrain the adoption of formaldehyde filtration in retail stores. A possible alternative would be a localized approach to filtration, where formaldehyde filters would be used only in the rooftop units servicing areas of the stores with major sources of formaldehyde.

5. Integration and broader impacts

The broad purpose of this research was to investigate volatile organic compounds of concern in the retail environment. The field sampling in fourteen retail stores conducted in phase 1 yielded VOC concentrations and ventilation parameters that were used as inputs in phases 2, 3 and 4. Disparities within the sorbent tube results used in phase 2 to calculate indoor-to-outdoor ratios and the Summa canister results used to explore the influence of store type, ventilation and seasonality on VOC concentrations in phase 2 were analyzed in phase 3. Results of phase 3 also presented available technologies for time-resolved measurements of formaldehyde. This finding, associated with the high emission rates for formaldehyde found for a majority of stores in phase 2, motivated the need to investigate formaldehyde removal strategies in phase 4.

The framework developed in phase 4 to evaluate the impact of implementing various removal strategies on formaldehyde concentrations and energy consumption in the U.S. retail stock could be used to investigate removal of other VOCs of potential concern in retail stores, particularly by filtration and local ventilation. For instance, examination of the dataset in phase 2 revealed that even though the vast majority of VOCs were present at relatively low concentrations in retail stores, occasionally high concentrations could be reached because of the store activity: cleaning appeared to cause high concentrations of terpenoids, and baking was suspected to raise acetaldehyde concentrations above selected guidelines, as well as ethanol. Envisioning solutions to control for these activity-driven VOC concentration peaks prompts the need for time-resolved VOC measurements. As evidenced in phase 3, a photoionization detector (PID) has the potential to be used to that intent if the device is calibrated or corrected to the specific targeted compounds.

Findings of all phases of this dissertation have contributed to investigate the trade-off between energy and indoor air quality. Previous studies have investigated how decreasing ventilation to reduce energy costs could negatively impact indoor air quality [92]. Conversely, others have modeled how increased ventilation could improve indoor air quality but simultaneously increase energy consumption. Recently, researchers have been working towards integrating indoor air quality considerations into the optimization of HVAC system [134]. Phase 2 of this research has demonstrated that formaldehyde should be a major component of such efforts in retail stores, as it has been in residences [91, 135]. The connection between energy use and formaldehyde concentrations was made indirectly by Ng et al. [94] who concluded from a modeling study that reduced formaldehyde emissions would allow for reduced ventilation rates, and therefore energy savings. Such reductions in emissions can be forced through regulations on formaldehyde emissions, such as the one instigated by the California Air Resources Board [136]. In phase 4 of this research, we explored if changes in relative humidity could also lead to significant reductions in formaldehyde emissions, but modeled results were not promising. Other researchers have started to investigate dynamic strategies to optimize HVAC energy and occupant comfort [134, 137]. Since phase 3 of this dissertation and others [138] have shown that there were reliable real-time devices to monitor formaldehyde concentrations, future research could explore the possibility of a dynamic control strategy that would rely on formaldehyde. However, slight differences in measured concentrations due to the selection of a measurement technique, as observed in phase 3, could then lead to situations where contaminants are left to accumulate in the space and reach unacceptable levels, or where the HVAC system operates when the quality of the air is already satisfying, therefore wasting energy.

As we slowly move away from prescribed ventilation rates [8] and other proxy approaches towards performance-based approaches to an acceptable indoor air quality [8, 134], information is needed on actual buildings and the composition of their air mixture. This dissertation takes part in this effort by characterizing VOC concentrations in fourteen U.S. retail stores, and evaluating alternative strategies for low-energy and healthy buildings.

6. Conclusions

The main objective of this dissertation was to improve existing knowledge related to exposure and control of volatile organic compounds in the retail environment, with the intent of balancing the need for an acceptable indoor air quality and the prospects of energy savings.

Measurements were made in fourteen retail stores in Texas and Pennsylvania, with six stores sampled multiple times, resulting in 24 test visits. Time-integrated measurements of volatile organic compounds were made using Summa canisters, Tenax-GR sorbent tubes, and 2,4-dinitrophenylhydrazine (DNPH) tubes. Time-resolved measurements were collected using photoionization detectors (PID) and colorimetric formaldehyde monitors (FMM). This work offered a better understanding of the state of VOCs in the retail sector, and demonstrated the impact of the instrumentation chosen on the identification and quantification of VOCs. Major conclusions from this effort include:

- The vast majority of VOCs are present in retail stores at low concentrations, but episodic activities such as cooking and cleaning can lead to relatively high indoor concentrations for ethanol, acetaldehyde, and terpenoids.
- Samples collected using Tenax GR-sorbent tubes indicated more possible exceedances of health guidelines compared to Summa canister samples, all of which were observed in general merchandise and home improvement stores.
- PID TVOC concentrations were not directly correlated with Summa canisters results even after correction for differential response to different VOCs. No standard mixture correction factor was found across store type. More agreeable results can only be expected if the PID is targeted to measure a subset of compounds for which the instrument is specifically calibrated.
- Formaldehyde monitors (FMM) results were strongly correlated with DNPH tube results.

This dissertation contributes new concentration and whole-building emission data to the literature, notably for future occupational exposure analysis in retail stores. This work emphasized the need to identify potential contaminants of concern before selecting the proper collection and analysis technique. Findings from this investigation also facilitate the development of precise guidelines on how to monitor air contaminants in retail environments, and inform building operators on the appropriate method to use to inspect the indoor air quality at locations and times of concern. Promising characteristics of the FMM were highlighted, supporting its further consideration as an indicator to control ventilation and/or environmental parameters in retail stores.

Another important finding of this field investigation was that formaldehyde was the most important VOC of concern in retail stores. All 14 stores sampled exceeded the most conservative health guideline for formaldehyde (OEHHA TWA REL= 7.3 ppb) during at least one sampling event. This finding motivated a modeling effort exploring strategies to reduce exposure to formaldehyde in retail buildings with a minimal energy penalty. In this modeling study, the viability of filtration, humidity control and local ventilation as formaldehyde removal strategies were investigated. The impact of various parameters on indoor formaldehyde concentrations was investigated and weighed against their influence on building energy consumption. Major conclusions from this investigation include:

- Filtration used under specific conditions led to the greatest reductions in formaldehyde concentrations. Local ventilation caused the most uniform improvements to indoor formaldehyde concentrations across building characteristics. Humidity control appeared to have a very limited impact given constraints on its variation for purposes of occupant comfort.

- Local ventilation was the only removal strategy investigated in this modeling effort to show the potential to decrease energy consumption while maintaining formaldehyde concentrations under the LEED reference limit.
- A case study for small, medium, and large retail buildings in three U.S. cities in different climate zones revealed that filtration was the least cost-intensive solution in all cities. Increased ventilation, when provided locally to areas of the store containing most formaldehyde sources, led to greater reductions in formaldehyde concentrations and cost four to five times less than ventilation raised uniformly for the whole store.

In the future, the framework developed can be used to assess and compare existing and emerging control strategies. Results from this dissertation provide guidelines to building designers looking to ally acceptable indoor air quality with energy efficiency, leading them to the most efficient control strategy for formaldehyde. Findings from this dissertation suggest that, ultimately, low-energy retail environments may require reduced formaldehyde emissions and air cleaning or localized ventilation to be healthier indoor environments.

Appendices

APPENDIX A: VOLATILE ORGANIC COMPOUNDS IN FOURTEEN U.S. RETAIL STORES.

Volatile organic compounds in fourteen U.S. retail stores.

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Abstract

Retail buildings have a potential for both short-term (customer) and long-term (occupational) exposure to indoor pollutants. However, little is known about VOC concentrations in the retail sector and influencing factors, such as ventilation, in-store activities, and store type. We measured VOC concentrations and ventilation rates in 14 retail stores in Texas and Pennsylvania. With the exception of formaldehyde and acetaldehyde, VOCs were present in retail stores at low concentrations well below health guidelines. Indoor formaldehyde concentrations ranged from 4.6 ppb to 67 ppb. The two mid-sized grocery stores in the sample had the highest levels of ethanol and acetaldehyde, with concentrations up to 2.6 ppm and 92 ppb, respectively, possibly due to the preparation of dough and baking activities. Indoor-to-outdoor concentration ratios indicated that indoor sources were the main contributors to indoor VOC concentrations for the majority of compounds. There was no strong correlation between ventilation and VOC concentrations across all stores. However, increasing the air exchange rates at two stores led to lower indoor VOC concentrations, suggesting that ventilation can be used to reduce concentrations for some specific stores.

Keywords: retail, volatile organic compounds, formaldehyde, acetaldehyde, indoor-to-outdoor ratio, ventilation.

Practical Implications

This study provides data from simultaneous measurements of air exchange rates and indoor and outdoor VOC concentrations for fourteen stores of various retail types. The data suggest that the vast majority of VOCs did not represent a serious health concern in the stores sampled. The main VOC sources identified were the merchandise sold (e.g. furniture) and store-based activities (e.g. food preparation, cleaning), each of which should be considered when improvements in indoor air quality are desired for a particular retail store.

Introduction

The retail sector has a potential for both short-term (customer) and long-term (occupational) exposure to indoor pollutants. Retail stores employ close to 10% of the U.S. labor force, and accommodate approximately 40% of the U.S. population who engage in shopping activities daily (U.S. Department of Labor, 2013a; U.S. Department of Labor, 2013b). Moreover, a multitude of sources of volatile organic compounds (VOCs) are common to the retail environment, including consumer goods, building materials, and cleaning and cooking activities (Wolkoff, 1995; Nazaroff and Weschler, 2004; Uhde and Salthammer, 2007). For the purposes of this analysis, organic compounds having an initial boiling point less than 250˚C are referred to as volatile organic compounds (VOCs) (U.S. EPA, 2014).

Health impacts associated with VOCs vary significantly between compounds. For example, benzene is a known human carcinogen (Dean, 1985; U.S. EPA, 2013a). Based on sufficient evidence in animals, the U.S. Environmental Protection Agency classifies formaldehyde as a probable human carcinogen, whereas the International Agency for Research on Cancer recognizes formaldehyde as a cause of cancer of the nasopharynx and leukaemia in humans (Feron et al., 1991; World Health Organization, 2006; U.S. EPA, 2013b). Many other VOCs are not considered a threat to human health at the concentrations typically observed in the indoor environment (Molhave, 2003), but can be respiratory, or eye, nose and throat irritants at elevated concentrations (Wolkoff et al., 2006; Nielsen et al., 2012).

Previous researchers have identified VOCs of potential concern in the retail environment, but little is known about the impact of store type or ventilation parameters on VOC concentrations. Previous research has focused on benzene, toluene, ethylbenzene, xylene (BTEX), and to a lesser extent styrene (BTEXS). Identified BTEXS sources include motor vehicle exhaust (Chao and Chan, 2001; Kim et al., 2001), newspaper ink (Lee and Hsu, 2007; Caselli et al., 2009), as well as building materials (Tang et al., 2005; Bruno et al., 2008). Reported concentrations of other VOCs in retail stores are surprisingly sparse. Halogenated compounds were found in a shopping mall in South China (Tang et al., 2005), mainly due to the use of chlorinated cleaning agents. Limonene, likely emitted by household cleaning products and scented consumer products, had the highest concentrations of all VOCs measured in two supermarkets studied by Bruno et al. (2008). Pressed wood products (Hotchi et al., 2006; Loh et al., 2006), and carpet (Wu et al., 2011) were identified as major sources of formaldehyde in retail stores.

At least four studies have explored the variation in VOC concentrations between types of retail stores (Tang et al., 2005; Loh et al., 2006; Eklund et al., 2008; Chan et al., 2012). Tang et al. (2005) and Eklund et al. (2008) observed spatial variability in BTEX concentrations within shopping malls in China and New Jersey, and evidence of cross-contamination amongst contiguous stores. In the Boston Exposure Assessment in Microenvironments (BEAM) study, toluene was the dominant VOC in multipurpose stores, formaldehyde in houseware and furniture stores, and acetaldehyde in grocery stores (Loh et al., 2006). Similar trends have been reported by

Chan et al. (2012) in two grocery stores and three furniture stores. Only three research teams have investigated the relationship between concentrations and ventilation rates. In a general merchandise store, Hotchi et al. (2006) observed increases in VOC concentrations ranging from 15% to 170% when decreasing ventilation rates by 30%. Grimsrud et al. (2011) investigated three general merchandise stores and suggested that ventilation rates could be lowered, while maintaining total volatile organic compound (TVOC as toluene measured using passive organic badges) and formaldehyde concentrations under reference levels recommended by ASHRAE Standard 62.1 (ASHRAE, 2010). However, Chan et al. (2012) found formaldehyde, acetaldehyde and acrolein concentrations exceeding their respective health guidelines in stores where air exchange rates complied with ASHRAE Standard 62.1.

For this paper, we monitored VOC concentrations, including formaldehyde and acetaldehyde, in fourteen retail stores. Volatile organic compounds with concentrations that exceed health guidelines, or levels typically found in common indoor environments were identified. The influences of store type, season and air exchange rate on indoor VOC concentrations were examined.

Methodology

The study was performed at fourteen retail stores in Pennsylvania and Texas, with six stores sampled two to four times over the course of a year, resulting in 24 test visits (Table 7). Stores varied in retail type, size and location. All stores but one (GeT) were standalone buildings, half of which were close to major roadways. Both furniture stores were two-story buildings. Two general merchandise stores, MiT and MiP, were selected for additional testing over two consecutive weeks. For the first week, the air exchange rate was set at about 50% higher than normal and returned to its normal condition during the second week. Samples were collected at both ventilation conditions in each store, but tests at the higher (not typical) ventilation rate are excluded from summary data.

Sampling and analysis. At each store, indoor and outdoor VOC concentrations, as well as the building air exchange rate, were measured simultaneously for a four-hour period, typically during the middle of the day. Indoor VOC samples were collected using a shopping cart or basket that was continuously pushed or carried through the retail space. Outdoor samples were typically collected on the roof of the retail space. In the event of rain, which occurred for two of the 24 test visits, outdoor samples were collected in protected spaces around the site. Three methods were used to collect VOCs: DNPH tubes, Summa canisters, and sorbent tubes. All techniques are described below.

Formaldehyde and acetaldehyde were collected and analyzed using the methods and procedures described in U.S. EPA Compendium Method TO-11A (1999a). Sorbent tubes packed with 2,4-dinitrophenylhydrazine (DNPH) were analyzed by two NELAP accredited laboratories. These two laboratories reported detection limits for acetaldehyde and formaldehyde of 100 ng and 500 ng, respectively. One laboratory reported uncertainties of ± 30% for both aldehydes, while the second reported uncertainties of ± 12.4% for formaldehyde and ± 14.4% for acetaldehyde. The second laboratory reported an incidence of breakthrough in the DNPH tube collected at test GeT1, suggesting that the concentrations reported for that test should be interpreted as a lower bound for the actual concentration. The DNPH tubes were successfully collected indoors during all sampling events, including 13 sets of duplicates, and were collected outdoors for two test visits.

Summa canister samples (1 L, 1.4 L or 6 L) were collected and analyzed according to U.S. EPA Compendium Method TO-15 (1999b). Two NELAP accredited laboratories conducted the analysis. Both laboratories maintained a target list of 74 VOCs, quantified with a reported ± 30% uncertainty. Compounds that were not on the target list were identified using a library compound search, and compared to the nearest internal standard for quantification with a ± 100% uncertainty. The analytical detection limit was generally 0.5 ppb. Indoor Summa canister samples were successfully collected at all test visits, as well as five sets of duplicates. Outdoor samples using Summa canisters were collected during three sampling events.

Sorbent tube samples were also collected using a modified version of the U.S. EPA Compendium Method TO-17 (1999c). The air sampling system consisted of a calibrated air pump (Buck VSS), vinyl tubing, a low flow adapter and a glass sorbent tube filled with at least 0.11 mg of Tenax GR. The nominal volumetric flow rate was 25 mL/min, producing sample volumes of 6.0 L.

Analysis of the sorbent tubes was accomplished in-house using a Hewlett-Packard (HP) gas chromatograph (GC) model number 5890 II outfitted with a HP 5971 mass selective detector (MS). The GC was outfitted with a 30-meter long RXi-624 Sil Ms column (Restek catalog number 13686) with 0.25 mm ID and a film thickness of 1.4 μm. The GC method included a 2-minute hold at 35 °C followed by an 8 °C/min temperature ramp to 75 °C. The temperature ramp was then increased to 20 °C/min to a final temperature of 280 °C. Samples were spiked with a known mass of an internal standard (4-bromofluorobenzene) and injected onto the column using an Optic II thermal desorption unit (TDU) manufactured by Atas. The TDU method employed an initial temperature of 50 °C followed by a 10 °C/s ramp to a final temperature 280 °C. The initial pressure for the carrier gas was 10 psi. Following a 2-minute hold at 10 psi, the carrier gas pressure was reduced to 7.5 psi. The carrier pressure was increased at a rate of 1 psi/min to a final pressure of 25 psi. All samples were analyzed using a split ratio of 3:1.

Individual VOCs with sample mass above 5 ng were statistically identified using a library compound search and compared to the internal standard for quantification assuming the response ratio of the compounds to the internal standard was equal to unity. However, since response ratios usually range from approximately 0.4 to 1.5, the uncertainty on VOC concentrations was assumed to be ± 100% (Katritzky et al., 1994).

Thirty indoor samples were successfully collected, including seven sets of duplicates. A total of 17 outdoor samples were also collected, three of which were at site MiT with artificially elevated air exchange rates. The quality assurance and quality control procedures for all VOC measurements are documented in Siegel et al. (2013).

Sampling for VOCs was completed simultaneously with a sulfur hexafluoride (SF_6) decay test to determine the air exchange rate in the space. Sulfur hexafluoride was released into the store by several field technicians emptying 1 to 5 L Tedlar bags filled with SF_6 throughout the sales floor over a 5- to 15-minute period. Over a 4-hour period, air samples were collected at nine to eighteen locations with 500 mL plastic syringes, and injected into 1 L Tedlar bags. Sample bags, trip blanks, and trip standard bags were analyzed using a Lagus Autotrac SF_6 analyzer. The measurement method is described in more detail in Siegel et al. (2013).

Data analysis. Across all sampling events, 288 VOCs were identified and quantified. To facilitate the analysis, VOCs were grouped into fourteen categories based on similarities in chemical structure and/or potential exposure characteristics (Table 8). Indoor VOC concentrations were averaged when replicate samples were collected.

The whole building emission rate (WBER) is the net amount of pollutant emitted per unit floor area per unit time. The whole building emission rate is derived from a time-averaged mass balance (Riley et al., 2002), under the following assumptions: (1) the space is well-mixed, (2) the penetration factor from outdoors to indoors of the contaminant is unity, and (3) losses by homogeneous and heterogeneous reactions are negligible when compared to removal by ventilation. Formaldehyde WBERs were calculated in accordance with Equation (1) using concentrations and air exchange rates measured during the sampling event:

$$WBER = \lambda \cdot \left(C_{in} - C_{out}\right) \cdot \frac{V}{A} \qquad (1)$$

where *WBER* is the formaldehyde whole building emission rate (μg/m^{2}h), λ is the air exchange rate (h^{-1}), C_{in} is the indoor concentration (μg/m^3), C_{out} is the outdoor concentration (μg/m^3), V is the volume of the store (m^3), and A is the retail floor area of the store (m^2). Since outdoor DNPH samples were not collected at all test visits, a range of formaldehyde WBERs was calculated by varying C_{out} between zero and the maximum outdoor formaldehyde concentration (3.4 ppb) measured in this study.

Results and Discussion

Indoor concentrations. Formaldehyde was detected indoors during every sampling event at concentrations that ranged from 4.6 ± 0.3 ppb at HaP1 to 67 ± 8.3 ppb at OhT (Figure 8). Office and furniture stores OhT and FfT exhibited the highest formaldehyde concentrations; it is likely that much of the formaldehyde originated from the pressed-wood furniture, displays, and carpet used in these stores. Acetaldehyde was detected during 17 of the 24 test visits (Figure 8), including in all grocery stores, at concentrations ranging from 3.1 ± 1.2 ppb at FfP to 92 ± 13 ppb at grocery store GeT1. The highest concentrations were measured in stores where bread baking was observed during the sampling event. Higher than average concentrations of acetaldehyde were also observed during test visits to one home improvement store (HaP2) and one general merchandise store (MbP1), where acetaldehyde was probably emitted by building materials and consumer products (e.g. adhesives, coatings, lubricants, and inks) that are commonly found in home improvement and general merchandise stores (Hodgson et al., 2002; Steinemann, 2009; Huang et al., 2011).

Ninety-five compounds from VOC Categories 3 through 14 (Table 8) were detected indoors using Summa canister sampling. Indoor concentrations of categorized VOCs measured using Summa canisters are presented in Table 9. Within each VOC category, concentrations vary by up to three orders of magnitude between stores, indicating that retail spaces are not easily generalized. The most common VOC categories detected using Summa canisters were acetone and BTEXS. Acetone is a light solvent commonly used in consumer products and building materials (Sack et al., 1992; Missia et al., 2010). It was observed at relatively high concentrations (122 – 370 ppb) at both of the home improvement stores. BTEX are common petroleum derivatives, whose ubiquity might be partially explained by the proximity of all sampling sites to parking lots, idling delivery trucks and major roadways. Styrene is a by-product of combustion, and also present in packaging and carpets (Hodgson et al., 1993; Vitrac and Leblanc, 2007).

Home improvement store HaP had relatively high concentrations of terpenoids and non-halogenated alkanes. Terpenoids are commonly associated with fragrances and are found in cleaning products (Singer et al., 2006). At HaP, α-pinene was the dominant terpenoid, making up 74 to 86% of total terpenoids. Pinene also naturally occurs in solid wood products (Jensen et al., 2001). Relative to other stores studied, total C_4-C_{10} carbonyls were also high at HaP. These compounds are often formed by oxidation of terpenoids and other unsatured organic compounds in air or on surfaces (Weschler, 2011). More than 60% of the C_4-C_{10} carbonyls observed at HaP consisted of hexanal and pentanal. Non-halogenated alkane concentrations were also relatively high at HaP. Related compounds are common components of gasoline, sealants, greases and floor waxes (Miksch et al., 1982; Tichenor, 1989; Sack et al., 1992). Numerous other compounds (VOC Category 14, Table 8) were observed at home improvement stores HaP and HaT. "Other" compounds observed at each store included methyl ester acetic acid (up to 41 ppb at HaT), tetrachloroethylene (up to 45 ppb at HaP1), carbonylsulfide (65 ppb at HaP2), and octamethylcyclotetrasiloxane (73 ppb at HaT).

High levels of ethanol were observed in mid-size grocery stores, with concentrations up to 2.6 ppm, and to a lesser extent in some general merchandise stores that had grocery sections. In the grocery stores investigated, baking and cooking took place before and/or during the sampling event. Ethanol was likely emitted by the preparation of dough and baking, and to a lesser extent from soaps and detergents, and ripening fruits (Wooley et al., 1990; Passant et al., 1993; Pesis et al., 2002; Kwon et al., 2008).

The lowest VOC concentrations measured by Summa canisters were found in all furniture stores. The absence of cooking and cleaning operations immediately before the mobile sampling event, and the absence of cleaning and fragrance products may have contributed to the low VOC concentrations observed. However, it should be noted that the furniture stores had relatively high formaldehyde concentrations. The remaining VOC categories show no obvious associations with store types.

An objective of this study was to investigate the variability in VOC concentrations at individual stores over the course of a year. When investigating the concentrations obtained at the same store across multiple visits, both formaldehyde and acetaldehyde concentrations exhibited large variations. The relative percent variance across that subsample averaged 44 ± 39 % and 76 ± 58 % for formaldehyde and acetaldehyde concentrations, respectively. The relative percent variance in air exchange rate averaged only 22 ± 22 %. This finding suggests that indoor activities and source strengths likely varied between visits. Considering VOCs from Categories 3 through 14 (Table 8), concentrations measured at general merchandise store MbP (test visits MbP1, MbP2, MbP3 and MbP4) mainly differed for ethanol, possibly indicating that baking activities that occurred in the store were not consistent during all sampling events. The general merchandise store in Texas (test visits MbT1, MbT2, MbT3, MbT4) had large variations in several VOC categories between visits, mainly ethanol and non-halogenated alkanes. At the electronics store (test visits EgP1 and EgP2), an elevated acetonitrile concentration was observed during the first visit but not during the second. Specific sources of acetonitrile at the site could not be identified, although there is a slim possibility of contamination by the DNPH tubes used for formaldehyde. At grocery store GeT (test visits GeT1 and GeT2), VOC concentrations varied considerably for ethanol and total terpenoids. The former was most likely generated by onsite baking activities, and the latter likely by cleaning activities witnessed when sampling occurred.

Comparison to other indoor environments. The VOC concentrations for each category defined in this study (Table 8) are consistent with VOC concentrations in retail environments previously reported in the literature, with a few exceptions. The stores sampled in this study exhibited, on average, higher concentrations of alkanes compared to those previously described in the literature (Chao and Chan, 2001; Hotchi et al., 2006; Bruno et al, 2008; Eklund et al., 2008; Caselli et al., 2009; Wu et al., 2011). This may be explained by the proximity of half the investigated stores to major roadways. The concentration of ethanol observed in this study is also higher than previously reported in the literature (Hotchi et al., 2006; Eklund et al., 2008), most likely as a result of baking activities in grocery and general merchandise stores.

Categorized VOC concentrations observed in this investigation were compared to those observed in the Relationships of Indoor, Outdoor, and Personal Air (RIOPA) study that surveyed 100 residences in each of three American cities (Weisel et al., 2005), and the Building Assessment Survey and Evaluation (BASE) study that surveyed 100 office buildings across the U.S. (Apte and Erdmann, 2002). Overall, categorized VOC concentrations observed in this investigation were similar to, or slightly lower than, concentrations typically observed in offices and residences for the BASE and the RIOPA studies, respectively. Average formaldehyde concentrations across all test visits in the current investigation (18.1 ± 13.8 ppb) were significantly higher (t-test, $p=0.05$) than concentrations observed in offices (13 ± 7 ppb in BASE study), but not significantly different ($p=0.83$) from concentrations in residences (21 ± 11 ppb in RIOPA study).

Comparison to health guidelines. Since there are no standards regulating indoor VOCs in non-industrial settings, selected VOC concentrations measured in this study are compared with occupational exposure limits recommended by various agencies. Of all contaminants identified in the retail stores sampled in this investigation only formaldehyde and acetaldehyde exceeded heath guidelines in some stores. Many organizations set exposure limits to indoor formaldehyde, and to a lesser extent to acetaldehyde. Table 10 lists the values of several relevant guidelines, with a focus on U.S. organizations. It should be noted that the aldehyde concentrations measured using DNPH are four-hour average concentrations, whereas the applicable guidelines use 15 minutes and 30 minutes (short-term or acute), eight hours (occupational) or one year (chronic).

The California Office of Environmental Health Hazard Assessment (CA OEHHA) prescribes the most conservative reference exposure level, set at 7.3 ppb (chronic and 8-hour average). Considering the uncertainty in the indoor concentrations, between 71% and 92% of the test visits in this study indicated exceedances of the OEHHA limit for formaldehyde (Figure 8). The time-weighted average recommended exposure limit (TWA REL) set by the National Institute for Occupational Safety and Health (NIOSH) and the Federal Emergency Management Agency (FEMA) for formaldehyde is 16 ppb. Formaldehyde concentrations exceeded this limit during half of all sampling events. Office supply store OhT was the only store to exceed the formaldehyde OEHHA acute reference concentration of 44.8 ppb. No store was found to exceed the 30-minute guideline set by the World Health Organization at 81.4 ppb to prevent sensory irritations and cancer effects (World Health Organization, 2010). For acetaldehyde, considering the uncertainty in the indoor concentrations, between one and three stores exceeded the chronic OEHHA limit of 78 ppb. All stores in which acetaldehyde was detected but FfP exceeded the inhalation reference concentration (RfC) for acetaldehyde set by the U.S. EPA at 5 ppb, although the RfC is defined as “an estimate with uncertainty spanning perhaps an order of magnitude” and assumes continuous inhalation exposure over a lifetime.

The National Institute for Occupational Safety and Health (NIOSH) publishes recommended exposure limits (RELs) for potential hazardous air contaminants in the workplace (CDC, 2007). The concentrations observed for individual VOCs in Categories 3 through 14 are well below their respective reference exposure limits (NIOSH RELs), suggesting no individual VOC in Categories 3 through 14 is a serious health concern for employees working in the stores sampled in this study. Benzene is the compound with the lowest TWA REL at 100 ppb. The maximum benzene concentration measured using Summa canisters was 0.78 ± 0.23 ppb at HaP1. The maximum VOC concentration observed in this study was 2.6 ± 0.8 ppm for ethanol at GeT1. Ethanol is a common indoor contaminant, for which the TWA REL is set at 1,000 ppm.

Outdoor concentrations and indoor-to-outdoor ratios. Outdoor formaldehyde and acetaldehyde samples were collected at test visits HaP1 and MbP2, where the formaldehyde outdoor concentrations were 3.4 ± 1.0 ppb (indoor-to-outdoor ratio = 1.4 ± 0.8) and 2.6 ± 0.3 ppb (indoor-to-outdoor ratio = 3.2 ± 0.8), respectively. Acetaldehyde was only detected outdoors at HaP1 with a concentration of 1.6 ± 0.5 ppb (indoor-to-outdoor ratio = 4.5 ± 1.9).

Sorbent tube samples were simultaneously collected indoors and outdoors at a subset of fourteen test visits to investigate VOCs from Categories 3 through 14 (Table 8). A total of 181 compounds were detected. Ninety-three compounds were detected exclusively indoors, suggesting those compounds originated from indoor sources. Related compounds include mainly non-halogenated alkanes, as well as benzene derivatives. Only thirty-two compounds were detected exclusively outdoors, suggesting those compounds originated from outdoor sources. Their concentrations were below 1 ppb 84% of the time. The relative importance of indoor and outdoor sources with respect to indoor concentrations was more intricate for the remaining fifty-six compounds. Figure 9 shows indoor and outdoor concentrations for a subset of these pollutants.

Over a majority of stores, outdoor sources of benzaldehyde and acetophenone appear to contribute significantly to indoor concentrations of these pollutants (Figure 9). Benzaldehyde is emitted by motor vehicle exhaust outdoors, and by fragranced products indoors (Namiesnik et al., 1992; Steinemann, 2009). It was present at relatively low concentrations both indoors and outdoors (< 2.5 ppb). Acetophenone concentrations followed a similar trend, at even lower concentrations (≤1.5 ppb). Acetophenone is found in emissions from vehicles, and is used in liquid waxes and as a flavoring agent (Knöppel and Schauenburg, 1989; Burdock, 2005).

For nonanal and undecane, indoor concentrations were likely dominated by the presence of indoor sources over a large majority of stores (Figure 9). Nonanal is a common by-product of indoor ozone chemistry (e.g., Poppendieck et al., 2007; Lamble et al., 2011; Cros et al., 2012). Nonanal was measured at low concentrations indoors (< 4 ppb), with an indoor-to-outdoor ratio higher than 2.0 at most visits, and was occasionally not detected outdoors. Undecane was detected only indoors for five test visits, and indoor-to-outdoor ratios were above 5.0 for most test visits. Undecane is common component of waxes, cleansers, adhesives, and buildings materials (Wallace et al., 1987). Furniture store FfT1 was the only test visit where indoor concentrations of all pollutants detected appeared to be dominated by the presence of indoor sources. Thirty-three pollutants were detected only indoors, and the remaining four compounds had indoor-to-outdoor ratios higher than 3.0.

Both indoor and, to a lesser extent, outdoor sources appear to contribute to indoor concentrations of toluene, xylene, ethylbenzene and hexanal (Figure 9). Toluene was present at relatively high concentrations indoors (median = 7.7 ppb), with indoor-to-outdoor ratios higher than 2.5 at 11 test visits but lower than 0.5 for two tests, suggesting the presence of both indoor and outdoor sources. Toluene is commonly emitted by gasoline and motor vehicle exhaust outdoors, and by inks and building materials indoors (Missia et al., 2010). Similarly, xylene is a standard component of household products such as paints and adhesives (Wallace et al., 1987), as well as gasoline, and exhibited the same behavior as toluene but at lower concentrations (median indoors = 5.0 ppb). Ethylbenzene is a common component of gasoline, and is also used indoors in household cleaners and polishes, as well as building materials (Sack et al., 1992; Missia et al., 2010). Hexanal results from incomplete combustion, and is commonly emitted indoors by air fresheners (Steinemann, 2009), or by oxidation reactions (Weschler, 2011).

Overall, the results suggested that indoor sources were the main contributors to indoor concentrations for not all, but a majority of contaminants encountered in the retail stores studied. Therefore, it seems appropriate to consider ventilation as a removal strategy (ASHRAE, 2010) for the VOCs considered herein and for locations with similar outdoor VOC concentrations.

Impact of ventilation. There were no significant associations between any speciated VOCs and air exchange rate across all sampling events, except for toluene (Spearman's rho=-0.7, p=0.0001). This finding further suggests the dominance of indoor sources of toluene. As examples, indoor concentrations of ethanol (measured using Summa canisters) and formaldehyde (measured using DNPH tubes) as a function of air exchange rate across all test visits are shown in Figure 10. The VOC uncertainty displayed is that reported by the laboratory conducting the analysis of the samples, and includes the variation between replicate samples where applicable. The calculation of the uncertainty in air exchange rates is described in Siegel et al. (2013). Such results do not indicate that ventilation has no impact on VOC concentrations, but rather that the variation in VOC source strengths across stores makes it difficult to find a relationship between ventilation rate and indoor concentrations in cross sectional studies. Additional factors, such as a potential dependence between store type and air exchange rate, may further confound the results.

This finding is limited by the structure of our dataset, which is based on a modest number of stores, with a small and inconsistent number of buildings within store types.

Whole-building emission rates (WBERs), presented in Figure 11, are an appropriate metric for comparison of formaldehyde source strengths per floor area. The box indicates the data calculated with outdoor formaldehyde concentrations ranging from 0 to 4.2 μg/m^3 (maximum outdoor concentration measured using DNPH tubes at home improvement store HaP1); the horizontal line indicates the mean WBER. To calculate these WBERs, stores were assumed to be well-mixed. Spatial variations in the stores were assessed by calculating the local age of air at each of the 9 to 18 SF_6 sampling locations for every test visit (Siegel et al., 2013). The coefficients of variation between locations at each store were generally small, suggesting that the well-mixed assumption seems to be reasonable for most buildings. Possible exceptions are the home improvement stores, and the Pennsylvania furniture store. Caution should be taken when interpreting the emission rates in these stores.

Formaldehyde WBERs exhibit the same variations as indoor concentrations. The highest WBER (205 - 217 μg/m^2.h) was seen at office supply store OhT that employed approximately one third of the retail floor space for the display and sale of office furniture, most of which was made from pressed-wood products.

To further isolate the impact of air exchange rate on indoor VOC concentrations and account for potentially confounding factors, such as variation in building characteristics, activity, or source strength, we conducted two sets of measurements at two stores, MiP and MiT, where ventilation rates were increased by 54% and 53%, respectively. The sum of VOC concentration (ΣVOC) was calculated at these stores by summing individual VOC concentrations measured using Summa canisters. The resulting reductions in ΣVOC concentrations of 60% and 56%, for stores MiP and MiT, respectively suggest a close to a one-to-one linear response of ΣVOC concentrations to changes in ventilation rates for both locations. Increasing the ventilation rate prevents indoor contaminants from accumulating and serves to dilute their concentrations. However, the reduction in indoor formaldehyde (38% and 22% for MiP and MiT, respectively) was not directly proportional to the increase in air exchange rate. This may have been due to a counter-active effect of increasing the airflow or changes in environmental conditions, leading to higher formaldehyde emissions, as noted by Hun et al. (2010). These general findings support the use of ventilation as a removal strategy in retail stores. However, indoor concentrations of speciated VOCs and other contaminants should be checked while doing so, since indoor concentrations of outdoor contaminants are expected to increase with air exchange rate.

Summary and Conclusions

Measurements were made in fourteen retail stores in Texas and Pennsylvania, with six stores sampled multiple times, resulting in 24 test visits. Summa canisters, sorbent tubes and DNPH tubes were used to collect samples of indoor and outdoor volatile organic compounds. The major conclusions from this effort include:

- Formaldehyde is the most important contaminant of concern in retail stores. In this study, all 14 stores exceeded the most conservative health guideline for formaldehyde (OEHHA TWA REL = 7.3 ppb) during at least one sampling event. Formaldehyde whole-building emission rates spanned two orders of magnitude amongst stores.
- The vast majority of VOCs are present in retail stores at low concentrations, but episodic activities such as cooking and cleaning can lead to relatively high indoor concentrations for ethanol, acetaldehyde, and terpenoids.
- Based on experiments in two stores, it appears that increased ventilation could reduce VOC concentrations in retail stores although the concentration decrease may not be proportional to the ventilation increase for some compounds.

To better understand the extent to which acceptable indoor air quality could be maintained through ventilation in retail stores, future studies would benefit from the collection of outdoor samples of targeted compounds, and greater control over HVAC systems.

Illustrations

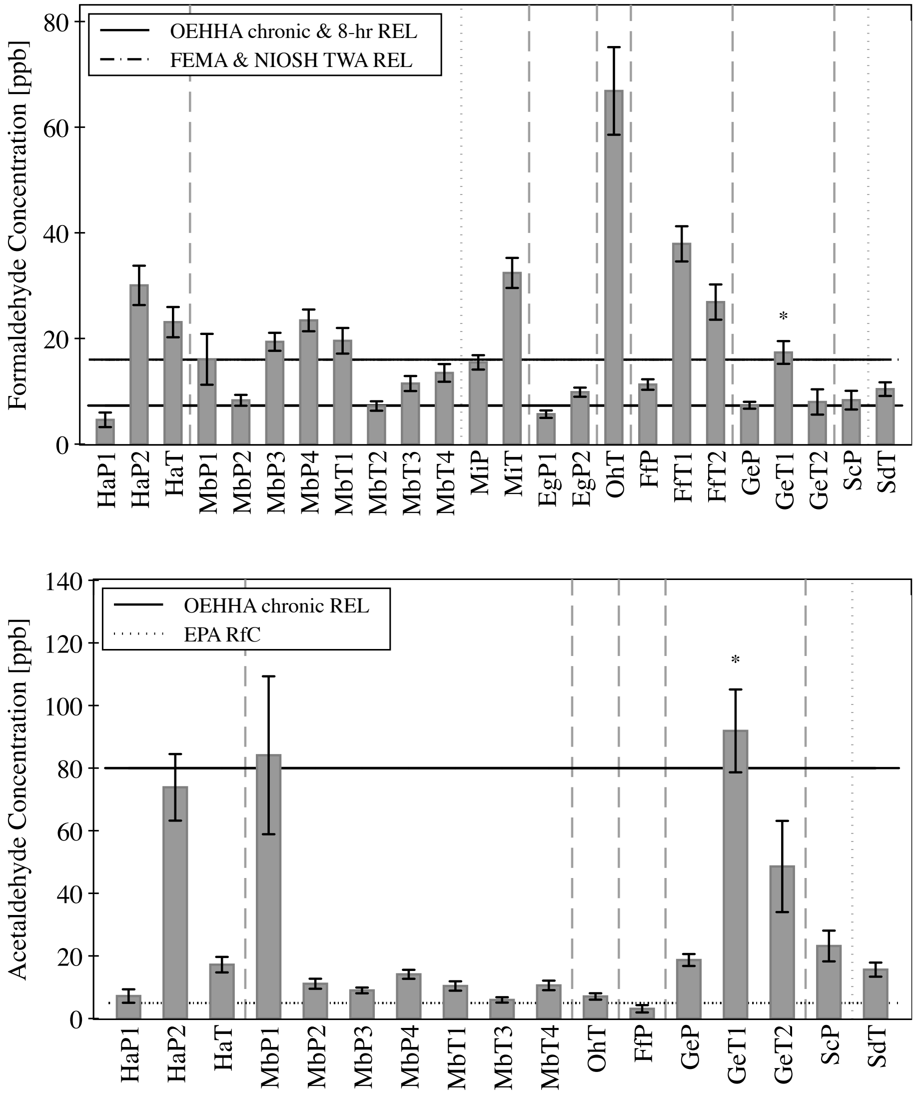

Figure 8: Formaldehyde and acetaldehyde indoor concentrations measured using DNPH tubes (dashed lines separate test visits by retail type; dotted lines separate stores of a same retail type by brand). The error bars represent the uncertainty reported by the laboratory that analyzed the DNPH tubes. The star indicates that the laboratory reported an incidence of breakthrough in the DNPH tube collected at GeT1, which means that these concentrations should be interpreted as a lower bound on the actual concentrations.

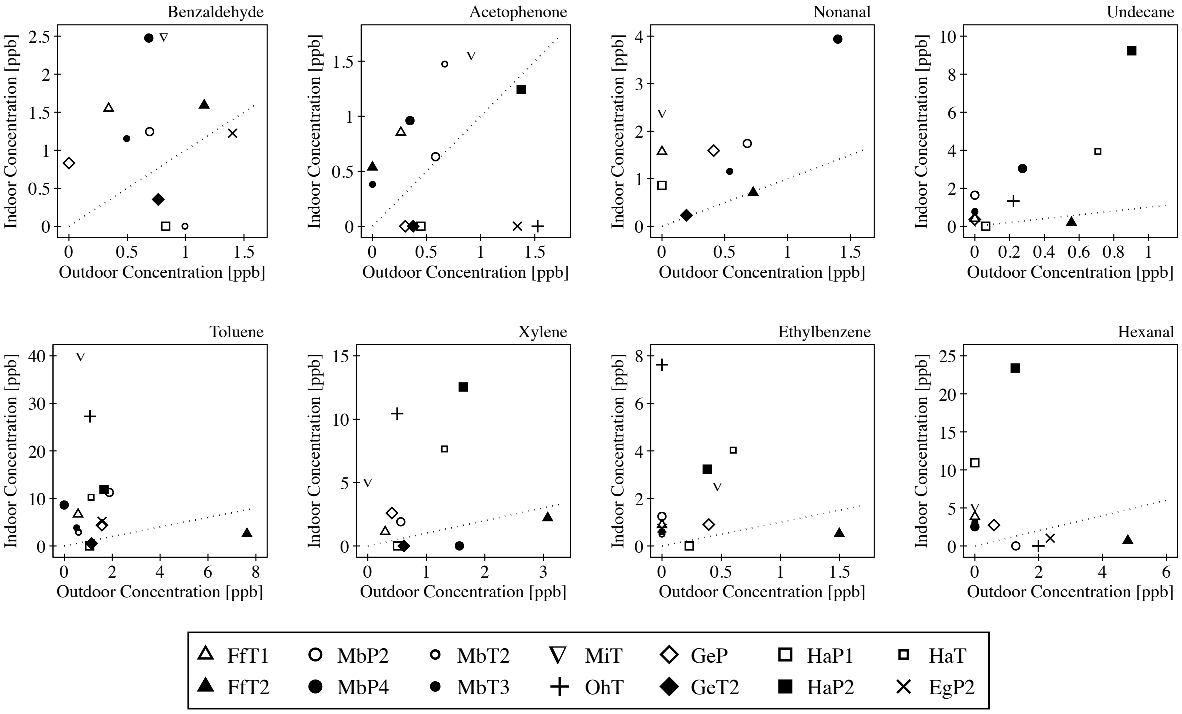

Figure 9: Indoor vs. outdoor concentrations measured using sorbent tubes for selected compounds with parity indicated with a dotted line. The relatively high indoor concentrations of undecane (38 ppb), toluene (159 ppb), xylene (181 ppb), and ethylbenzene (99 ppb) measured at HaT1 were excluded from the plots for clarity.

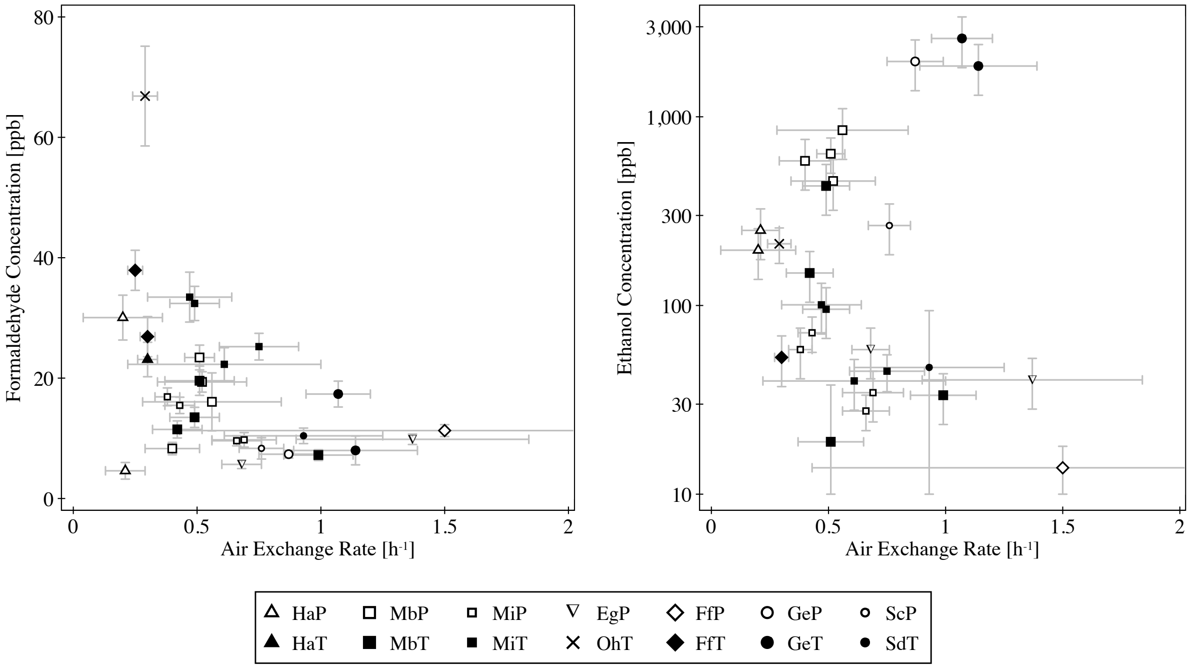

Figure 10: Indoor concentration as a function of air exchange rate for selected compounds (measured using DNPH tubes and Summa canisters, respectively).

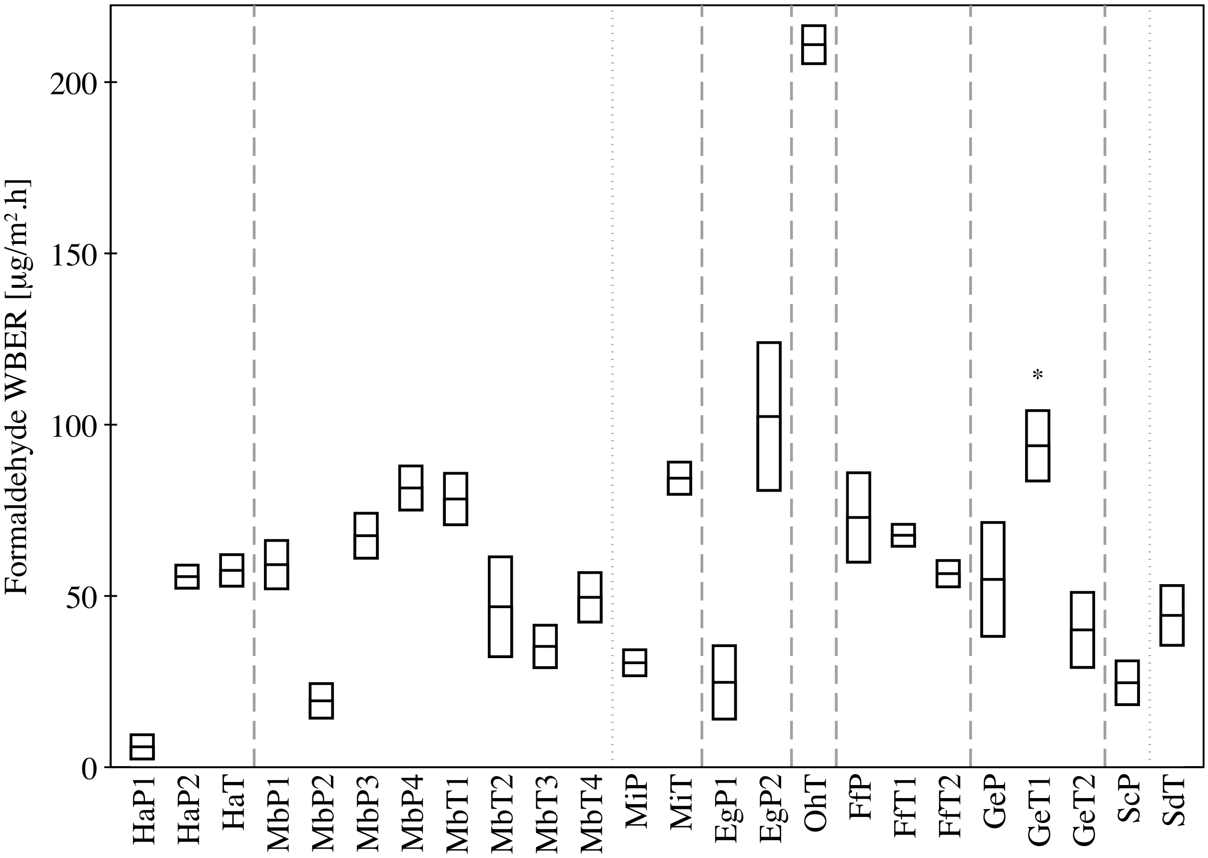

Figure 11: Formaldehyde whole building emission rates (dashed lines separate test visits by retail type; dotted lines separate stores of a same retail type by brand). The star indicates that the laboratory reported an incidence of breakthrough in the DNPH tube collected at GeT1, which means that these values should be interpreted as a lower bound on the actual whole building emission rates.

Tables

Table 7: Summary information about the retail stores sampled.

Store code[a]	Number of Test Visits[b]	Type	Location	Months Tested	Volume [m^3]
HaP	2	Home improvement	PA	May, Nov	93,400
HaT	1	Home improvement	TX	Jun	91,800
MbP	4	General merchandise	PA	Sep, Jan, May, Jul	99,500
MbT	4	General merchandise	TX	Jul, Oct, Feb, Apr	61,200
MiP	1[c]	General merchandise	PA	Apr	66,800
MiT	1[c]	General merchandise	TX	Apr	55,200
EgP	2	Electronics	PA	Feb, Jun	20,300
OhT	1	Office supply	TX	May	20,700
FfP	1	Furniture	PA	Mar	8,170
FfT	2	Furniture	TX	Oct, Feb	19,800
GeP	1	Grocery (mid-size)	PA	Jul	25,300
GeT	2	Grocery (mid-size)	TX	Sep, Jan	14,900
ScP	1	Grocery (small)	PA	Aug	3,340
SdT	1	Grocery (small)	TX	Aug	5,390

[a] Three-character code that identifies a unique store. The first letter identifies the store type (H for home improvement, M for general merchandise, E for electronics, O for office supply, F for furniture, G for grocery (mid-size) and S for small grocery); the second letter differentiates the brand of the store; and the third letter the location of the store (P for Pennsylvania and T for Texas).

[b] At stores where multiple visits occurred, sampling events are identified with a four-character code composed of the store code and a number (1-4) referring to the test visit considered.

[c] Stores MiP and MiT were selected for additional testing. Two sampling events occurred at each store; the first sampling event was conducted at artificially elevated ventilation conditions (results excluded from summary data), and the second sampling event was conducted at normal ventilation conditions.

Table 8: VOC categories and their occurrence on the sales floor across test visits.

Category	n[a]	Indoor Occurrence
1 - Formaldehyde	1	24/24[b]
2 - Acetaldehyde	1	17/24[b]
3 - Ethanol	1	22/24[c], 7/20[d]
4 - Non-halogenated alkanes	73	23/24[c], 20/20[d]
5 - Acetone	1	24/24[c], 2/20[d]
6 - Total terpenoids	15	20/24[c], 11/20[d]
7 - Acetonitrile	1	17/24[c], 0/20[d]
8 - Isopropyl alcohol	1	23/24[c], 4/20[d]
9 - C_4-C_{10} carbonyls	55	22/24[c], 19/20[d]
10 - BTEXS	5	24/24[c], 20/20[d]
11 - Halogenated alkanes	13	23/24[c], 0/20[d]
12 - Non-BTEXS aromatics	17	8/24[c], 16/20[d]
13 - C_4-or-greater alcohols	28	5/24[c], 18/20[d]
14 - Other	40	15/24[c], 20/20[d]

[a] Number of compounds in categories found across all sampling events, sampling techniques and locations.
[b] DNPH tube samples.
[c] Summa canister samples.
[d] Sorbent tube samples.

Table 9: Indoor categorized VOC concentrations (ppb) found by Summa canisters for all test visits[b].

VOC Category	HaP1	HaP2	HaT	MbP1	MbP2	MbP3	MbP4	MbT1	MbT2	MbT3	MbT4	MiP	MiT	EgP1	EgP2	OhT	FfP	FfT1	FfT2	GeP	GeT1	GeT2	ScP	SdT
Ethanol	250	196	<DLa	849	584	456	637	18.9	33.4	149	430	71.6	95.5	58.4	40.3	212	13.8	<DL	53.1	1,960	2,600	1,860	265	46.9
Non-halogenated alkanes	183	411	14.1	38.2	24.0	29.4	42.7	84.2	<DL	39.8	195	18.1	165	10.5	8.8	231	15.8	0.9	45.7	117	16.4	18.8	150	22.4
Acetone	370	122	168	14.7	17.3	21.0	24.4	99.6	7.2	22.7	29.5	10.1	17.3	6.3	5.5	192	5.1	13.5	13.1	12.2	27.4	18.1	16.8	16.0
Total terpenoids	348	267	19.9	6.1	4.5	3.9	3.3	8.2	<DL	1.7	5.4	2.5	2.2	<DL	<DL	8.5	2.7	<DL	7.9	8.3	173	21.5	5.6	2.8
Acetonitrile	52.9	1.8	<DL	<DL	<DL	<DL	0.7	6.5	0.6	5.2	4.1	<DL	65.5	149	<DL	50.6	24.4	<DL	21.4	2.6	89.3	34.5	7.7	7.0
Isopropanol	18.0	195	15.9	13.0	6.5	6.9	13.6	68.8	25.6	4.9	20.3	7.7	5.7	3.3	5.3	8.3	5.7	18.7	6.9	12.2	12.6	9.8	4.9	<DL
C4-C10 carbonyls	47.5	50.3	3.7	5.1	2.3	5.8	11.6	9.7	<DL	4.1	11.1	5.8	11.5	1.3	<DL	11.4	4.5	0.5	7.9	9.7	9.2	3.4	10.4	7.0
BTEXS	55.5	34.5	14.2	5.3	2.7	6.4	5.3	7.6	0.6	2.3	5.1	19.0	22.6	1.8	1.3	17.8	0.9	3.7	10.1	1.6	0.7	1.3	5.6	2.0
Halogenated alkanes	8.1	13.5	3.7	13.9	14.4	7.2	15.4	5.1	2.7	45.0	34.7	7.9	3.4	2.5	8.8	0.7	<DL	0.5	0.6	5.5	8.5	6.8	0.7	0.7
Non-BTEXS aromatics	6.8	2.7	<DL	<DL	<DL	<DL	0.7	1.8	2.4	<DL	<DL	<DL	0.6	<DL	<DL	<DL	<DL	0.2	<DL	<DL	<DL	<DL	<DL	53.2
C4-or-greater alcohols	1.2	8.1	<DL	<DL	1.1	<DL	0.7	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	2.3	<DL	<DL	<DL	<DL	<DL
Other	93.1	101	114	<DL	<DL	1.0	7.5	25.8	2.9	<DL	19.6	2.4	3.4	1.8	<DL	7.4	<DL	<DL	<DL	<DL	11.2	<DL	2.7	14.7

[a] Detection limit (DL) = 0.5 ppb for most compounds.

[b] The first letter identifies the store type (H for home improvement, M for general merchandise, E for electronics, O for office supply, F for furniture, G for grocery (mid-size) and S for small grocery); the second letter differentiates the brand of the store; and the third letter the location of the store (P for Pennsylvania and T for Texas). At stores where multiple visits occurred, sampling events are identified with a four-character code composed of the store code and a number (1-4) referring to the test visit considered.

Table 10: Exposure limits for formaldehyde and acetaldehyde.

Organization	Formaldehyde Exposure Limit [ppb]	Acetaldehyde Exposure Limit [ppb]
OSHA[a] PEL[h] TWA[m]	750	200,000
OSHA STEL[i]	2,000	/
OSHA action level[n]	500	/
NIOSH[b] REL[j] TWA	16	/
NIOSH ceiling[n]	100	/
ACGIH[c] TLV[k] TWA	300	25,000
OEHHA[d] REL acute[o]	44.8	262
OEHHA REL 8-hour	7.3	167
OEHHA REL chronic[p]	7.3	78
FEMA[e] TWA	16	/
EPA[f] RfC[l]	/	5
WHO[g] 30-min	81.4	/

[a] Occupational Safety and Health Administration.

[b] National Institute for Occupational Safety and Health.

[c] American Conference of Governmental Industrial Hygienists.

[d] Office of Environmental Health Hazard Assessment.

[e] Federal Emergency Management Agency.

[f] Environmental Protection Agency.

[g] World Health Organization recommended guideline.

[h] Permissible exposure limit.

[i] Short-term exposure limit (15-minute average).

[j] Recommended exposure limit.

[k] Threshold limit value.

[l] Inhalation reference concentration (lifetime).

[m] Time-weighted average (8-hour average).

[n] 30-minute average.

[o] 1-hour average.

[p] 1-year average.

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References

Apte, M. G., and Erdmann, C. A. (2002) Associations of indoor carbon dioxide concentrations, VOCs, environmental susceptibilities with mucous membrane and lower respiratory sick building syndrome symptoms in the BASE study: Analyses of the 100 building dataset, Report No. 51570.

ASHRAE (2010) ANSI/ASHRAE Standard 62.1-2010. Ventilation for acceptable indoor air quality, Atlanta, GA, American Society of Heating, Refrigerating, and Air Conditioning Engineers, Inc.

Bruno, P., Caselli, M., de Gennaro, G., Iacobellis, S., and Tutino, M. (2008) Monitoring of volatile organic compounds in non-residential indoor environments, Indoor Air, 18, 250–256.

Burdock, G. A. (2005) Fenaroli's Handbook of Flavor Ingredients - 5th edition, Boca Raton, FL, CRC Press.

Caselli, M., de Gennaro, G., Saracino, M. R., and Tutino, M. (2009) Indoor contaminants from newspapers: VOCs emissions in newspaper stands, Environmental Research, 109, 149–157.

Center for Disease Control and Prevention. (2007) NIOSH Pocket Guide to Chemical Hazards, 1–454.

Chan, W., Sidheswaran, M. A., Sullivan, D. P., Cohn, S., and Fisk, W. J. (2012) Contaminant levels and source strengths in U.S. retail stores - A pilot study, Report No. 5547E1–8.

Chao, C. Y., and Chan, G. Y. (2001) Quantification of indoor VOCs in twenty mechanically ventilated buildings in Hong Kong, Atmospheric Environment, 35, 5895–5913.

Cros, C. J., Morrison, G. C., Siegel, J. A., and Corsi, R. L. (2012) Long-term performance of passive materials for removal of ozone from indoor air, Indoor Air, 22, 43–53.

Dean, B. J. (1985) Recent findings on the genetic toxicology of benzene, toluene, xylenes and phenols, Mutation Research, 153–181.

Eklund, B. M., Burkes, S., Morris, P., and Mosconi, L. (2008) Spatial and temporal variability in VOC levels within a commercial retail building, Indoor Air, 18, 365–374.

Feron, V. J., Til, H. P., De Vrijer, F., Woutersen, R. A., Cassee, F. R., and Van Bladeren, P. J. (1991) Aldehydes: occurrence, carcinogenic potential, mechanism of action and risk assessment, Mutation Research/Genetic Toxicology, 259, 363–385.

Grimsrud, D., Carlson, N., Bridges, B., Springman, T., and Williams, S. (2011) Investigation of appropriate ventilation rates for retail stores, In: Proceedings for the Conference Indoor Air 2011.

Hodgson, A. T., Wooley, J. D., and Daisey, J. M. (1993) Emissions of volatile organic compounds from new carpets measured in a large-scale environmental chamber, Air and Waste, 43, 316–324.

Hodgson, A. T., Beal, D., and McIlvaine, J. (2002) Sources of formaldehyde, other aldehydes and terpenes in a new manufactured house, Indoor Air, 12, 235–242.

Hotchi, T., Hodgson, A. T., and Fisk, W. J. (2006) Indoor air quality impacts of a peak load shedding strategy for a large retail building, LBNL, Report No. 59293.

Huang, Y., Ho, S. S. H., Ho, K. F., Lee, S.-C. C., Yu, J. Z., and Louie, P. K. K. (2011) Characteristics and health impacts of VOCs and carbonyls associated with residential cooking activities in Hong Kong, Journal of Hazardous Materials, 186, 344–351.

Hun, D. E., Corsi, R. L., Morandi, M. T., and Siegel, J. A. (2010) Formaldehyde in residences: long-term indoor concentrations and influencing factors, Indoor Air, 20, 196–203.

Jensen, L. K., Larsen, A., Molhave, L., Hansen, M. K., and Knudsen, B. (2001) Health evaluation of volatile organic compound (VOC) emissions from wood and wood-based materials, Archives of Environmental Health: An International Journal, 56, 419–432.

Katritzky, A. R., Ignatchenko, E. S., Barcock, R. A., Lobanov, V. S., and Karelson, M. (1994) Prediction of gas chromatographic retention times and response factors using a general qualitative structure-property relationships treatment, Analytical Chemistry, 66, 1799–1807.

Kim, Y. M., Harrad, S., and Harrison, R. M. (2001) Concentrations and sources of VOCs in urban domestic and public microenvironments, Environmental Science and Technology, 35, 997–1004.

Knöppel, H., and Schauenburg, H. (1989) Screening of household products for the emission of volatile organic compounds, Environment International, 15, 413–418.

Kwon, K. D., Jo, W. K., Lim, H. J., and Jeong, W. S. (2008) Volatile pollutants emitted from selected liquid household products, Environmental Science and Pollution Research, 15, 521–526.

Lamble, S. P., Corsi, R. L., and Morrison, G. C. (2011) Ozone deposition velocities, reaction probabilities and product yields for green building materials, Atmospheric Environment, 45, 6965–6972.

Lee, C. W., and Hsu, D. J. (2007) Measurements of fine and ultrafine particles formation in photocopy centers in Taiwan, Atmospheric Environment, 41, 6598–6609.

Loh, M. M., Houseman, E. A., Gray, G. M., Levy, J. I., Spengler, J., and Bennett, D. H. (2006) Measured concentrations of VOCs in several non-residential microenvironments in the United States, Environmental Science and Technology, 40, 6903–6911.

Miksch, R. R., Hollowell, C. D., and Schmidt, H. E. (1982) Trace organic chemical contaminants in office spaces, Environment International, 8, 129–137.

Missia, D. A., Demetriou, E., Michael, N., Tolis, E. I., and Bartzis, J. G. (2010) Indoor exposure from building materials: A field study, Atmospheric Environment, 44, 4388–4395.

Molhave, L. (2003) Organic compounds as indicators of air pollution, Indoor Air, 13, 12–19.

Namieśnik, J., Gorecki, T., and Łukasiak, J. (1992) Indoor air quality (IAQ), pollutants, their sources and concentration levels, Building and Environment, 27, 339–356.

Nazaroff, W. W., and Weschler, C. J. (2004) Cleaning products and air fresheners: exposure to primary and secondary air pollutants, Atmospheric Environment, 38, 2841–2865.

Nielsen, G. D., Larsen, S. T., and Wolkoff, P. (2012) Recent trend in risk assessment of formaldehyde exposures from indoor air, Archives of Toxicology, 87, 73–98.

Passant, N. R., Richardson, S. J., Swannell, R. P., Gibson, N., Woodfield, M. J., van der Lugt, J. P., Wolsink, J. H., and Hesselink, P. G. (1993) Emissions of volatile organic compounds (VOCs) from the food and drink industries of the European community, Atmospheric Environment. Part A. General Topics, 27, 2555–2566.

Pesis, E., Dvir, O., Feygenberg, O., Arie, R. B., Ackerman, M., and Lichter, A. (2002) Production of acetaldehyde and ethanol during maturation and modified atmosphere storage of litchi fruit, Postharvest Biology and Technology, 26, 157–165.

Poppendieck, D. G., Hubbard, H. F., Weschler, C. J., and Corsi, R. L. (2007) Formation and emissions of carbonyls during and following gas-phase ozonation of indoor materials, Atmospheric Environment, 41, 7614–7626.

Riley, W. J., McKone, T. E., Lai, A. C. K., and Nazaroff, W. W. (2002) Indoor particulate matter of outdoor origin: importance of size-dependent removal mechanisms, Environmental Science and Technology, 36, 200–207.

Sack, T. M., Steele, D. H., Hammerstrom, K., and Remmers, J. (1992) A survey of household products for volatile organic compounds, Atmospheric Environment, 26A, 1063–1070.

Siegel, J. A., Srebric, J., Crain, N., Nirlo, E. L., Zaatari, M., Hoisington, A., Urquidi, J., Shu, S., Kim, Y. S., and Jareemit, D. (2013) Ventilation and indoor air quality in retail stores, Report No. 1596-RP.

Singer, B. C., Destaillats, H., Hodgson, A. T., and Nazaroff, W. W. (2006) Cleaning products and air fresheners: emissions and resulting concentrations of glycol ethers and terpenoids, Indoor Air, 16, 179–191.

Steinemann, A. C. (2009) Fragranced consumer products and undisclosed ingredients, Environmental Impact Assessment Review, 29, 32–38.

Tang, J., Chan, C. Y., Wang, X., Chan, L. Y., Sheng, G., and Fu, J. (2005) Volatile organic compounds in a multi-storey shopping mall in Guangzhou, South China, Atmospheric Environment, 39, 7374–7383.

Tichenor, B. A. (1989) Measurement of organic compound emissions using small test chambers, Environment International, 15, 389–396.

U.S. Department of Labor. (2013a) Retail trade: NAICS 44-45, www.bls.gov. http://www.bls.gov/iag/tgs/iag44-45.htm, February 18, 2013.

U.S. Department of Labor. (2013b) American time use survey: Purchasing goods and services, www.bls.gov. http://www.bls.gov/tus/current/purchasing.htm, February 18, 2013.

U.S. EPA. (1999a) Compendium Method TO-11A, Center for Environmental Research Information Office of Research and Development, U.S. Environmental Protection Agency Cincinnati, OH 45268.

U.S. EPA. (1999b) Compendium Method TO-15, Center for Environmental Research Information Office of Research and Development, U.S. Environmental Protection Agency Cincinnati, OH 45268.

U.S. EPA. (1999c) Compendium Method TO-17, Center for Environmental Research Information Office of Research and Development, U.S. Environmental Protection Agency Cincinnati, OH 45268.

U.S. EPA. (2013a) Integrated risk information system - benzene, www.epa.gov. http://www.epa.gov/iris/subst/0276.htm, November 6, 2013.

U.S. EPA. (2013b) Integrated risk information system - formaldehyde, www.epa.gov. http://www.epa.gov/iris/subst/0419.htm, February 26, 2013.

U.S. EPA. (2014) Volatile organic compounds (VOCs) - Technical overview, www.epa.gov. http://www.epa.gov/iaq/voc2.html, January 7, 2014.

Uhde, E., and Salthammer, T. (2007) Impact of reaction products from building materials and furnishings on indoor air quality—A review of recent advances in indoor chemistry, Atmospheric Environment, 41, 3111–3128.

Vitrac, O., and Leblanc, J. C. (2007) Consumer exposure to substances in plastic packaging. I. Assessment of the contribution of styrene from yogurt pots, Food Additives and Contaminants, 24, 194–215.

Wallace, L. A., Pellizzari, E., Leaderer, B., Zelon, H., and Sheldon, L. (1987) Emissions of volatile organic compounds from building materials and consumer products, Atmospheric Environment, 21, 385–393.

Weisel, C. P., Zhang, J. J., Turpin, B. J., Morandi, M. T., Colome, S., Stock, T. H., Spektor, D. M., Korn, L., Winer, A. M., and Kwon, J. (2005) Relationships of indoor, outdoor, and personal air (RIOPA) Part I. Collection methods and descriptive analyses, Health Effects Institute, Report No. 130.

Weschler, C. J. (2011) Chemistry in indoor environments: 20 years of research, Indoor Air, 21, 205–218.

Wolkoff, P. (1995) Volatile organic compounds: sources, measurements, emissions, and the impact on indoor air quality, Indoor Air, 5 (S3), 5–73.

Wolkoff, P., Wilkins, C. K., Clausen, P. A., and Nielsen, G. D. (2006) Organic compounds in office environments - sensory irritation, odor, measurements and the role of reactive chemistry, Indoor Air, 16, 7–19.

Wooley, J., Nazaroff, W. W., and Hodgson, A. T. (1990) Release of ethanol to the atmosphere during use of consumer cleaning products, Journal of the Air and Waste Management Association, 40, 1114–1120.

World Health Organization. (2006) International Agency for Research on Cancer Monographs on the Evaluation of Carcinogenic Risks to Human, Volume 88: Formaldehyde, 2-Butoxyethanol and 1-tert-Butoxy-2-propanol, World Health Organization, Lyon.

World Health Organization. (2010) WHO guidelines for indoor air quality: selected pollutants, WHO Regional Office for Europe, Copenhagen.

Wu, X. M., Apte, M. G., Maddalena, R., and Bennett, D. H. (2011) Volatile organic compounds in small- and medium-sized commercial buildings in California, Environmental Science and Technology, 45, 9075–9083.

APPENDIX B: FIELD EVALUATION OF FIVE VOC MEASUREMENT TECHNIQUES: IMPLICATIONS FOR GREEN BUILDING DECISION-MAKING.

Field evaluation of five VOC measurement techniques: Implications for green building decision making

Elena L. Nirlo, Neil Crain, Richard L. Corsi, Jeffrey A. Siegel

ABSTRACT

Measurements of volatile organic compounds (VOCs) can be necessary to ensure healthy indoor environments. Many methods exist to collect and analyze VOCs, and each technique is associated with characteristic issues that affect the identification and quantification of some VOCs. In this study, simultaneous samples of VOCs were collected during 30 test visits in fourteen retail stores. Time-integrated measurements were made using Summa canisters, Tenax-GR sorbent tubes, and 2,4-dinitrophenylhydrazine (DNPH) tubes. Time-resolved measurements were collected using photoionization detectors (PID) and colorimetric formaldehyde monitors. Sampling with Summa canisters is less field-intensive than with sorbent tubes, however samples collected using Tenax GR-sorbent tubes indicated more possible exceedances of health guidelines compared to Summa canister samples. PID total volatile organic compound concentrations were not directly correlated with Summa canisters results even after correction for differential response to different VOCs. Formaldehyde monitor results were strongly correlated with DNPH tube results and the two sampling techniques agreed on all exceedances of the National Institute for Occupational Safety and Health chronic recommended exposure limit (REL = 16 ppb), but not on exceedances of the stricter

Office of Environmental Health Hazard Assessment chronic REL (7.3 ppb) at two stores. The formaldehyde monitor showed promising characteristics, supporting its further consideration as an indicator to control ventilation and/or environmental parameters in buildings where formaldehyde concentrations are of concern. The overall results suggest the sampling approach for VOCs can determine compliance with green building standards for VOC concentrations.

INTRODUCTION

In the past decade, energy efficiency has become the most important control parameter for building design and operation. A recent shift in interest from green to healthy buildings strives to refocus building design and operation to include the health, comfort and productivity of occupants (Kim, 2012; Teichman et al., 2013). For these reasons, green building standards, certifications, and rating systems, such as the Leadership in Energy & Environmental Design program (LEED: USGBC, 2013), are evolving to promote an integrated approach to sustainable design that includes indoor environmental quality. Indoor air quality is a decisive component of healthful environments (Spengler and Chen, 2000). Volatile organic compounds (VOCs), defined as having a boiling point below 250 °C (US EPA, 2013), are a broad class of chemicals ubiquitous in the indoor environment. While exposure to most VOCs at typical indoor concentrations has not been shown to negatively impact human health, specific compounds have been associated with a variety of adverse health effects. Such outcomes may include mucosal irritations, lower respiratory symptoms, central nervous system symptoms, and cancers (Norback et al., 1995; WHO, 2010; Nielsen et al., 2012; Wolkoff, 2013). Exposure to VOCs is a particular concern in specific indoor environments. In the retail sector, VOC exposure is a potential concern for its 15 million employees, and 101 million daily customers (US Department of Labor, 2014a, 2014b). Common sources of VOCs in retail stores include merchandise, displays, building materials, as well as cooking and cleaning activities (Wallace, 1991; Nazaroff and Weschler, 2004; Uhde and Salthammer, 2007).

Assessing exposure to VOCs requires information about the compounds present in the air and their concentrations at a specific location and time. Although the US Environmental Protection Agency (EPA) and the American Society for Testing and Materials (ASTM) Subcommittee D22.05 on indoor air quality publish standardized methods and protocols for measuring indoor air pollutants (US EPA, 2003; ASTM, 2007; ASTM, 2009a; ASTM, 2009b), VOC measurements are not widely practiced. Multiple guides, such as the Performance Measurement Protocols for Commercial Buildings published by ASHRAE (2010), or the Building Air Quality: A Guide for Building Owners and Facility Managers (Appendix A: Common IAQ Measurements: A General Guide) published by the US EPA and the National Institute for Occupational Safety and Health (1991), warn facility managers, operators, technicians and consultants about the price associated with sampling, the necessity of selecting an appropriate technique and representative time, duration and location of sampling, as well as the complexity of interpreting the results. Therefore, direct measurements are only advised as a last resort (ASHRAE, 2010), and simpler techniques are commonly used as proxies to evaluate indoor air quality (Teichman et al., 2013). Indoor air quality investigations triggered by a complaint are typically limited to a site assessment and/or a perception survey, and can be accompanied with measurements of ventilation rates and environmental parameters (e.g., temperature, relative humidity, CO2 concentrations) (ASHRAE, 2010). Information obtained through these indirect methods is not always sufficient to design and operate a

VOC removal strategy that may be needed to create and maintain a healthy environment. If information on indoor air quality is required during the modeling phase of the removal system, the designer is encouraged to compare the space studied to similar existing environments (ASHRAE, 2013). However, cross-studies comparisons of VOC concentrations are problematic as studies differ in sampling method, time and duration, and the buildings sampled differ in merchandise carried and layout (e.g., Zaatari et al., 2014).

While many studies have compared the output of two analytical procedures used simultaneously in a controlled environment with gas mixtures of known concentrations (e.g., Kumar et al., 2005), few studies have used field data to compare sampling methodologies (Stock et al., 1999; Coy et al., 2000; Dobos, 2000; Pfeffer and Breuer, 2000; Kim et al., 2005; Pratt et al., 2005). Such studies were specific to a targeted subset of compounds, mainly benzene, toluene, ethylbenzene, xylene, and styrene (BTEXS), and to the environment sampled (cokery: Pfeffer and Breuer, 2000; newly-built apartments: Kim et al., 2005; construction sites with painting jobs: Coy et al., 2000). None of these studies were conducted in retail stores, and less than twenty compounds were investigated. Most of the investigations published compared passive to active collection techniques (canister vs. organic vapor monitor (OVM): Stock et al., 1999; Pratt et al., 2005; sorbent vs. OVM: Dobos, 2000; Pfeffer et al., 2000).

This paper identifies the advantages and limitations of five measurement methods used in a large field investigation on ventilation and indoor air quality in retail stores (Siegel et al., 2013; Nirlo et al., 2014) Simultaneous measurements of VOCs by Summa canisters (CAN), Tenax-GR sorbent tubes (SOR), photoionization detectors (PID), DNPH tubes, and colorimetric formaldehyde monitors (FMM) are compared. Differences in identification and concentration of compounds of interest are discussed. This work explores how the selection of a VOC sampling method may impact compliance with green building standards. Results indicate what method, if any, could be used to monitor or control a VOC removal strategy.

BACKGROUND

Many collection and analysis techniques exist to measure VOCs, and each method is associated with advantages and limitations. The collection of Summa canisters (CAN) consists of introducing air into a specially-prepared stainless steel canister, and does not require the presence of skilled personnel. Blank samples are not required. Sorbent tube (SOR) sampling consists of pulling a known volume of air through a sorbent packing to collect VOCs. Additional material and skilled personnel are necessary to set up the sampling system and calibrate the pump before and after sampling, although some laboratories offer to send pre-calibrated pumps. Extra sorbent tubes also need to be collected for quality control purposes. Moreover, tubes need to be handled with caution to avoid contamination and must be maintained below 4°C during shipping.

Both CAN and SOR samples can be sent to certified laboratories for analysis, although a brief web search for “laboratory TO-17 analysis” and “laboratory TO-15 analysis” reveals that fewer laboratories offer SOR services, and that the current cost of analysis for CAN and SOR samples is approximately 300 USD and 200 USD, plus shipping, respectively. The analysis is conducted using gas chromatographic column (GC), coupled to a mass spectrometer (MS) (Compendium TO-15: US EPA, 1999a; Compendium TO-17: US EPA, 1999b). Identification and quantification of VOCs on a mass spectrum is based of the fragmentation pattern of ions of individual peaks. If the speciation of the air sampled is already known, customized target lists can be created for both CAN and SOR analysis to improve identification and quantification of the selected compounds (SI 4). Compounds that were not on the target list are identified using a library compound search (LCS), and compared to the nearest internal standard for quantification. Both the identification and quantification of LCS compounds is associated with a greater uncertainty than that of targeted compounds.

A variant of sorbent tube sampling used to collect light aldehydes requires the use of adsorbent cartridges coated with 2,4-dinitrophenylhydrazine (2,4-DNPH), followed by the separation and analysis of the hydrazone derivative by high performance liquid chromatography with ultraviolet (UV) detection (Compendium TO-11A: US EPA, 1999c). DNPH tubes are a reliable but field-intensive sampling technique. Current cost of analysis by a certified laboratory is approximately 100 USD.

A photoionization detector (PID) is an easy-to-use instrument that can be plugged in a fixed location for extended periods of time, or carried around for 4 to 5 hours. PIDs use high-energy UV light to ionize molecules in the sampled airstream. The instrument measures the current produced by the electrically charged gas and converts the signal to the concentration, providing rapid onsite screening for total volatile organic compounds (TVOC). In addition to the initial price of the instrument (above 5,000 USD), additional costs are associated with the use of consumables needed for the instrument calibration before and after sampling.

A formaldehyde multimode monitor (FMM) is an extremely easy-to-use, self-calibrating instrument that can be used plugged in, or on battery for up to five hours. Measurements with this instrument have the potential to be automated, and therefore be connected to a real-time control strategy. However, the FMM requires consumables (sensor assemblies) to be changed every 4 days (if measuring concentrations around 20 ppb). The current cost of the instrument is approximately 1500 USD and approx. 90 USD for a sensor assembly. The main limitation of this instrument concerns its use for concentrations under 20 ppb, commonly found in indoor environments, that has not been verified by the manufacturer. However, tests conducted in a controlled environment by Carter et al. (2013) indicated a good performance of the FMM at 5 and 10 ppb. The authors also reported a decreased accuracy at high concentrations, and some inconsistency amongst sensor batches.

METHODS

This study was performed at fourteen retail stores in Texas and central Pennsylvania. Six out of the fourteen stores studied were sampled two to four times over the course of a year, for a total of 30 sampling events. More details on the sample of buildings selected were published elsewhere (Nirlo et al., 2014).

Sampling and Analysis

Time-resolved and time-integrated instruments were placed in shopping carts (or baskets) that were continuously pushed (carried) through the retail floor over a period of four hours. Five methods were used to measure VOC, aldehyde, and TVOC concentrations: Summa canisters (CAN), sorbent tubes (SOR), photoionization detectors (PID), DNPH tubes (DNPH), and formaldehyde multimode monitors (FMM). The instruments used for each type of measurement, along with the manufacturer/laboratory reported uncertainty, detection limit, and resolution are summarized in Table 11. The quality assurance and quality control procedures for all VOC measurements are documented in the SI (SI 1). All techniques were discussed previously (Siegel et al., 2013; Nirlo et al., 2014), and are presented briefly here.

Table 11: Instrumentation used in the present investigation

Concentrations Measured	Time Resolution	Instrument	Detection Principle	Uncertainty	Detection Limit	Resolution
Speciated VOCs	Integrated 4 hrs	Summa canisters, analyzed by CL1[a], CL2[a]	Gas chromatography, mass spectrometry	±30% (TC)[b] ±100% (LSC)[c]	0.5 ppb	
	Integrated 4 hrs	Tenax-GR sorbent tubes, analyzed in-house	Thermal desorption, gas chromatography, mass spectrometry	±100%	2 ng	1 ng
TVOC	Continuous 5 min	RAE Systems ppbRAE Plus PGM-7240	UV absorption	Greater of ± 20 ppb and 10% of the reading	1 ppb	1 ppb
Formaldehyde	Integrated 4 hrs	DNPH tubes, analyzed by CL1, CL3[a]	High-performance liquid chromatography	±30% (CL1) ±12.4% (CL3)	100 ng	
	Continuous 30 min	Shinyei Formaldehyde Multimode Monitor	UV absorption	±10% at 40, 80, 160 ppb[d]	20 ppb[d]	1 ppb

[a] Commercial laboratories.

[b] Targeted compounds.

[c] Library search compounds.

[d] Manufacturer only calibrates device to 20 ppb. Readings below 20 ppb were made using special software provided by the manufacturer for this investigation. The uncertainty associated with these readings is also assumed to be ± 10%.

Indoor Summa canister samples were successfully collected at all sampling events. Five sets of duplicate samples were also collected. Sorbent tube samples were collected using a modified version of the US EPA Compendium Method TO-17 (1999b) and analyzed in-house. Thirty-one indoor sorbent tube samples were collected, including eight sets of duplicates. The sorbent tube sampling system was successfully collocated in the shopping cart or basket with the Summa canister for twenty-three sampling events.

Photoionization detectors (ppbRAE Plus PGM-7240, RAE Systems) were used for each test to measure 5-minute averages of the total volatile organic compound (TVOC) concentration. The PID was successfully collocated in the shopping cart or basket with the Summa canister for twenty-seven mobile sampling events. Several issues arose with the PID over the course of this investigation, notably a concentration drift after 3 days of use that required additional regular re-calibrations.

DNPH tubes were successfully collected during all sampling events, including 13 sets of duplicates. Concurrently, formaldehyde multimode monitors (FMM) manufactured by Shinyei Corp. were used at fourteen test visits to measure 30-minute averages of the formaldehyde concentration. Even though the instrument is advertised as having a detection limit of 20 ppb, readings below 20 ppb were made using special software provided by the manufacturer for this investigation. The uncertainty associated with these readings (10%) is assumed to be that reported by the manufacturer at 40, 80, and 160 ppb.

Data Analysis

Time-Integrated Measurements: CAN, SOR, and DNPH

Analysis of the duplicate samples collected by Summa canisters, sorbent tubes, and DNPH tubes is detailed in the Supporting Information (SI 1). In general, the relative variance between the concentrations obtained by the sets of replicates was well within the uncertainty published by the laboratory conducting the analysis of the samples. For this reason, indoor VOC concentrations in this study were averaged when replicate samples were collected. If the compound was not detected in one of the replicate sample, which occurred in less than 20% of both CAN and SOR measurements, the missing concentration was replaced by half the detection limit.

Time-Resolved Measurements: PID and FMM

For every test, data points where the concentration was not within three standard deviations of the overall mean were flagged as potential outliers, and removed from the time series data after a visual check (SI 2). For the PID, outliers were mostly caused by the instrument sensitivity to vertical movements, by power interruptions, or by logging issues. As a way to compare results obtained from the different techniques, time-resolved concentrations were averaged over the four-hour mobile sampling period where real-time monitoring (PID, FMM) was concurrent with time-integrated measurements (CAN, SOR, and DNPH).

PID results are compared to a total volatile organic compound (TVOC) concentration calculated by summing the individual concentrations obtained by the Summa canisters (C_{CAN}^{TVOC}). PID results are also compared to an estimated TVOC concentration calculated by combining Summa canister and the sorbent tubes results ($C_{estimated}^{TVOC}$) in an attempt to circumvent the biases inherent to CAN results and approach the "real" composition of the air mixture sampled. Further comparisons are conducted using PID TVOC concentrations adjusted to the specific air mixture sampled. Mixture correction factors (CF_{mix}) are calculated for each sample using mole fractions determined by Summa canisters, and by the estimated air mixture. Detailed calculations are available in Supporting Information (SI 3).

RESULTS AND DISCUSSION

Measurements of Speciated VOCs

Two hundred and thirty-nine distinct compounds were identified in the 23 paired Summa canister (CAN) and sorbent tube (SOR) samples. The resulting 1,112 concentrations are shown in Figure 12, where all CAN and SOR VOC concentrations are organized by the molecular weight (MW) of the corresponding compound. A list of all VOCs identified over the course of this investigation by either sampling technique can be found in the Supporting Information (SI 4).

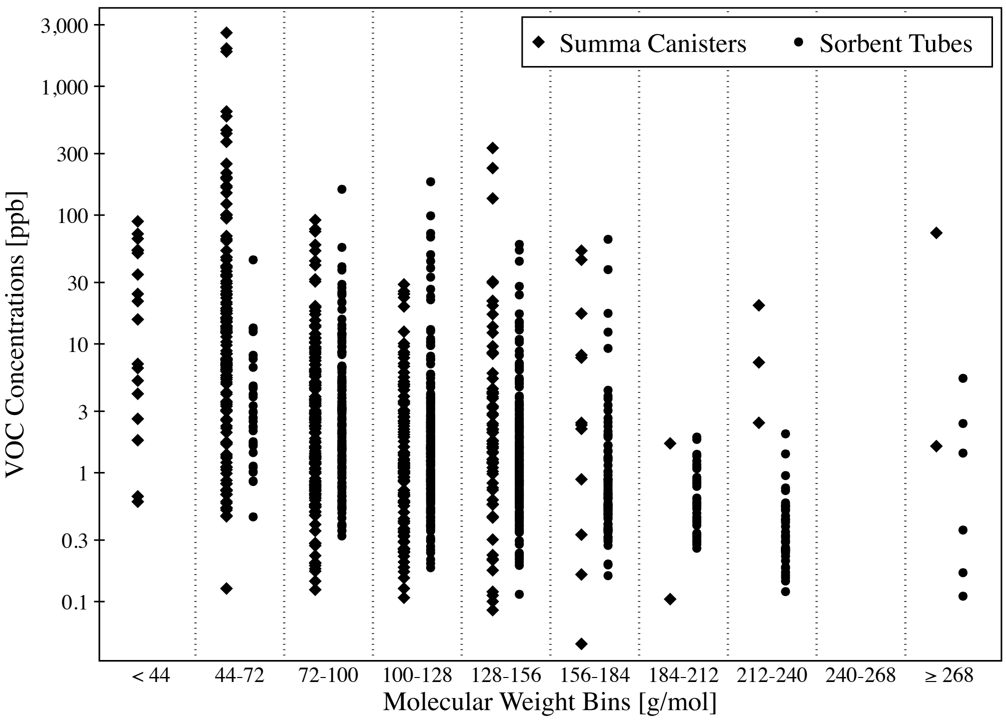

Figure 12: Comparison of all VOC concentrations measured simultaneously by Summa canisters and sorbent tubes across all test visits, displayed by molecular weight.

Summa canisters appear to prevail amongst low molecular weight compounds (< 72 g/mol). The first bin consisted of a single compound, acetonitrile (41 g/mol), which was only observed in CAN samples. The second bin (44≤MW<72 g/mol) was also dominated by Summa canisters, in terms of instances quantified (151 measurements vs. 35 for sorbent tubes), diversity of VOCs identified (15 compounds vs. 5 for sorbent tubes), and range of concentrations measured (4 orders of magnitude covered vs. 2 for sorbent tubes). The highest VOC concentration observed was for ethanol, which was measured at 2.6 ppm in a Summa canister sample, but was found to be only 8.1 ppb in the sorbent tube sample from the same site. In all samples, sorbent tubes under-estimated concentrations of ethanol and isopropanol when compared to CAN results by a factor of

132 and 31 on average, respectively (Figure 13). These findings are consistent with the physical properties of the sorbent used in this investigation. Tenax GR is a relatively low surface area sorbent and is not adapted to collect compounds with fewer than four carbon atoms and relatively high vapor pressures (US EPA, 1999c). The Tenax GR's low affinity for low-molecular weight compounds may also explain the SOR underestimation of ethylacetate (88 g/mol) concentrations when compared to Summa canisters (Figure 13) (Harper, 2000).

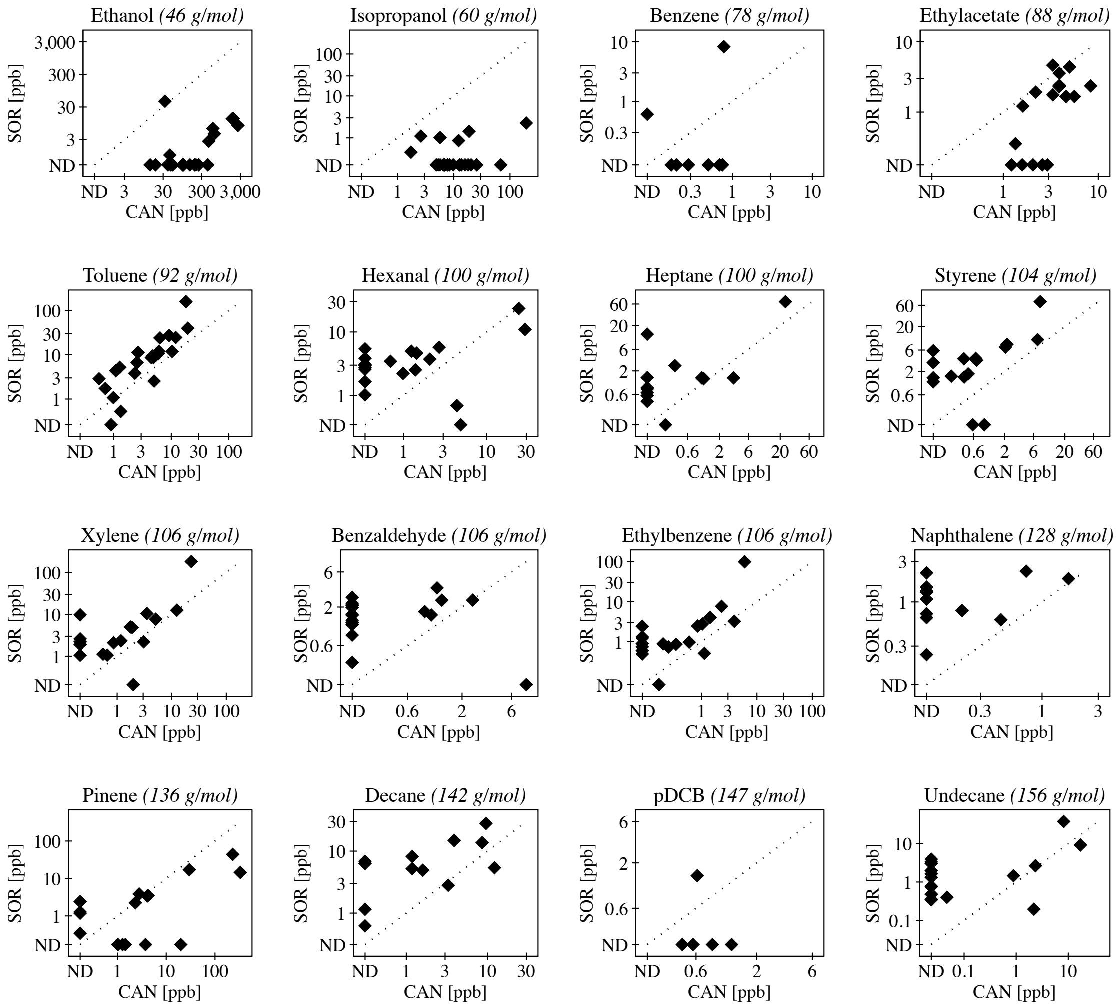

Figure 13: Sorbent tube (SOR) vs. Summa canister (CAN) concentrations for 16 prevalent compounds. Note that compounds are displayed by increasing molecular weight.

The following three bins (72≤MW<156 g/mol) hold the most datapoints and compounds, for both techniques. Sorbent tubes showed more diversity as 149 individual VOCs were identified in SOR samples vs. 69 in CAN samples, and SOR concentrations appear generally higher than CAN concentrations. For instance, benzene, a target compound, was identified more often in CAN samples, at very low concentrations (< 0.8

ppb), but was measured at a higher concentration in the SOR sample when found by both techniques (Figure 13). Although SOR and CAN results were in good agreement in 63% of the samples, SOR concentrations for styrene were on average higher than CAN concentrations by a factor of 5, even though styrene was on the CAN target list (Figure 13). However, when considering the uncertainty of the techniques on specific compounds, SOR and CAN results were in good agreement for targeted compounds such as toluene, heptane, xylene, and ethylbenzene in more than three quarters of the samples, and for LCS compounds such as hexanal, benzaldehyde, decane, undecane, and to a lesser extent, naphthalene (Figure 13). *p*-Dichlorobenzene (*p*DCB) was one of four compounds presented in Figure 13 whose concentrations crossed the parity line in less than a fourth of the samples in which they were identified by either technique. *p*DCB was identified 5 times in CAN samples but only once in a SOR sample, at very low concentrations (< 1.2 ppb). Both collection techniques also appeared to perform erratically regarding the quantification of pinene (Figure 13). In a third of the samples, pinene was identified in CAN samples only, at concentrations ranging from 1 to 20 ppb. In another third of the samples, pinene was found by both techniques where CAN concentrations were on average 6 times higher compared to SOR concentrations. Pinene was found at low concentrations (< 2.5 ppb) in SOR samples only in the remaining third of the samples, which may be explained by the relatively low recovery of alkenes in canisters (Wai-mei Sin et al., 2001; Batterman et al., 1998).

Sorbent tubes dominated over the remaining five bins (MW≥156 g/mol), with the exception of one bin (240≤MW<268 g/mol) that contained no compound. Three to 10 times as many compounds were identified per bin in SOR samples as were in CAN samples, for a total of 160 measurements for SOR samples vs. 19 for CAN samples. Sorbent tubes may be more suitable to sample for high molecular weight compounds since they allow for the deposition of particles onto which low vapor pressure compounds may have sorbed, whereas a filter prevents such particles from entering Summa canisters. Low vapor pressure compounds may also adhere to the walls of the canisters and are not thermally desorbed since canisters are not heated for analysis (Brymer et al., 1996).

It should be noted that this comparison is influenced by the fact that all compounds in SOR samples were identified through a library search, while CAN analysis targeted 70 compounds (shown in SI 4), and was complemented by a limited library search to identify up to the 20 largest non-target concentration peaks per sample. Therefore it is possible that other compounds were captured by the Summa canisters but did not appear in the analysis report.

This analysis illustrates the need to identify potential contaminants of concern in advance to select the appropriate sorbent to be used in SOR sampling (US EPA, 1999b; Harper, 2000), and create customized target lists for both CAN and SOR analysis. Acrolein can further demonstrate this point. Acrolein is a VOC commonly emitted when heating cooking oil that has been found in grocery stores in other studies (Dutton et al., 2013). It is suspected to be associated with serious health effects at concentrations in the ppt range (OEHHA, 2014). Since such concentrations would represent less than 1% of the internal standard peak, acrolein would not be reported as a CAN LCS compound. Moreover, acrolein is too light (56 g/mol) to be captured by Tenax GR in sorbent tubes. Therefore, the fact that acrolein was not identified in neither CAN nor SOR samples does not mean that acrolein was not present at any store sampled in this investigation. If the speciation of the air to be sampled is not known or suspected before sampling, compounds of potential interest can be missed.

Measurements of TVOC

Figure 14 explores the correlation between the 4-hour average PID TVOC concentration and the integrated TVOC concentration calculated by summing the speciated VOC concentrations based on collection with Summa canisters (CAN) (Figure 14.a) and sorbent tubes (Figure 14.c). It also documents further attempts at improving this correlation by the use of correction factors (Figures 14.b and 14.d).

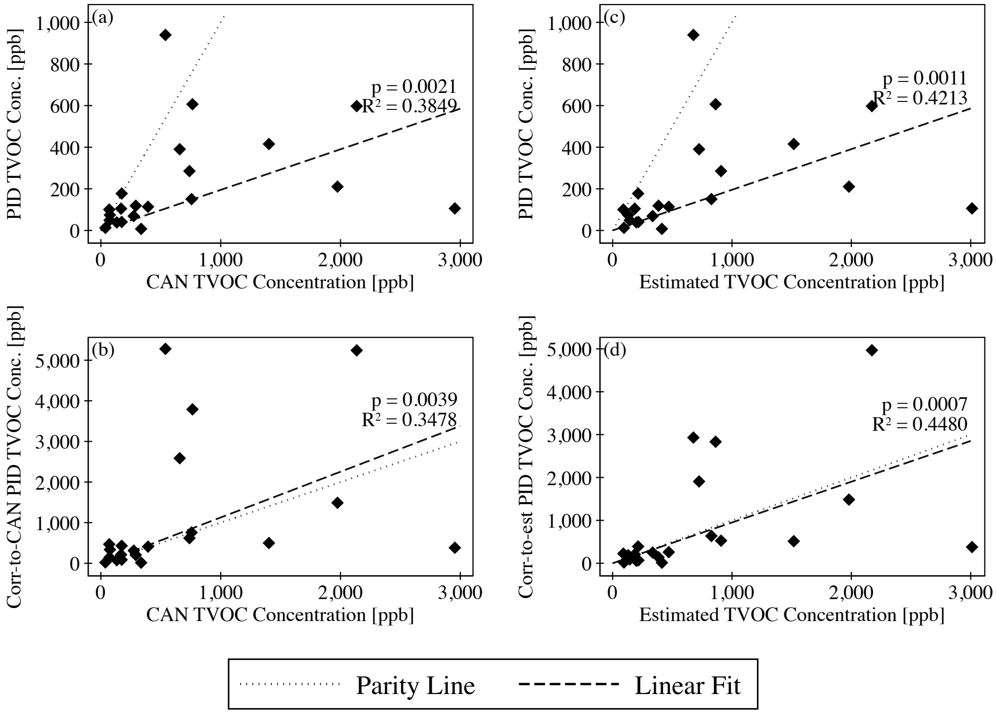

Figure 14: Parity plots of the results of the PID, averaged over four hours (a) as monitored versus TVOC calculated from collocated Summa canisters (CAN TVOC), (b) corrected to the CAN results versus CAN TVOC, (c) as monitored versus TVOC calculated from an estimation of the air mixture sampled, and (d) corrected to the estimated air mixture versus TVOC calculated from an estimation of the air mixture sampled. Note that the dotted line is the parity line, and the dashed line the best linear fit.

A linear regression indicates that the PID TVOC concentration is significantly but poorly correlated (p=0.0021, R^2=0.39, coefficient=0.2) with the CAN TVOC concentration (Figure 14.a). 34% of PID results are within ±50% of CAN results, but all PID results lay within ±100% of CAN results. A possible explanation for this dispersion is the choice of isobutylene as the calibration gas. The molecular structure of isobutylene is very different compared to the observed compounds that had the highest concentrations, such as ethanol or isopropanol. Using a dissimilar calibration gas may have generated a calibration curve that under-estimated the concentrations of these compounds. In order to account for that difference, mixture correction factors can be applied to the PID value (Figure 14.b).

Corrected PID TVOC concentrations are 1.2 to 8.8 times higher after correction to the air mixture compared to Summa canister results. The correlation between corrected-to-CAN PID TVOC concentrations and CAN TVOC concentrations is still significant but poorer (p=0.0039, R^2=0.35). Consistent with higher corrected PID TVOC concentrations, a linear regression gives a coefficient higher than one. A minority of high concentrations (>1.5 ppm by either technique) found at one brand of grocery stores and one brand of general merchandise stores strongly influence this fit. A linear regression omitting the six corresponding data points gives a significant and much stronger correlation (p=0.0018, R^2=0.64, coefficient=0.54). This assessment of the PID accuracy is based on Summa canister results. However, as previously evidenced, Summa canisters do not identify all compounds present in the air. In an attempt to approach the “real” composition of the air mixture sampled, sorbent tubes results were added to CAN results to create an estimated air mixture. The rest of the analysis is carried with this estimated air mixture as a reference (Figure 14.c and 14.d).

The PID TVOC concentration is significantly and slightly more strongly correlated (p=0.0011, R^2=0.42) with the estimated TVOC concentration (Figure 14.c) than with the CAN TVOC concentration. However, the coefficient of fit and the dispersion of PID TVOC results around estimated TVOC concentrations are the same. The best regression results across all tests are obtained between corrected-to-estimated PID TVOC concentrations and estimated TVOC concentrations (p=0.0007, R^2=0.45), with a coefficient of fit closest to unity (0.95) (Figure 14.d).

After correction, PID TVOC concentrations increase by a factor of 1.2 to 8.3. These mixture correction factors are significantly different (Wilcoxon matched-pairs signed-ranks test, p=0.0001) from those calculated based on Summa canisters results. The relative percent difference across all samples averaged (SD) 25% (21%).

These corrections of the PID results must be considered while being mindful of the fact that both CAN- and estimated- mixture correction factors are based on biased characterizations of the air sampled, as illustrated in the previous section. Moreover, both the CAN TVOC concentration and the estimated TVOC concentration likely represent an underestimation of the actual TVOC concentration since they were calculated by summing concentrations of identified compounds, and not by integrating the total area under the chromatographic curve of the GC/MS assuming a single response factor. Additional uncertainty in the calculation of mixture correction factors comes from the fact that the manufacturer does not provide correction factors for all compounds observed. The detection principle of the PID may have also influenced the results. Equipped with a 10.6 eV lamp, the instrument cannot detect organic compounds whose ionization potential is greater than 10.6 eV, such as halogenated compounds (e.g., Freons, methylene chloride, chlorinated alkanes) or methanol (Coy et al., 2000; Haag, 2005).

Overall, no strong correlation could be found between PID TVOC concentrations, uncorrected or corrected, and CAN- or estimated- TVOC concentrations. Linear regressions conducted by store type between corrected-to-estimated PID TVOC concentrations and estimated TVOC concentrations lead to strong significant results ($p=0.0011$, $R^2=0.67$) for general merchandise stores only, with a coefficient of fit of 2.1. For this study, the PID had a general tendency to under-predict TVOC concentrations when compared with CAN TVOC concentrations (86% of all tests) and estimated TVOC concentrations (90% of all tests). This tendency may be influenced by the characteristics of time-resolved vs. time-integrated techniques. Summa canisters are a whole-air sampling technique, and can capture compounds that the sampling apparatus may have encountered for a small period of time, whereas these peak concentrations would not be reflected in 4-hour averaged PID results.

After correction, the PID tends to over-predict TVOC concentrations when compared with CAN TVOC concentrations, but has a slight tendency to under-estimate TVOC concentrations when corrected to the estimated air mixture (62% of all tests). The inconsistent effect of correcting PID TVOC concentration is particularly apparent on samples with initially high concentrations (C_{CAN}^{TVOC} > 1.9 ppm). For the first test ($\overline{C}_{PID}^{TVOC}$ =1975 ppb ; C_{CAN}^{TVOC} =210 ppb), the initial ratio of PID-to-CAN TVOC concentration (P-to-C) was 11%, and rose to 75% after correction. At the second grocery store ($\overline{C}_{PID}^{TVOC}$ =106 ppb ; C_{CAN}^{TVOC} =2955 ppb), the correction had little effect, the P-to-C increasing from 4% to 13%. For the third test ($\overline{C}_{PID}^{TVOC}$ =597ppb ; C_{CAN}^{TVOC} =2136 ppb), the correction worsened the PID agreement with CAN results, as the P-to-C increased from 28% to 245%. This inconsistency may be explained by the complexity of the air mixture and its composition. In the first case, the calculation for the mixture correction factor was relatively straightforward and lead to good results. The air mixture was among the simplest studied

(12 compounds), and was dominated by a single compound, ethanol. In the second and third case, the mixture was more complex (22 and 20 compounds, respectively), and the calculation for the mixture correction factor was dominated by multiple compounds. Similar findings were obtained when considering the estimated air mixture as a reference. These results suggest that a reliable use of the PID could be made if the focus is on a few selected compounds for which the instrument was specifically calibrated.

An a posteriori correction can only be made to the PID TVOC concentration if information is available regarding the composition of the air mixture sampled. If generic mixture correction factors were readily available for specific environments, their use would prevent the need for concurrent PID and speciated VOC samples. This part of the analysis explores the dataset of mixture correction factors based on Summa canister results ($CF_{mix(CAN)}$) that were used to calculate the corrected PID TVOC concentrations displayed in Figure 14.b in hopes of finding such trends (Figure 15).

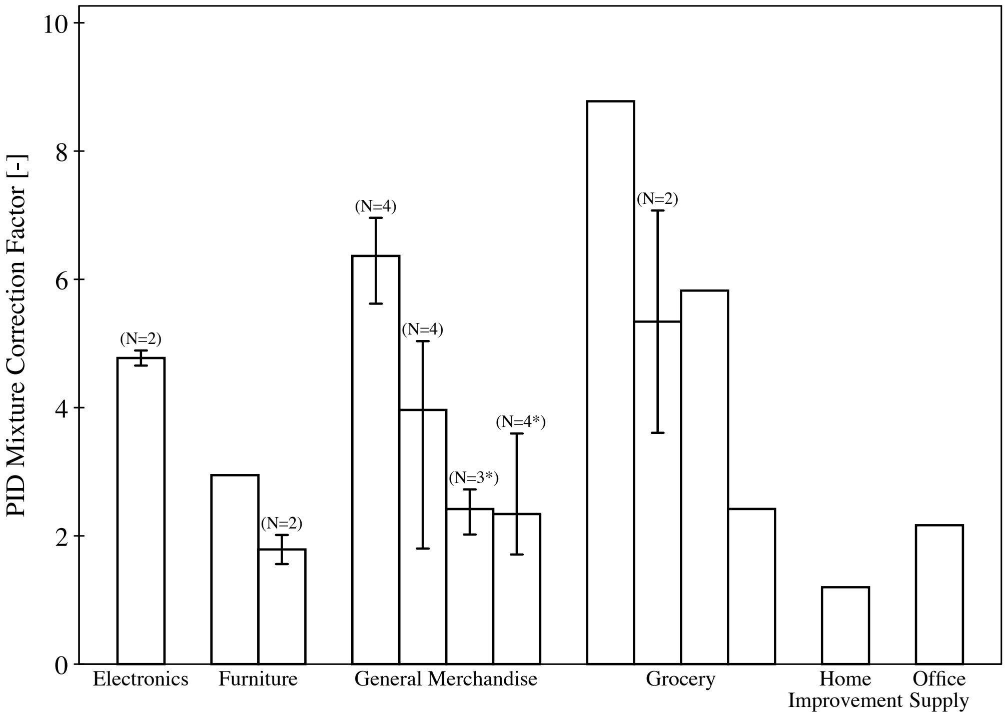

Figure 15: Correction factors for mixtures (CF_{mix}) for the stores sampled in this investigation by store type. For stores that were sampled multiple times over the course of the year, N is the number of test visits, the bar represents the mean CF_{mix} over test visits, and the whiskers indicate the minimum and maximum CF_{mix} found across test visits. The star indicates two stores where the multiple test visits occurred at different ventilation conditions over the course of 2 consecutive weeks.

Overall, mixture correction factors varied widely. Values ranged from 1.2 at a home improvement store to 8.8 at a grocery store, with a mean (SD) of 3.9 (2.2), and a median of 2.9. With the exception of the furniture stores, mixture correction factors varied widely within store type as well. In grocery stores, CF_{mix} ranged from 2.4 to 8.8, with a mean of 5.6. In general merchandise stores, CF_{mix} averaged 3.8 but ranged from 2.3 to 6.4.

The mixture correction factors even show little consistency among various test visits at a same store. At two general merchandise stores that were sampled 4 times each and a grocery store sampled twice, the CF_{mix} had a relative percent difference (RPD) ranging from 65% to 94%. However, mixture correction factors were relatively constant at the electronics store, one of the furniture stores, and the two remaining general merchandise stores, for which the RPD ranged from 4% to 23%.

Based on our small sample, it does not appear that generic mixture correction factor could be used to adjust PID TVOC concentrations measured in these retail stores. Therefore, if building operators wish to use quantitative results from a PID, the characterization of the air mixture sampled must either be known a priori to calibrate the instrument accordingly, or estimated simultaneously by speciated VOC techniques to correct the PID results. In the absence of resources to do so, the PID may still provide useful information regarding temporal variations of TVOC concentration, but caution should be used because of the issues raised above.

Temporal Profiles

The temporal profiles of TVOC concentrations for three selected stores are displayed in Figure 16. During the three-day period presented here, the monitors remained at a fixed location in the stores.

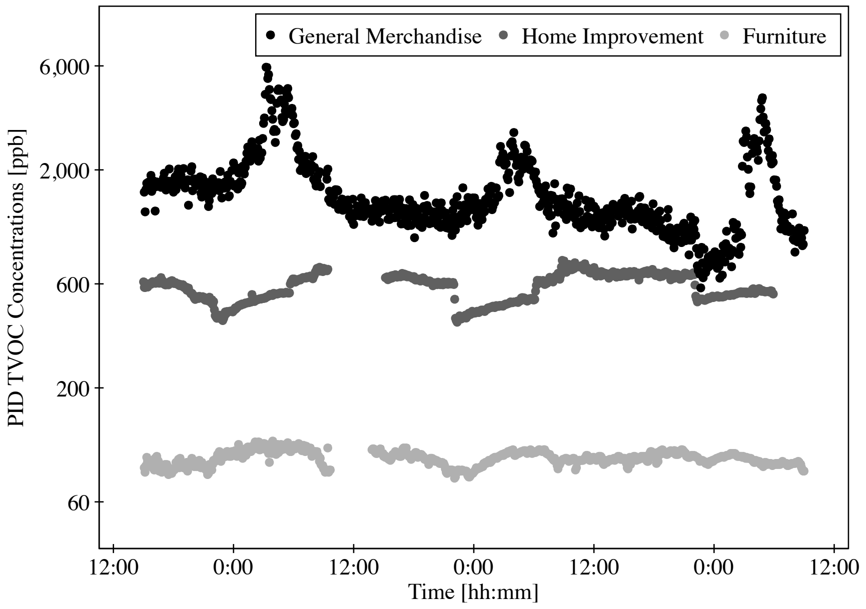

Figure 16: Temporal variations of TVOC concentrations monitored by the PID for selected stores over the course of three non-concurrent days. On the abscissa, *12:00* refers to noon and *0:00* to midnight. Note that the concentrations are displayed on a logarithmic scale. Data acquisition was momentarily interrupted by a power outage in the home improvement store, and a logging error in the furniture store.

TVOC concentrations at the furniture store remained relatively low and constant over time, ranging from 77 ppb to 114 ppb, with a coefficient of variation of 7% (Figure 16). This finding may be explained by the absence of VOC-inducing activities in the store, such as cleaning and cooking, and an absence of fragranced products. At the home improvement store, TVOC concentrations ranged from 400 ppb to 769 ppb, with a mean (SD) of 581 (83) ppb. The highest concentrations were obtained in the middle of the day. The profile is discontinuous on the second and third day at 10pm, where the concentration dropped within 30 minutes by 200 ppb and 150 ppb, respectively, for reasons that could not be identified.

The highest TVOC concentrations and the widest temporal variations were observed at a general merchandise store, where concentrations ranged from 575 ppb to 5915 ppb, with a coefficient of variation of 46 %. The temporal profile shows a cyclical pattern over the three days displayed. The TVOC concentration starts increasing around midnight, peaks between 3am and 4am, and reaches its lowest point between 8am and 10am. Daytime concentrations remain relatively constant. The regularity of the pattern suggests either a constant source or a change in ventilation operation or a combination of these two factors. This store conducted their cleaning activities overnight, which may be a contributor to increased VOC concentrations and generally reduced their ventilation air flow rate during unoccupied periods. These factors suggest the potential for occupational exposure during overnight cleaning and stocking activities.

The pattern and depth of temporal TVOC variations are highly dependent on the store ventilation strategy and the activities occurring in the store. Even though the PID does not provide accurate TVOC concentrations if the air sampled is not fully characterized through other sampling techniques, this instrument provides relevant information on the daily variation of the TVOC concentration.

Measurements of Formaldehyde

Formaldehyde concentrations were measured simultaneously using the FMM and DNPH tubes for fourteen tests are shown in Figure 17. Since the FMM has a time resolution of 30 minutes, the results presented were calculated as an average over the four hours of collocation with the DNPH tubes. During this time period, the FMM produced only between 3 and 5 data points, therefore, the uncertainty displayed for the FMM results is the uncertainty given by the manufacturer for the instrument (Table 11). The uncertainty associated with the DNPH results is the uncertainty reported by the laboratory that performed the analysis (Table 11).

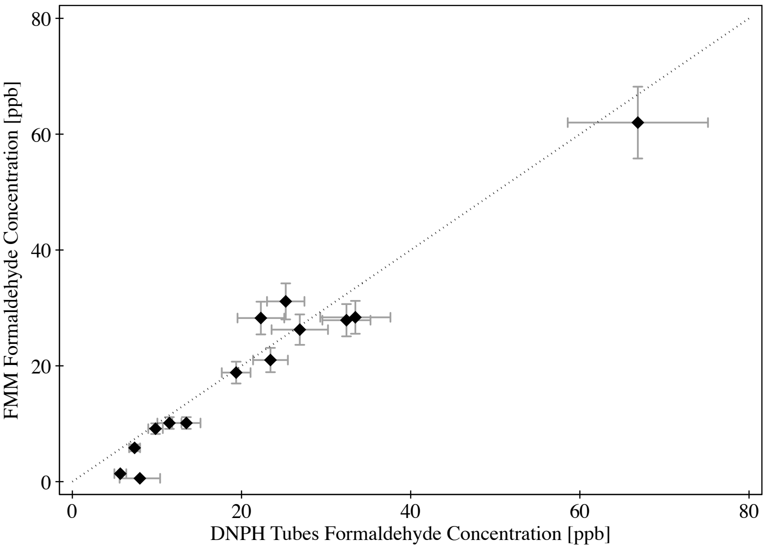

Figure 17: Parity plot of the results of the formaldehyde multimode monitor (FMM), averaged over four hours, versus collocated DNPH tubes. Note that the uncertainty displayed for the FMM formaldehyde concentrations below 20 ppb is assumed to be that published by the manufacturer for concentrations above 20 ppb.

Examination of the graph in Figure 6 indicates that the FMM tended to under report formaldehyde concentrations compared to DNPH results, but agreed well with DNPH results considering the uncertainties. A linear regression across all FMM measurements gave the following relationship (Equation 1), with a R^2 of 0.94.

$$C_{FMM} = 0.98\, C_{DNPH} - 1.35 \qquad \text{(Equation 1)}$$

Where:

C_{FMM} is the 4-hour average concentration as sampled by the FMM (ppb), and

C_{DNPH} is the concentration as sampled by DNPH tubes (ppb).

If the dataset is restricted to concentrations above the FMM's official detection limit of 20 ppb (7 out of 14 datapoints), a linear regression with DNPH results gives a slightly lower coefficient of fit of 0.83, and maintains a strong R^2 of 0.91. A similar analysis conducted by Carter et al. (2013) on concurrent FMM and DNPH measurements in chamber experiments for concentrations ranging from 5 to 50 ppb led to a similar coefficient of fit, with a R^2 of 0.98.

The FMM can be further used to provide relevant information on the daily variation of the formaldehyde concentration in stores. Figure 18 is the temporal profile of formaldehyde at two selected stores in Austin, TX over the course of three days. Variations of temperature and relative humidity measured by the FMM are also shown on the graphs. Most of the sampling occurred from a fixed location with the exception of a 4-hour period, noted *M**, during which the FMM was continuously moved across the sales floor to capture spatial variations in the stores.

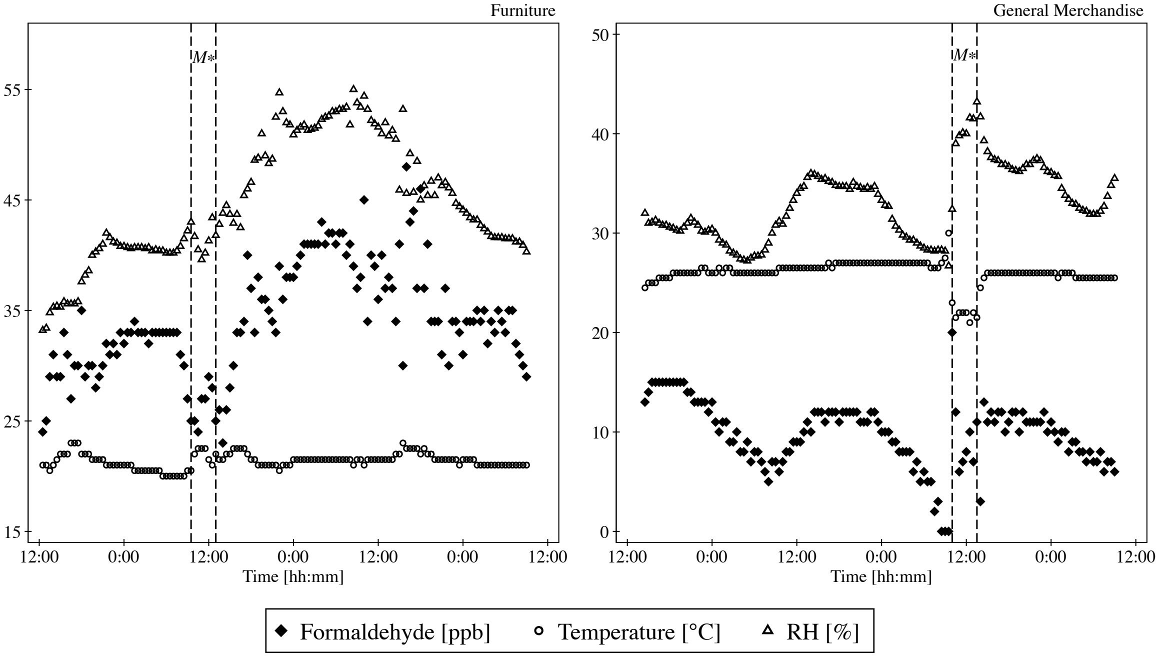

Figure 18: Temporal variations of formaldehyde concentrations, temperature and relative humidity (RH) monitored by the formaldehyde multimode monitors (FMM) for selected stores over the course of three days. On the abscissa, *12:00* refers to noon and *0:00* to midnight. Note that most of the monitoring occurred from a specific location on the sales floor (fixed sampling), but that the monitors were continuously moved through the sales floor for up to four hours (mobile sampling *M**).

At the furniture store, formaldehyde concentrations showed wide variations but no cyclical pattern, ranging from 23 ppb to 48 ppb, with a mean (SD) of 34 (5) ppb (Figure 18). Local concentration maxima were reached during nighttime and early mornings. Pressure sensors placed in rooftop units indicated that the ventilation system was cycling on and off overnight. This suggests that the air exchange rate was at its lowest at that time, allowing for the accumulation of formaldehyde in the store (Siegel et al., 2013). The formaldehyde concentration was lower during the mobile sampling event, suggesting that the air in the store may not have been well mixed, as the fixed sample location was situated in a corner of the store. This finding is also supported by separate mixing calculations from the tracer gas ventilation measurements (Siegel et al., 2013).

To further explore spatial variations at this store, a second FMM was placed in the store for three days. Since the furniture store was a building with two floors communicating trough a large open atrium, the two instruments were placed on different levels. Formaldehyde profiles for the two instrument followed roughly similar patterns of variation. The relative percent difference (RPD) was calculated to capture the difference between the two monitors over time, as the ratio of the absolute difference to the mean of concentrations at the two locations. The RPD ranged from 0 to 26%, with a mean (SD) of 7.9 (5)%. Although the mean RPD is within the instrument uncertainty, RPD values higher than 10% confirm temporary spatial variations of formaldehyde concentrations across both stories of the store.

The temporal profile of formaldehyde at the general merchandise store shows a cyclical pattern (Figure 18). Overall, concentrations averaged 9.8 ppb with a standard deviation of 3.3 ppb. Formaldehyde concentrations decreased in the morning, reaching a minimum around 9am every day, then increased steadily to reach their maximum in the afternoon. At the beginning of the mobile sampling period, the formaldehyde concentration peaked at 20 ppb but averaged 10 ppb over the 4-hour period, which was consistent with concentrations obtained at a similar time on previous days. It should be noted that all concentrations measured at this store were below the instrument's detection limit of 20 ppb. These readings were made possible thanks to a special software made available by the manufacturer, and are likely associated with a greater uncertainty.

At the furniture store, the temperature was relatively constant, ranging from 20ºC to 23ºC with a mean (SD) of 21.4 (0.7)ºC (Figure 18). However, the relative humidity (RH) varied widely, from 33.2% to 55%, in a pattern similar to the formaldehyde profile.

The formaldehyde concentration at the general merchandise also followed RH variations closely. This finding may be explained by the fact that pressed-wood products were likely the main sources of formaldehyde at both stores. Previous studies have shown that changes in temperature and relative humidity have significant impacts on formaldehyde emissions from various pressed-wood products (Andersen et al., 1975; Myers, 1985; van Netten et al., 1989; Parthasarathy et al., 2011). At the furniture store, displays and building materials were made out of pressed wood, while the general merchandise store had a section with large amounts of pressed-wood furniture.

Impact on Decision-Making

Each VOC collection and analysis technique was shown to produce a biased evaluation of the composition of the air sampled. Therefore, the choice of sampling approach can significantly affect decisions made by building operators on strategies to maintain an acceptable indoor air quality.

There is no consensus over what is acceptable indoor quality (Molhave et al., 1997). One approach is to restrict the concentrations of various contaminants believed to be associated with negative health effects. Many organizations set health guidelines for indoor environments, however these are mostly for industrial settings. The California Office of Environmental Health Hazard Assessment (OEHHA) publishes recommended exposure limits (RELs) for 99 gas-phase contaminants (OEHHA, 2014). The ASHRAE literature (e.g. Performance Measurement Protocols for Commercial Building, chapters of the ASHRAE Handbook) commonly refers to ASHRAE Standard 62.1, “Ventilation for acceptable indoor air quality” (ASHRAE, 2009, 2013). In this standard, an informative appendix gives a subset of air quality guidelines for various exposure durations set by OEHHA and by the Agency for Toxic Substances and Disease Registry (ASTDR). The

Leadership in Energy & Environmental Design (LEED) rating system for green buildings includes indoor environmental quality credits, and recently developed a compliance alternative path (EQpc68) establishing minimum standards for indoor air quality (USGBC, 2013). The concentration limits for 33 VOCs found in EQpc68 are also a subset of OEHHA chronic (1-year average) guidelines. For these reasons, the following analysis will be conducted with the strictest guidelines introduced in the ASHRAE 62.1 Standard, and with LEED EQpc68 guidelines (SI 4). It should be noted that none of the store sampled intended to comply with these guidelines, and the comparison is conducted here for illustrative purposes.

Assessing Exposure to VOCs with CAN, SOR and PID.

There were fifteen exceedances of either LEED EQpc68 or ASHRAE 62.1 guidelines (Table 12), four of which were observed in CAN samples and fourteen in SOR samples (including four in both measurements). All compounds other than naphthalene were part of the CAN target list.

Table 12: Exceedances of VOC concentration limits referenced by LEED EQpc68 and ASHRAE 62.1 in SOR and CAN samples.

			LEED EQpc68			ASHRAE 62.1		
Compound	**C_{SOR} [ppb]**	**C_{CAN} [ppb]**	**C_{ref} [ppb]**	**Exc. in SOR**	**Exc. in CAN**	**C_{ref} [ppb]**	**Exc. in SOR**	**Exc. in CAN**
Benzene	8.3 ± 8.3	0.8 ± 0.2	18.8			3[a]	X	
Toluene	158.5 ± 158.5	18 ± 5.4	79.6	X		79.6[b]	X	
Xylenes	181.4 ± 140	22.9 ± 5.6	161.2	X		50[a]	X	
Tetrachloroethene	64.8 ± 64.8	45 ± 13.5	5.2	X	X	5.2[b]	X	X
Tetrachloroethene	4.4 ± 4.4	7.8 ± 2.3	5.2		X	5.2[b]		X
Tetrachloroethene	17.3 ± 17.3	*ND*	5.2	X		5.2[b]	X	
Naphthalene	1.1 ± 1.1	*ND*	1.7			0.7[a]	X	
Naphthalene	2.2 ± 1.6	*ND*	1.7	X		0.7[a]	X	
Naphthalene	2.3 ± 2.3	0.7 ± 0.2	1.7	X		0.7[a]	X	X
Naphthalene	1.5 ± 1.5	*ND*	1.7			0.7[a]	X	
Naphthalene	1.3 ± 1	*ND*	1.7			0.7[a]	X	
Naphthalene	1.3 ± 0.9	*ND*	1.7			0.7[a]	X	
Naphthalene	0.8 ± 0.2	0.2 ± 0.1	1.7			0.7[a]	X	
Naphthalene	0.7 ± 0.7	*ND*	1.7			0.7[a]	X	
Naphthalene	1.9 ± 1.9	1.6 ± 0.5	1.7	X		0.7[a]	X	X

[a]: ATSDR MRL Chronic.

[b]: CA OEHHA REL Chronic.

Sorbent tubes samples were the only testing technique where benzene, toluene, and xylenes were measured at concentrations exceeding their exposure limit. There were three exceedances of both guidelines for tetrachloroethylene (PCE): one detected by both sampling techniques, one observed in a CAN sample only, and one in a SOR sample only. Naphthalene concentrations were measured above the LEED EQpc68 guideline by sorbent tubes alone three times. Out of the nine exceedances of the ASHRAE 62.1 guideline for naphthalene, the two sampling approaches agreed twice. The remaining seven exceedances were observed in SOR samples only. This finding may be partially explained by the fact that naphthalene was the only compound with concentrations measured above health guidelines in this investigation that was not part of the CAN target list. Therefore, naphthalene may have been captured by Summa canisters but not been reported because napthtalene concentrations were lower compared to the 20 largest peaks identified by a library search in these samples. There were no other exceedances of the OEHHA chronic RELs.

Overall, more exceedances were observed in sorbent tube samples. Depending on the sampling technique chosen, the number of spaces with unacceptable levels of VOCs (excluding formaldehyde) varies from 3 to 10. These results suggest that naphthalene should be added to the CAN target list when used for similar investigations.

The PID does not provide information on the speciation of the air sampled, and therefore does not allow for comparison to exposure limits. Based on the inconsistency of the measure, most of the scientific community agrees not to set target concentrations for TVOC concentrations (Molhave et al., 1997, ASHRAE, 2013). The LEED (v4) credit 3.2 (indoor air quality assessment after construction: USGBC, 2014) sets a guideline for TVOC concentrations at 500 µg/m3. However, there is no specific definition of TVOC in the credit, and not all testing methods recommended for use (e.g., US EPA, 1999a and 1999b) mention how to calculate TVOC concentrations. Moreover, PID results would not qualify for comparison with this guideline, as real-time devices are not part of the testing methods recommended in the LEED credit. The PID is recommended for use as a screening tool for sensory effects at most by Molhave (2003). However, as seen in Figure 16, continuous measurements of TVOC concentrations by the PID can be necessary to identify the time of critical exposure.

Assessing Exposure to Formaldehyde with DNPH and FMM

Parametric (paired t-test) and non-parametric (Wilcoxon signed rank sum test) tests performed on formaldehyde concentrations obtained by DNPH tubes and the FMM indicate that results from both techniques were not significantly different (p=0.108 and p=0.084, respectively). However, if one considers the most conservative guideline for formaldehyde set by OEHHA at 7.3 ppb for chronic (24-hour average) and occupational exposure (8-hour average), then 11 out of the 14 samples exhibit exceedances when looking at the FMM results, as opposed to 13 out of 14 according to the DNPH results. Conversely, the FMM indicated more exceedances of the LEED EQpc68 limit of 27 ppb than the DNPH tubes, 5 vs. 3, respectively. However, both methods point to the same spaces as being in non-attainment when considering the Federal Emergency Management Agency (FEMA) and NIOSH chronic guideline of 16 ppb. Based on these findings, it appears that both methods could lead to similar assessments of indoor air quality if FMM readings below 20 ppb are made available to all, depending on the reference concentration chosen.

This analysis, because it is based on average FMM results, fails to take advantage of the information given by the FMM on temporal and spatial variations of formaldehyde concentrations. For instance, formaldehyde concentrations shown in Figure 18 for the furniture store are consistently above the OEHHA chronic and occupational REL (7.3 ppb) and the NIOSH and FEMA chronic REL (16 ppb), as were the average FMM and the DNPH tube concentrations during the mobile sampling period. However, three concentrations measured by the FMM also exceeded the acute (1-hour average) OEHHA REL (44.8 ppb). This exceedance was missed by the DNPH tubes because of the time of sampling selected. Conversely, for the general merchandise store in Figure 18 the DNPH sampling occurred during the time of maximum concentrations. DNPH and FMM formaldehyde concentrations exceeded the CA OEHHA chronic and 8-hour average during mobile sampling. However, continuous measurements of formaldehyde by the FMM indicate that the store was not consistently in non-attainment over the three days of sampling (78% of the time). This suggests both the importance of selecting sampling time and possible opportunities to adjust ventilation strategies when considering this contaminant.

CONCLUSION

This study demonstrated the impact of the instrumentation chosen on the identification and quantification of VOCs during up to 30 test visits at fourteen retail stores in Texas and central Pennsylvania. Sampling with Tenax GR-sorbent tubes was more field-intensive but revealed more exceedances of health guidelines compared to Summa canister samples, all of which were observed in general merchandise and home improvement stores. The TVOC concentration measured by the photoionization detector (PID) was not directly correlated to Summa canisters results, even after correction. No standard mixture correction factor was found across store type. More agreeable results can only be expected if the PID is targeted to measure a subset of compounds for which the instrument is specifically calibrated. Even though the formaldehyde multimode monitor (FMM) was strongly correlated to the DNPH tubes results, the two sampling techniques did not agree on exceedances of the OEHHA chronic recommended exposure limit at two stores.

Findings of this investigation suggested the sampling approach for VOCs could determine compliance with green building standards for VOC concentrations, emphasizing the need to identify potential contaminants of concern before selecting the proper collection and analysis technique. Promising characteristics of the FMM were highlighted, supporting its further consideration as an indicator to control ventilation and/or environmental parameters.

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REFERENCES

Andersen, I. B., Lundqvist, G. R., and L. Molhave. 1975. Indoor air pollution due to chipboard used as a construction material. Atmospheric Environment 9:1121–1127.

ASHRAE. 2009. Chapter 10: Indoor Environmental Health, In 2009 ASHRAE Handbook - Fundamentals. Atlanta, GA: American Society of Heating, Refrigerating, and Air Conditioning Engineers, Inc.

ASHRAE. 2010. Performance Measurement Protocols for Commercial Building. Atlanta, GA: American Society of Heating, Refrigerating, and Air Conditioning Engineers, Inc.

ASHRAE/ANSI. 2013. Standard 62.1: Ventilation for acceptable indoor air quality. Atlanta, GA: American Society of Heating, Refrigerating, and Air Conditioning Engineers, Inc.

ASTM International. 2007. Standard test method for determination of volatile organic chemicals in atmospheres (canister sampling methodology). D54661. West Conshohocken, PA: ASTM International.

ASTM International. 2009a. Standard practice for selection of sorbents, sampling, and thermal desorption analysis procedures for volatile organic compounds in air. D6196. West Conshohocken, PA: ASTM International.

ASTM International. 2009b. Standard test method for determination of formaldehyde and other carbonyl compounds in air (active sampler methodology). D5197. West Conshohocken, PA: ASTM International.

Batterman, S., Zhang, G., and M. Baumann. 1998. Analysis and stability of aldehydes and terpenes in electropolished canisters. Atmospheric Environment 32:1647–1655.

Brymer, D.A., Ogle, L.D., Jones, C.J. and D.L. Lewis. 1996. Viability of using SUMMA polished canisters for the collection and storage of parts per billion by volume level volatile organics. Environmental Science and Technology 30:188–195.

Carter, E. M., Jackson, M. C., Katz, L. E., and G.E. Speitel. 2013. A coupled sensor-spectrophotometric device for continuous measurement of formaldehyde in indoor environments. Journal of Exposure Science and Environmental Epidemiology 1–6.

Coy, J. D., Bigelow, P. L., Buchan, R. M., Tessari, J. D., and J.O. Parnell. 2000. Field evaluation of a portable photoionization detector for assessing exposure to solvent mixtures. AIHAJ-American Industrial Hygiene Association 61:268–274.

Dobos, R. T. 2000. Field investigation comparing diffusion badge and charcoal tube monitoring for styrene, Applied occupational and environmental hygiene 15:673–676.

Dutton, S. M., Chan, W., Mendell, M. J., Barrios, M., Parthasarathy, S., Sidheswaran, M. A., Sullivan, P. S., Eliseeva, K., and W. J. Fisk. 2013. Evaluation of the indoor air quality procedure for use in retail buildings. Berkeley, CA: Ernest Orlando Lawrence Berkeley National Laboratory.

Haag, W. R. 2005. Rapid, continuous TVOC measurements using ppb-level PIDs. In: Proceedings for the conference Indoor Air 2005.

Harper, M. 2000. Sorbent trapping of volatile organic compounds from air. Journal of Chromatography A 885:129–151.

Kim, J. T. 2012. Sustainable and healthy buildings. Energy and Buildings 46:1–2.

Kim, K., Lee, J., Hong, Y., and Y. Choi. 2005. Evaluation of a PID-based portable detection system for TVOC as an indoor pollution analyzer. In: Proceedings for the conference Indoor Air 2005.

Kumar, A., and I. Viden. 2005. Simultaneous use of tube and canister system for sampling of volatile organic compounds (VOCs) in the atmosphere. 2076–2080. In: Proceedings for the conference Indoor Air 2005.

Molhave, L. 2003. Organic compounds as indicators of air pollution. Indoor Air 13:12–19.

Molhave, L., Clausen, G., Berglund, B., Ceaurriz, J. D. E., Kettrup, A., Lindvall, T., Maroni, M., Pickering, A. C., Risse, U., Rothweiler, H., Seifert, B., and M. Yunes. 1997. Total volatile organic compounds (TVOC) in indoor air quality investigations. Indoor Air 7(4):225–240.

Myers, G. E. 1985. The effects of temperature and humidity on formaldehyde emission from UF-bonded boards: a literature critique. Forest Products Journal 9:20–31.

Nazaroff, W. W., and C. J. Weschler. 2004. Cleaning products and air fresheners: exposure to primary and secondary air pollutants. Atmospheric Environment 38:2841–2865.

Nielsen, G. D., Larsen, S. T., and P. Wolkoff. 2012. Recent trend in risk assessment of formaldehyde exposures from indoor air. Archives of Toxicology 87:73–98.

Nirlo, E. L., Crain, N., Corsi, R. L., and J. A. Siegel. 2014. Volatile organic compounds in fourteen retail stores. Indoor Air. Published online March 15, 2014.

Norback, D., Björnsson, E., Janson, C., Widström, J., and G. Boman. 1995. Asthmatic symptoms and volatile organic compounds, formaldehyde, and carbon dioxide in dwellings. Occupational and environmental medicine 52:388–395.

Office of Environmental Health Hazard Assessment. 2014. All OEHHA acute, 8-hour and chronic reference exposure levels (chRELs) as of January 2014, www.oehha.ca.gov. http://oehha.ca.gov/air/allrels.html, January 27, 2014.

Parthasarathy, S., Maddalena, R. L., Russell, M. L., and M. G. Apte. 2011. Effect of temperature and humidity on formaldehyde emissions in temporary housing units, Journal of the Air & Waste Management Association 61:689–695.

Pfeffer, H.-U., and L. Breuer. 2000. BTX measurements with diffusive samplers in the vicinity of a cokery: Comparison between ORSA-type samplers and pumped sampling, Journal of Environmental Monitoring 2:483–486.

Pratt, G. C., Bock, D., Stock, T. H., Morandi, M. T., Adgate, J. L., Ramachandran, G., Mongin, S. J., and K. Sexton. 2005. A field comparison of volatile organic compound measurements using passive organic vapor monitors and stainless steel canisters, Environmental Science & Technology 39:3261–3268.

Siegel, J. A., Srebric, J., Crain, N., Nirlo, E. L., Zaatari, M., Hoisington, A., Urquidi, J., Shu, S., Kim, Y. S., and D. Jareemit. 2013. ASHRAE RP-1596: Ventilation and indoor air quality in retail stores. Atlanta, GA: American Society of Heating, Refrigerating, and Air Conditioning Engineers, Inc.

Spengler, J., and Q. Chen. 2000. Indoor air quality factors in designing a healthy building. Annual Review of Energy and the Environment 25:567–600.

Stock, T. H., Morandi, M. T., Pratt, G. C., Bock, D., and J. H. Cross. 1999. Comparison of the results of VOC monitoring with diffusive samplers and canisters. Indoor Air 99:443-448.

Teichman, K., Persily, A. K., and S. J. Emmerich. 2013. Indoor Air Quality in High-Performing Building Case Studies: A Wealth of Intent, A Dearth of Data. High Performing Buildings 34–43.

Uhde, E., and T. Salthammer. 2007. Impact of reaction products from building materials and furnishings on indoor air quality—A review of recent advances in indoor chemistry. Atmospheric Environment 41:3111–3128.

US Department of Labor. 2014a. Retail trade: NAICS 44-45, www.bls.gov. http://www.bls.gov/iag/tgs/iag44-45.htm, January 3, 2014.

US Department of Labor. 2014b. American Time Use Survey: Purchasing Goods and Services, www.bls.gov. http://www.bls.gov/tus/current/purchasing.htm, January 3, 2014.

US EPA and NIOSH. 1991. Building Air Quality: A Guide for Building Owners and Facility Managers - Appendix A: Common IAQ Measurements: A General Guide, EPA 402-F-91-102, 109-119.

US EPA. 1999a. Compendium Method TO-15, Center for Environmental Research Information Office of Research and Development, U.S. Environmental Protection Agency Cincinnati, OH 45268.

US EPA. 1999b. Compendium Method TO-17, Center for Environmental Research Information Office of Research and Development, U.S. Environmental Protection Agency Cincinnati, OH 45268.

US EPA. 1999c. Compendium Method TO-11A, Center for Environmental Research Information Office of Research and Development, U.S. Environmental Protection Agency Cincinnati, OH 45268.

US EPA. 2003. A standardized EPA protocol for characterizing indoor air quality in large office buildings. Washington, DC: U.S. Environmental Protection Agency.

US EPA. 2013. VOC definition, www.epa.gov. http://www.epa.gov/iaq/voc2.html#definition, April 1, 2013

US Green Council Building. 2013. LEED pilot credit EQpc68: Indoor air quality procedure - alternative compliance path, www.usgbc.org. http://www.usgbc.org/node/2616403?return=/pilotcredits, January 1, 2014

US Green Council Building. 2014. LEED v4 credit: Indoor air quality assessment, www.usgbc.org.

http://www.usgbc.org/node/2614245?return=/credits/retail---new-construction/v4/indoor-environmental-quality, April 8, 2014

van Netten, C., Shirtliffe, C., and J. Svec. 1989. Temperature and humidity dependence of formaldehyde release from selected building materials. Bulletin of Environmental Contamination and Toxicology 42:558–565.

Wai-mei Sin D., Wong Y. C., Sham W. C., and D. Wang. 2001. Development of an analytical technique and stability evaluation of 143 C3–C12 volatile organic compounds in Summa canisters by gas chromatography–mass spectrometry. Analyst. 126(3):310–321.

Wallace, L. A. 1991. Comparison of risks from outdoor and indoor exposure to toxic chemicals. Environmental Health Perspectives 95:7-13.

Wolkoff, P. 2013. Indoor air pollutants in office environments: Assessment of comfort, health, and performance. International Journal of Hygiene and Environmental Health 216:371–394.

World Health Organization. 2010. WHO guidelines for indoor air quality: selected pollutants. Copenhagen, Denmark: WHO Regional Office for Europe.

Zaatari M., Nirlo E.L., Jareemit D., Crain N., Srebric J., and J. A. Siegel. 2014. Ventilation and indoor air quality in retail stores: A critical review (RP-1596). HVAC&R Research 20:276–94.

SUPPORTING INFORMATION

SI 1: Quality assurance/quality control

To ensure the high quality of the VOC measurements conducted, a robust quality assurance program was developed. Quality assurance controls such as instrument calibration, calibration check standards, replicate samples, field and laboratory blanks, and instrument co-location were employed. Additionally, EPA certified commercial laboratories were used where possible. The quality assurance methods used for this study are presented below.

1. VOCs - Summa Canisters

VOC samples collected using summa canisters were analyzed by Centek Laboratories, Syracuse, NY and EMSL Analytical Chicago, IL. EMSL Analytical analyzed 35 of 39 canisters. The quality controls employed at EMSL are summarized in Table 13. Similar controls were employed at Centek Laboratories.

Table 13: Quality Controls for EMSL Analytical – TO-15 Laboratory

QC Description	Frequency	QC Acceptance Limits
Internal standard (IS) injection	First injection of every 24 hr sequence	Area response must be within ± 40% of the mean area response of the IS in the most recent valid calibration
Continuing calibrations	Immediately following the Internal Standard injection	100% of the target list compounds must have recoveries of 70 to 130%
Reporting limit standard of 0.5 ppbv	Once every 24 hour sequence	90% of compounds must have recoveries of 60-140%
Method blank	Every sequence prior to analyzing samples	All target compounds must be <0.5 ppbv with the following exceptions: propylene and para and meta xylene <1.0 ppbv
Initial calibration (5-6 points)	As needed when continuing calibration does not pass of after maintenance	All compounds must have a %RSD < 30% with 2 target compounds allowed up to a 40% RSD
Initial calibration verification standard	Immediately following initial calibration	90% of target compounds must have recoveries of 70 to 130%
Internal standard	Included in every injection	Response area upper limit < 140% of daily 10 ppbv calibration level of IS Response area lower limit 60% of daily 10 ppbv calibration level of IS Retention time upper limit +0.33 min of daily 10 ppbv calibration level of IS Retention time lower limit -0.33 min of daily 10 ppbv calibration level of IS
Summa canister batch certification following cleaning	1 composite can from batch must be analyzed after passing leak check	All target compounds must have concentrations <0.2 ppbv except for ethanol, isopropyl alcohol and acetone, which must be <0.5ppbv.

In addition to the laboratory quality controls, 5 replicate Summa canisters were collected. The relative variance between the samples was calculated for each of the fifteen categories of VOCs monitored for this study. The relative difference was calculated using Equation 1.

$$\text{Relative Variance} = \frac{\left|rep1 - rep2\right|}{\frac{rep1 + rep2}{2}} \times 100 \qquad \text{(Eq. 1)}$$

where
rep1 = the cumulative molar concentration for VOC category$_i$ measured in canister 1, and
rep2 = the cumulative molar concentration for VOC category$_i$ measured in canister 2
If rep1=0 and rep2≠0, rep1 is replaced by half the detection limit (0.5ppbv).
If rep1=0 and rep2=0, the percentage is set non-detect (ND).

The results of these calculations for categories 3 through 14 along with the cumulative statistics can be found in Table 14.

Table 14: Relative variance (%) between VOC category concentrations in replicate Summa canisters.

		VOC Categories[a]												Cumulative Statistics			
Site	**Test**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**Mean**	**SD**	**Min**	**Max**
OhT	18	20.0	13.2	2.2	13.6	35.3	14.6	22.2	5.1	ND	ND	ND	24.0	16.7	10.1	2.2	35.3
MbP4	22	ND	2.4	6.9	11.8	36.4	3.0	25.4	16.4	6.7	28.6	18.2	41.5	17.9	13.5	2.4	41.5
MiPI	23_2	19.2	0.7	ND	ND	81.7[b]	6.0	0.3	ND	4.3	ND	ND	ND	18.7	31.6	0.3	81.7
MiP	23_4	7.4	13.3	8.3	ND	ND	31.6	14.2	2.9	0.6	ND	ND	95.1	21.7	31.1	0.6	95.1
MiTi	24_2	60.4	11.6	37.3	ND	16.7	35.3	28.9	3.8	33.5	29.5	ND	119.1	37.6	32.6	3.8	119.1

[a] VOC categories: 3=ethanol, 4=non-halogenated alkanes, 5=acetone, 6=total terpenoids, 7=acetonitrile, 8=isopropanol, 9=C4-C10 carbonyls, 10=BTEXS, 11=halogenated alkanes, 12=non-BTEXS aromatics, 13=C4 or greater alcohols, and 14=other. Categories 1 (formaldehyde) and 2 (acetaldehyde) were omitted.
[b] The concentration of the VOC category in one of the replicates was non-detect. For these calculations the concentration was assumed to be half the detection limit (DL=0.5ppb).

2. VOCs – Sorbent Tubes

VOC samples collected using sorbent tubes were analyzed at The University of Texas at Austin. All samples were analyzed using BFB as an internal standard. The relative standard deviation for the response area of the IS for 132 of the samples analyzed was ± 16%. In addition to monitoring the response area for the IS, 8 replicate samples were collected. The relative variance between the samples was calculated for thirteen of the fifteen categories of VOCs monitored for this study using Equation 1. The results for the other two categories, formaldehyde and acetaldehyde are presented in section 4. The results of these calculations along with the cumulative statistics for the calculations can be found in Table 15.

Table 15: Relative variance (%) between VOC category concentrations in replicate sorbent tubes.

		VOC Categories[a]												Cumulative Statistics			
Site	**Test**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**Mean**	**SD**	**Min**	**Max**
MbT1	3	ND	14.0	ND	14.0	ND	ND	18.2	5.7	ND	21.5	30.6	22.6	18.1	7.9	5.7	30.6
FfP	16	ND	1.5	ND	ND	ND	ND	1.4	1.0	ND	ND	27.9	9.1	8.2	11.5	1.0	27.9
MbP3	17	191.39[b]	5.0	ND	ND	ND	ND	95.0	3.9	ND	32.5	36.1	10.1	53.4	68.5	3.9	191.4
MbT4	19	ND	6.3	ND	13.8	ND	ND	3.4	11.9	ND	11.0	4.3	3.7	7.8	4.4	3.4	13.8
MiTI	24_1	ND	19.1	ND	ND	ND	3.8	11.3	0.9	ND	7.7	5.9	11.4	8.6	6.0	0.9	19.1
MiTI	24_2	179.36[b]	60.4	ND	ND	ND	162.8[b]	14.1	8.0	ND	9.3	110.2	25.8	71.2	70.6	8.0	179.4
MiT	24_3	ND	191.7[b]	ND	7.2	ND	ND	19.3	0.8	ND	ND	4.3	7.6	38.5	75.3	0.8	191.7
MiT	24_4	ND	6.8	ND	ND	ND	183.4[b]	9.5	29.4	ND	88.2	5.1	18.2	48.7	66.1	5.1	183.4

[a] VOC categories: 3=ethanol, 4=non-halogenated alkanes, 5=acetone, 6=total terpenoids, 7=acetonitrile, 8=isopropanol, 9=C4-C10 carbonyls, 10=BTEXS, 11=halogenated alkanes, 12=non-BTEXS aromatics, 13=C4 or greater alcohols, and 14=others. Categories 1 (formaldehyde) and 2 (acetaldehyde) were omitted.

[b] The concentration of the VOC category in one of the replicates was non-detect. For these calculations the concentration was assumed to be half the detection limit (DL=2.0 ng).

3. VOCs – Photoionization Detector

Prior to each use, the PID was calibrated using procedure and calibration gases supplied by the manufacturer. Following calibration, a verification standard was processed and the results recorded. The relative variance between the PID response and the concentration of the calibration gas was calculated using an equation similar to Equation 1. The results for these calculations are shown in Table 16.

Table 16: Relative variance (%) between the PID response and the concentration of the calibration gas

QC Description	Mean	Standard Deviation	N
UT initial calibration verification standard	0.2	0.3	10
UT continuing calibration verification standard	7.9	7.7	5
PSU initial calibration verification standard	1.2	0.9	10

4. Aldehydes – DNPH Tubes

EMSL Analytical Chicago, Illinois and Bureau Veritas, Novi, Michigan analyzed the DNPH tubes collected for this study. 39 of the 45 samples were analyzed by Bureau Veritas. The quality controls employed by Bureau Veritas are summarized in Table 17. Similar quality controls were employed by EMSL.

Table 17: Quality Control Bureau Veritas – TO 11A Laboratory

QC Description	Frequency	QC Acceptance Limits
Initial calibration (3 to 5 points)	Until failure or machine maintenance	
Method blank	Prior to each sampling sequence	Reporting and 3 times the reporting limit depending on the samples
Laboratory control spike batch	For every preparation	Recovery for acetaldehyde 83 to 103% Recovery for formaldehyde 85 to 103%
Duplicate laboratory control spike	For every preparation	Recovery for acetaldehyde 83 to 103% Recovery for formaldehyde 85 to 103%
Continuing calibration verification standard	Every 10 injections	±10% from theoretical
Reporting level spike	Once per sampling sequence	Recovery ±50% reporting limit

The uncertainty for DNPH analysis reported by Bureau Veritas was ± 12.4% for formaldehyde, and ± 14.4% for acetaldehyde.

In addition to the quality controls maintained by Bureau Veritas, 12 replicate DNPH tubes were collected as a part of this study. The relative variance in concentrations between the samples was calculated for formaldehyde and acetaldehyde using Equation 1. The results of these calculations can be found in Table 18.

Table 18: Relative variance (%) between formaldehyde and acetaldehyde concentrations in replicate DNPH tubes

Site	Test	Formaldehyde	Acetaldehyde	Mean
ScP	4	7.0	2.5	4.8
FfT1	8	12.3	ND	12.3
FfP	16	9.3	13.1[a]	11.2
MbP3	17	10.0	0.4	5.2
EgP2	20	0.4	ND	0.4
GeP	21	18.9	12.4	15.6
MbP4	22	11.0	1.8	6.4
MiPI	23_2	6.8	ND	6.8
MiP	23_3	3.7	ND	3.7
MiP	23_4	10.6	ND	10.6
MiTI	24_2	7.1	ND	7.1
MiT	24_4	6.5	ND	6.5

[a] The concentration of one of the replicates was non-detect. For these calculations the concentration was assumed to be half the detection limit. Formaldehyde DL=100ng and acetaldehyde DL = 500ng.

5. Aldehydes – Formaldehyde Monitors

Shinyei Formaldehyde Multimode Monitors were also used for a portion of this study. When two monitors were available, the pair of Shinyei monitors was collocated with each other. The relative variance between the monitors was calculated for formaldehyde and acetaldehyde using Equation 1. The results of these calculations can be found in Table 19.

Table 19: Relative variance (%) between formaldehyde concentrations in collocated monitors.

Concentration Range	Mean	Standard Deviation	Number of Hours of Collocation
< 20 ppb	36	38	62
≥ 20 ppb	9	9	249

SI 2: Data analysis: detection of outliers

The detection of outliers for time series data is a complex issue. Outliers generally occurred following a temporary movement or misuse of the instrument, power failures or problems in the logging process. For every test, data points where the concentration was above the overall mean plus three standard deviations were flagged as potential outliers. The data points were then rejected after a visual check confirming their outlier status. Table 20 lists the number of outliers detected per test for the PID. Outliers represent less than 2% of the data collected in every site.

Table 20: Outliers for the photoionization detectors (PIDs).

Test	Location	Num. of data points	Num. of outliers	Outlier detection technique
4	indom	57	1	> overall mean+3SD
5	indof	778	1	> overall mean+3SD
6	indof	279	1	> overall mean+3SD
7	indom	10	1	> overall mean+3SD
10	indof	295	1	> overall mean+3SD
12	indof	558	4	> overall mean+3SD
13	indof	1018	3	> overall mean+3SD
15	indof	823	2	> overall mean+3SD
17	indom	49	1	> overall mean+3SD
18	indom	51	1	> overall mean+3SD
19	indom	48	1	> overall mean+3SD
21	indof	233	5	> overall mean+3SD
21	indom	47	1	> overall mean+3SD
24	indof	4061	1	> overall mean+3SD

Outliers in the ozone data arose from power failures and problems in the logging process. For every test, data points where the concentration was above the overall mean plus three standard deviations, or below the overall mean minus three standard were flagged as potential outliers. As the ozone data can be highly variable over time, the process was repeated on local section of the data that exhibited less variability. The data points were then rejected after a visual check confirming their outlier status. Table 21 lists the number of outliers detected per test for the ozone data. Outliers represent less than 2.5% of the data collected in every site. When outdoor ozone concentrations were obtained from the Texas Commission on Environmental Quality (TCEQ) or the Pennsylvania Department of Environmental Protection (PA DEP), the data was not further analyzed for outliers as those institutions publish certified data.

Table 21: Outliers for the ozone monitors:

Test	Location	Num. of data points	Num. of outliers	Outlier detection technique
1	indof	860	1	> overall mean+3SD
2	indof	270	2	> overall mean+3SD
2	outdr	866	8	< local mean-3SD
6	indof	540	2	> local mean+3SD
9	indof	818	2	> overall mean+3SD
10	indof	612	1	> overall mean+3SD
10	outdr	45	1	< overall mean-3SD
12	indof	613	1	> overall mean+3SD
13	indof	1120	1	> overall mean+3SD
18	indof	333	1	> local mean+3SD
19	indof	820	2	> local mean+3SD
20	indof	224	1	> local mean+3SD
22	indof	1141	1	> local mean+3SD
23	indof	3137	1	> overall mean+3SD

No outliers were detected in the data collected by the formaldehyde multimode monitors.

SI 3: Calculations of mixture correction factors

PID results are compared to a TVOC concentration calculated by summing the individual concentrations obtained by the Summa canisters (C_{CAN}^{TVOC}) and to an estimated TVOC concentration calculated by combining Summa canister and the sorbent tubes results ($C_{estimated}^{TVOC}$). Further comparisons are conducted using PID TVOC concentrations adjusted to the specific air mixture sampled. Mixture correction factors (CF_{mix}) are calculated for each sample using mole fractions determined by Summa canisters, and by the estimated air mixture.

There is no standard method to estimate the concentration of total volatile organic compounds. The PID results will first be compared to a TVOC concentration calculated by summing the individual concentrations obtained by the Summa canisters, C_{CAN}^{TVOC}. In an attempt to get a more comprehensive assessment of the air mixture composition at the time of sampling, and to circumvent some of the issues encountered with Summa canister sampling, the Summa canister and the sorbent tubes results are then combined using the following equation to calculate an estimated TVOC concentration (Equation 1).

$$C_{estimated}^{TVOC} = \sum_{i|C_{SOR}^{i}=0} C_{CAN}^{i} + \sum_{j|C_{CAN}^{j}=0} C_{SOR}^{j} + \sum_{k|C_{CAN}^{k}\neq C_{SOR}^{k}\neq 0} \max(C_{CAN}^{k}, C_{SOR}^{k}) \qquad \text{(Equation 1)}$$

Where:

$C_{estimated}^{TVOC}$ is the estimated TVOC concentration (ppb),

C_{CAN} is the concentration of a compound as measured in the CAN samples (ppb),

C_{SOR} is the concentration of a compound as measured in the SOR samples (ppb),

i refers to compounds that were not detected in the SOR samples,

j refers to compounds that were not detected in the CAN samples, and

k refers to compounds that were detected in both CAN and SOR samples.

The biases introduced by the use of C_{CAN}^{TVOC} and $C_{estimated}^{TVOC}$ as bases for comparison of the PID results will be discussed in the results section.

Since the PID was used in parallel with other techniques that characterize individual compounds, the PID TVOC concentration can be adjusted to the specific air mixture sampled. Correction factors for many individual compounds have been determined by the PID manufacturer (RAE Systems, 2010), and can be combined to obtain the correction factor for a mixture according to Equation 2.

$$CF_{mix} = \frac{1}{\frac{x_1}{CF_1} + \frac{x_2}{CF_2} + \ldots + \frac{x_i}{CF_i}} \qquad \text{(Equation 2)}$$

Where:

CF_{mix} is the correction factor for a mixture [-],

$x_1, x_2, \ldots, x_i$ are the mole fractions of each component of the mixture [-], and

CF_i is the correction factor for compound *i* of the mixture [-].

First, the mole fractions are calculated from the CAN results. Since a correction factor has not been determined for some compounds detected and quantified by the Summa canisters, the mole fractions are calculated in regards to the sum of VOCs for which correction factors are known, instead of to C_{CAN}^{TVOC} (Equation 3). For 22 out of 27 samples, VOCs without a correction factor represent less than 20% on a molar basis of all the compounds detected in the CAN samples. Therefore, this approximation is believed have limited impact on the present analysis for most of the sampling events. For the remaining 5 samples, compounds without a correction factor account for 42 to 65% of all VOCs on a molar basis, and these findings should be interpreted with caution.

$$x_i = \frac{C^{i}_{CAN}}{\sum_{j|\exists CF_j} C^{j}_{CAN}} \qquad \text{(Equation 3)}$$

The mixture correction factor obtained, $CF_{mix(CAN)}$, is then applied to the averaged PID TVOC concentration as seen in Equation 4 to obtain the averaged PID TVOC concentration corrected-to-Summa canisters, $\overline{C}^{TVOC,corr-to-CAN}_{PID}$.

$$\overline{C}^{TVOC,corr-to-CAN}_{PID} = \overline{C}^{TVOC}_{PID} \cdot CF_{mix(CAN)} \qquad \text{(Equation 4)}$$

A similar analysis (Equations 2 – 4) is conducted using the estimate of the air mixture introduced in Equation 1 to calculate mixture correction factors and obtain an average PID TVOC concentration corrected-to-estimated air mixture, $\overline{C}^{TVOC,corr-to-est}_{PID}$.

SI 4: List of compounds found in this investigation, on target list for TO-15 and TO-17 analyses, and for which various health guidelines are available

COMPOUND	FOUND IN SOR	FOUND IN CAN	TO17 EAS Target List	TO15 EPA Target List	TO15 EMSL Target List	LEED EQpc68 List	ASHRAE 62.1	OEHHA RELs
1,4-Dichlorobenzene	X	X	X	X	X	X	X	X
Acetaldehyde	X	X		X		X	X	X
Benzene	X	X	X	X	X	X	X	X
Carbon disulfide		X	X	X	X	X	X	X
Carbon tetrachloride	X	X	X	X	X	X	X	X
Chloroform		X	X	X	X	X	X	X
Ethylbenzene	X	X	X	X	X	X	X	X
Formaldehyde				X		X	X	X
Hexane	X	X	X	X	X	X	X	X
Isopropanol	X	X	X		X	X	X	X
Methylene Chloride		X	X	X	X	X	X	X
Naphthalene	X	X				X	X	X
Phenol	X			X		X	X	X
Styrene	X	X	X	X	X	X	X	X
Tetrachloroethene	X	X	X	X	X	X	X	X
Toluene	X	X	X	X	X	X	X	X
Trichloroethene		X	X	X	X	X	X	X
Xylenes	X	X	X	X	X	X	X	X
1,2-Dichloroethane		X	X	X	X		X	X
2-Butanone	X	X	X	X	X		X	X
Bromomethane		X	X	X	X		X	X
Ethylene glycol monobutyl ether (2-Butoxyethanol)	X						X	X
Epichlorohydrin (1-chloro-2,3-epoxy propane)				X		X		X
N,N-Dimethylformamide	X			X		X		X
Methyl isocyanate				X				X
Phthalic anhydride								X
Acetone	X	X	X		X		X	
1,1-Dichloro-1-fluoroethane		X						
1,1-Difluoroethane		X	X					
1,2,4-Trimethylbenzene	X	X	X		X			
1,2,4-Trimethylcyclohexane	X							
1,2-Butanediol	X							
1,2-Diethylcyclobutane	X							
1,3,5-Trimethylbenzene		X	X		X			
1,3-Dichlorobenzene	X		X		X			
1,3-Dimethylcyclopentane	X							
1,3-Hexadien-5-yne	X							
1,4-Butanediamine	X							
1-(2-Butoxyethoxy)-ethanol	X							
1-(2-Ethoxypropoxy)-2 propanol	X							
1-(2-Methoxypropoxy)-2-propanol	X							
1-Butanol	X	X						
1-Butoxy-2-propanol	X							
1-Chloro-1,1-difluoroethane		X						
1-Chloro-4-trifluoromethane benzene	X	X						
1-Decene	X							
1-Ethenyl-3-methylene cyclopentene	X							
1-Ethoxypentane	X							
1-Ethyl-2-methylbenzene	X							
1-Ethyl-3-methylbenzene	X							
1-Ethyl-4-methylcyclohexane	X							
1-Hexanol	X	X						
1-Methanol-3-cyclohexene	X							
1-Methoxy-4-(2-propenylbenzene)	X							
1-Methyethylcyclohexane	X							
1-Methyl-2-(1-methylethyl)benzene		X						
1-Methyl-2-(3-methylcyclopropane)	X							
1-Methyl-4-(10m)-1,4-cyclohexadiene	X							
1-Methylpropyl ester acetic acid	X							
1-Pentadecanol	X							
1-Pentanol	X							
2,2,3,3-Tetramethylpentane	X							

2,2,4,4-Tetramethylpentane	X							
2,2,4-Trimethyldecane	X							
2,2,4-Trimethylhexane	X							
2,2,4-Trimethylpentane	X	X	X	X	X			
2,2,5-Trimethylhexane	X	X						
2,2,6,6-Tetramethylheptane	X							
2,3,3-Trimethylpentane	X	X						
2,3,4-Trimethylpentane	X							
2,3,6-Trimethyldecane	X							
2,3-Butanedione	X							
2,3-Dimethyloctane	X							
2,4,6-Trimethyloctane	X							
2,4-Dimethylheptane	X							
2,4-Dimethylheptene	X							
2,4-Dimethylhexane	X	X						
2,5-Dimethyloctane	X							
2,6,7-Trimethyldecane	X							
2,6-Dimethyl-7-octen-2-ol	X							
2,6-Dimethylheptane	X							
2,6-Dimethylnonane	X							
2,6-Dimethyloctane	X							
2,6-Dimethylundecane	X							
2,7,10-Trimethyldodecane	X							
2,8-Dimethylundecane	X							
2-(2-Ethoxyethoxy)-ethanol	X							
2-Butanamine	X							
2-Ethyl-1-butanol	X							
2-Ethyl-1-decanol	X							
2-Ethyl-1-dodecanol	X							
2-Ethyl-1-hexanol	X							
2-Ethylhexyl ester acetic acid	X							
2-Heptanone	X							
2-Hexanone		X	X		X			
2-Hexoxyethanol	X							
2-Methyl-1,3-butadiene		X						
2-Methyl-1-butanol	X							
2-Methyl-1-propanol	X							
2-Methyl-1-propene		X						
2-Methyl-2,2-dimethylpropanoic acid	X							
2-Methyl-3-hydroxypropanoic acid	X							
2-Methylbutanal	X							
2-Methylbutane		X						
2-Methylheptane	X							
2-Methylhexane	X	X						
2-Methylnonane	X	X						
2-Methyloctane	X							
2-Methylpentane		X						
2-Methylpropylacetic acid ester	X							
2-Methylpropylbutanoic acid ester	X							
2-Pentanol	X							
2-Pentanol acetate	X	X						
2-Pentanone	X							
2-Trimethylsilyloxy Benzoic Acid	X							
3,3,5-Trimethylheptane	X							
3,3,6-TrimethylBicyclo[3.1.0]hexan-2-one	X							
3,3-Dimethylhexane	X							
3,3-Dimethylpentane		X						
3,4-Dimethylheptane	X							
3-Carene	X	X						
3-Decen-2-one	X							
3-Ethoxy-1-butene	X							
3-Ethyl-2-methylheptane	X							
3-Ethyl-4-methylhexane	X							
3-Ethylhexane	X							
3-Ethylpentane		X						
3-Methyl-1-butanol	X							
3-Methyl-1-butanolacetate	X							
3-Methyl-2-butanolacetate	X							
3-Methyl-2-butanone	X							
3-Methylbutanal	X							

3-Methyldodecane	X							
3-Methylheptane	X							
3-Methylhexane	X	X						
3-Methylnonane	X							
3-Methyloctane	X							
3-Methylpentane	X	X						
3-Methylundecane	X							
4,6,8-Trimethylnonene	X							
4,6-Dimethylundecane	X							
4-Ethoxy-1-butanol	X							
4-Ethyltoluene		X	X		X			
4-Methyl-1-bicyclo[3.1.0]hex-2-ene	X							
4-Methyl-1-bicyclo[3.1.1]hexane	X							
4-Methyl-2-pentanone	X	X	X	X	X			
4-Methyl-4-penten-2-one	X							
4-Methyldecane	X							
4-Methylnonane	X							
4-Methyloctane	X							
5-Ethyl-2-methylheptane	X							
5-Ethyldecane	X							
5-Methyl-1-hexene	X							
5-Methyl-2-(1-methyl)cyclohexanol	X							
5-Methyl-2-(1methylene)cyclohexanol	X							
5-Methyl-2-hexene-4-ol	X							
Acetic acid	X							
Acetonitrile (cyanomethane)		X		X	X			
Acetophenone	X			X				
Alpha Cedrene	X							
Alpha Terpineol	X							
Azulene	X							
Benzaldehyde	X	X						
Benzophenone	X							
Benzyl alcohol	X							
Beta Phellandrene	X							
Bornyl Acetate	X							
Butanal		X						
Butane		X						
Butyl ester acetic acid		X						
Butyl ester butanoic acid	X							
Butyl ester hexanoic acid	X							
Campene	X							
Camphor	X							
Carbonyl sulfide		X		X				
Carvone	X							
Chloromethane		X	X	X	X			
Cyclohexane		X	X		X			
Cyclohexanone	X	X						
Cyclopentane		X						
Decanal	X							
Decane	X	X						
Dichlorodifluoromethane		X	X		X			
Diethylbenzene	X							
Difluorochloromethane		X						
Dodecane	X							
Eicosane	X							
Ethanol	X	X			X			
Ethyl ester butanoic acid	X							
Ethylacetate	X	X			X			
Ethylcyclohexane	X							
Ethylcyclopentane	X	X						
Eucalyptol	X							
Freon 113		X	X		X			
Heptamethylnonane	X							
Heptanal	X							
Hexadecane	X							
Hexadecanoic acid methyl ester	X							
Hexamethylcyclotrisiloxane	X	X						
Hexanal	X	X						
Hexyl ester acetic acid	X							
Isobutane		X						

Isomenthol	X							
Limonene	X	X						
Linalool	X							
Menthol	X							
Methenamine	X							
Methyl ester acetic acid		X						
Methyl ester benzoic acid	X							
Methyl ester butanoic acid	X							
Methyl methacrylate		X		X				
Methylbutylcyclohexane	X							
Methylcyclohexane	X	X						
Myrcene	X							
Nonanal	X	X						
Nonane	X	X						
Norflurane		X						
Octamethylcyclotetrasiloxane		X						
Octanal	X	X						
Octane	X	X						
Pentadecane	X							
Pentanal	X	X						
Pentane	X	X						
Phenylmethyl ester acetic acid	X							
Pinene	X	X						
Propanamide	X							
Propane		X						
Propylcyclohexane	X	X						
Propylene Glycol	X							
Tertiary butyl alcohol	X	X			X			
Tetradecanal	X							
Tetradecane	X	X						
Tetrahydrofuran	X	X	X		X			
Tetramethyl silicic acid	X							
Thujopsene	X							
Trichlorofluoromethane		X	X		X			
Tricycloheptane	X							
Tridecane	X							
Trimethylbenzene	X							
Trimethylpropanoatesilanol		X						
Undecane	X	X						
n-Heptane	X	X	X		X			
n-Propylbenzene	X		X					

APPENDIX C: FORMALDEHYDE CONTROL STRATEGIES FOR U.S. RETAIL BUILDINGS.

Formaldehyde control strategies for U.S. retail buildings

Elena L. Nirlo, Richard L. Corsi, Jeffrey A. Siegel

Abstract

Retail buildings are important from both occupational health and energy perspectives. Of particular concern to worker and customer exposure is formaldehyde, a hazardous air pollutant that is widespread in indoor environments. In this modeling study, the viability of filtration, humidity control and local ventilation as formaldehyde removal strategies are investigated. The impact of various parameters on indoor formaldehyde concentrations was investigated and weighed against their influence on building energy consumption. Local ventilation caused the most uniform improvements to indoor formaldehyde concentrations across building characteristics. Filtration used under specific conditions could lead to larger decreases in formaldehyde concentrations. Humidity control appeared to have a very limited impact given constraints on its variation for purposes of occupant comfort. A case study for small, medium, and large retail buildings in three U.S. cities in different climate zones revealed that filtration and local ventilation were the most promising strategies in terms of energy cost-to-unit of formaldehyde removed. Ultimately, healthy low-energy retail environments may require reduced formaldehyde emissions and filtration or localized ventilation.

Keywords

indoor air quality, model, energy, relative humidity, filtration, local ventilation

1. Introduction

Buildings use nearly 40% of all the energy consumed in the U.S. [1]. The retail sector, with 443,000 buildings occupying up to 401 million m^2 of floorspace [2,3], is a major component of the U.S. building stock. According to the last commercial building energy consumption survey, retail space cooling, heating, and ventilation alone used 148 trillion BTUs, which amounted to 46% of the total energy consumed by U.S. retail buildings [4]. Reducing ventilation in retail buildings could therefore lead to considerable energy savings.

The retail sector also has a significant potential for both short-term and occupational exposure to indoor pollutants. More than 15 million employees work in retail stores [5], and every day 36% of the U.S. civilian population engages in consumer goods purchases. Consumers spend approximately one hour on average in retail environments [6]. These shopping activities are highly lucrative; during the last quarter of 2013 (adjusted for seasonal variation), U.S. retail sales exceeded $380 billion monthly [7]. Not only would changes in indoor air quality have an impact on the health of retail workers and customers, but it could also influence the customer shopping experience, leading to a potentially significant economic benefit for stores [8,9].

Formaldehyde is widespread in indoor environments. Common indoor sources of formaldehyde include pressed-wood products (particle board, plywood, medium-density fiber board), insulation materials (mineral wool), flooring materials (carpet, laminate), coating materials (latex paint), combustion (wood burning, cooking, cigarette smoke), and office equipment (computers, printers) [10]. In retail stores, merchandise, displays, and building materials can emit formaldehyde. Six investigations of air quality in retail stores have included formaldehyde sampling [11-16]. Relatively high formaldehyde concentrations (> 50 $\mu g/m^3$) were measured in houseware stores [12], an office supply store [16], and furniture stores [15,16]. Formaldehyde was also deemed a dominant contaminant of concern in general merchandise stores [11,12,14,16].

Exposure to formaldehyde is a concern for retail workers and customers because of its adverse health effects. Acute exposure can cause nausea, headaches, and irritation of the skin, eyes, and mucous membranes [17]. Due to its high water solubility, formaldehyde is absorbed in upper airways and leads to sensory irritation [18]. Although the formaldehyde sensory irritation threshold has been determined to be approximately 0.6-1 mg/m^3, environmental, occupational, or personal risk factors can intensify the effects at lower concentrations [19]. Researchers have not reached a consensus regarding the adverse health effects of chronic exposure to formaldehyde at typical indoor concentrations. Some studies have shown that formaldehyde concentrations as low as 37 to 86 $\mu g/m^3$ were responsible for long-term allergic sensitization and non-negligible respiratory effects in sensitive individuals, particularly children [17,20]. However, some have noticed the absence of a convincing association between formaldehyde exposure and asthma or other airway effects in children [21,22]. Based on extensive evidence in rats, formaldehyde is classified as a probable human carcinogen by the U.S.

Environmental Protection Agency [23]. The International Agency for Research on Cancer further considers that there is sufficient evidence of formaldehyde causing nasopharyngeal cancer and leukaemia, and limited evidence of sinonasal cancer in humans to classify formaldehyde as a human carcinogen [24].

Ventilation is the most common strategy for removal of harmful pollutants of indoor origin [25]. There is some evidence that increased ventilation rates can help to reduce formaldehyde concentrations in retail stores [11,15,16]. Previous modeling studies have investigated the use of ventilation as a solution to improve indoor air quality in residences [26] and in commercial buildings [27-29]. The U.S. EPA [27] conducted an extensive modeling effort to evaluate the energy costs associated with various ventilation scenarios. The study simulated the impacts on thermal comfort but not on pollutant concentrations, and guided to building designers and operators towards "indoor air quality-compatible" measures to reduce HVAC energy. Ng et al. [29] investigated the impact of reducing or doubling ventilation rates on formaldehyde concentration and energy consumption in a model stand-alone retail building, and concluded on the importance of first reducing emissions. Apte et al. [28] modeled the influence of ventilation and other removal strategies, such as air cleaning and local ventilation, on the concentrations of 36 contaminants of concern. The authors suggested that reduced ventilation rates combined with air cleaning and local ventilation could lead to significant decreases in formaldehyde concentrations and energy use. However, the simulation was conducted on a model "big box" retail store, and was limited to Californian cities.

In this paper, we apply a mass balance model with multiple parameters to estimate the indoor concentration of formaldehyde in retail stores. With a parametric framework, we assess the feasibility of filtration, local ventilation and humidity control as strategies to reduce exposure to formaldehyde in U.S. retail buildings. The model provides an estimate of the penalty associated with each removal strategy in terms of energy consumption and cost. We examine the influence of building characteristics, source strengths, climate, and ventilation conditions.

2. Controlling the Fate of Indoor Formaldehyde

The main processes influencing the fate of formaldehyde in retail stores are illustrated in Figure 19.

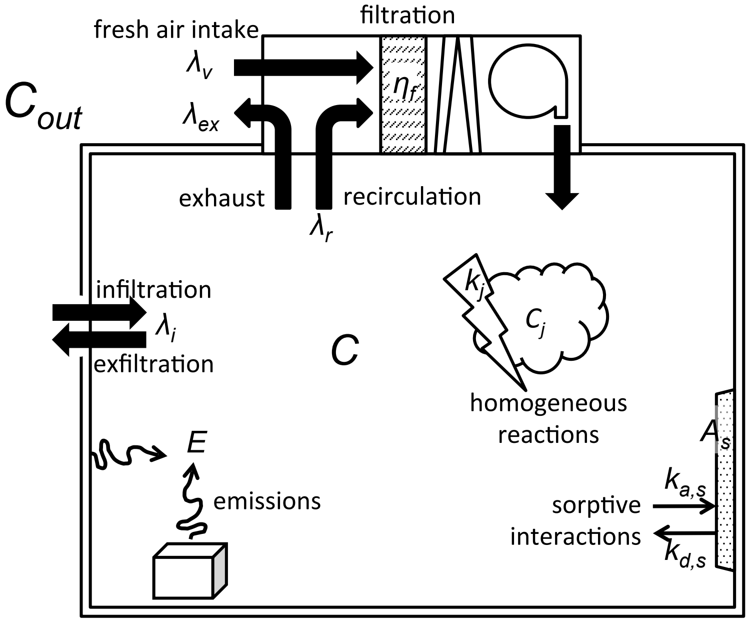

Figure 19: Schematic for modeling of indoor formaldehyde concentration in retail stores. Block arrows represent airflows.

In Figure 19, C is the indoor formaldehyde concentration (µg/m^3), C_{out} is the ambient formaldehyde concentration (µg/m^3), E is the formaldehyde emission rate (µg/m^2.h), λ_v is the make-up ventilation rate at which outdoor air is introduced into the space by the HVAC system (h^{-1}), λ_{ex} is the air exhaust rate (h^{-1}), λ_r is the air recirculation rate (h^{-1}), λ_i is the infiltration rate at which air enters and exits the space through the building envelope (h^{-1}), η_f is the efficiency of a filter designed to remove formaldehyde (-), k_j is the rate at which formaldehyde reacts with a compound j found at a concentration C_j (µg/m^3), $k_{a,s}$ is the adsorption rate coefficient (m/h) and $k_{d,s}$ the desorption rate coefficient (h^{-1}). The latter two parameters represent sorptive interactions between formaldehyde and indoor materials with surface area A_s (m^2).

2.1. Modeling indoor formaldehyde concentrations

Assuming a single well-mixed environment, the mass balance for formaldehyde with the HVAC system running is presented in Equation 1.

$$\frac{dC}{dt} = E\frac{A}{V} + \left(1-\eta_f\right)\left(\lambda_v C_{out} + \lambda_r C\right) + \lambda_i C_{out} + \sum_s k_{d,s}\frac{A_s}{V}M_s - \left(\lambda_{ex} + \lambda_r\right)C - \lambda_i C - \sum_s k_{a,s}\frac{A_s}{V}C \pm \sum_j k_j C_j C \qquad \text{(Eq. 1)}$$

Where V is the volume of the store (m^3), A is the floor area of the retail space (m^2) and M_s the mass of formaldehyde per unit area of surface (µg/m^2). All other variables are as described above. Equation 1 can be time-averaged by assuming that all parameters are constant and independent over a 1-hour period [30]. These parameters are varied in a parametric analysis to explore their relative influence on hourly concentrations of indoor formaldehyde.

2.1.1. Emission rates

The release of formaldehyde from a material is a three-step process. Formaldehyde is first produced in the bulk material, then transported through the bulk material, and finally out of the material and into the atmosphere [31]. A few researchers have reported the net amount of formaldehyde emitted per unit floor area of a retail store, or whole-building emission rate (WBERs) [13,14,16].

Three levels of WBERs were selected for the current paper from the dataset obtained through a field study conducted in 14 retail stores published elsewhere [16]. The 10th percentile (24.7 $\mu g/m^2.h$) is taken to be representative of a WBER of a store with no obvious formaldehyde sources but displays and building materials. The arithmetic mean WBER (61 $\mu g/m^2.h$) represents a store with a limited furniture section. The 90th percentile (91 $\mu g/m^2.h$) is taken to represent a store offering primarily furniture. These values are consistent with previously published WBERs [13,14].

2.1.2. Ambient concentrations

Formaldehyde is mainly an indoor pollutant, but can be found outdoors [32]. Sources of ambient formaldehyde include ozone chemistry, ethanol fuel combustion, and industrial flares [33,34]. Ambient concentrations in this study were varied from zero to the maximum concentration (4.2 $\mu g/m^3$) measured in a field study conducted in retail stores in Texas and Pennsylvania [16]. The selected values are consistent with the average outdoor concentration (3.8 $\mu g/m^3$) reported in the RIOPA study for three major U.S. cities in New Jersey, Texas, and California [35].

2.1.3. Building characteristics

Building characteristics recommended by the U.S. Environmental Protection Agency [36] in the 2011 Exposure Factor Handbook were selected for this study. A building height of 3.7m is suggested for commercial buildings (excluding warehouses and enclosed shopping malls). Low (510 m^3), medium (3310 m^3) and high (6116 m^3) building volumes are taken to be the 10th percentile, mean, and 90th percentile values, respectively, of a dataset collected during the last commercial building energy consumption survey (CBECS) conducted by the U.S. Energy Information Agency in 2003.

2.1.4. Ventilation parameters

2.1.4.1. HVAC operation

Packaged rooftop units commonly assure the introduction of fresh air in retail spaces [37]. In this study, we investigate the impact of reducing ventilation rates at night. For simplicity, transient effects induced by HVAC systems switching operating modes are neglected, and daily formaldehyde concentrations are calculated according to Equation 2.

$$C = f_{oper} C_{operating} + (1 - f_{oper}) C_{closed} \qquad \text{(Eq. 2)}$$

Where f_{oper} is the fraction of time the HVAC system runs on full operating mode, $C_{operating}$ is the indoor formaldehyde concentration in the store during operating hours (μg/m^3), C_{closed} is the indoor formaldehyde concentration in the store during closed hours (μg/m^3). Since operating hours are assumed to be from 7AM to 12PM everyday of the week, the parameter f_{oper} is set to 0.7 when the HVAC system is set to run with reduced airflows at night, and to 1 when the HVAC system runs continuously.

2.1.4.2. Total outdoor air exchange rates

While the amount of fresh air to be delivered to a store is influenced by codes and standards [25], there are little published measurements of total outdoor air exchange rates in retail stores [38]. The U.S. EPA Exposure Factor Handbook [36] refers to measurements conducted in commercial buildings (non-retail) in 1987 [39] that averaged 1.5±0.87 h^{-1}. The three levels selected for this study are the 10th percentile (0.26 h^{-1}), mean (0.60 h^{-1}), and 90th percentile (1.05 h^{-1}) of a dataset of total outdoor air exchange rates measured with tracer gas techniques in 14 retail stores in the United States [40].

2.1.4.3. Ventilation and infiltration rates

For the purposes of this study, ventilation corresponds to the mechanical introduction of outdoor air through air handling units (make-up air), and infiltration corresponds to outdoor air that enters the retail space through cracks in the building envelope and actual openings (entrance doors, loading dock entrances). Bennett et al. [41] reported infiltration rates for buildings that keep doors mostly open as six times those that keeps doors closed of the time. For the latter, the authors measured that on average 71% of fresh air was introduced to the retail space through ventilation and the remaining through infiltration.

2.1.4.4. Recirculation rates

Recirculation rates in this study were computed based on the 10th percentile (40%), mean (65%), and 90th percentile (90%) of a dataset of percentage of recirculated air as a fraction of supplied air measured with CO_2 sensors in 14 retail stores in the United States [40]. Table 22 summarizes all airflows selected for the current modeling study.

Table 22: Definition of airflow cases.

Air exchange rates (h^{-1})	**40RA**			**65RA**			**90RA**		
	low	**med**	**high**	**low**	**med**	**high**	**low**	**med**	**high**
λ_i	0.08	0.17	0.3	0.08	0.17	0.3	0.08	0.17	0.3
λ_v	0.18	0.43	0.75	0.18	0.43	0.75	0.18	0.43	0.75
λ_r	0.12	0.29	0.5	0.33	0.8	1.39	1.62	3.87	6.75

2.1.5. Sorptive interactions and homogeneous reactions

Building materials can act as sources and sinks for gas-phase pollutants [42,43], affecting transient concentrations of formaldehyde. For simplicity, the effects of sorptive interactions on time-averaged concentrations of formaldehyde are neglected in this study.

Formaldehyde can be consumed by reactions with highly reactive species such as hydroxyl radicals and ozone [10], and formed as ozone reacts with unsaturated organic compounds [44]. However, rates of removal and formation for reasonable indoor reactant concentrations are negligible compared to losses by ventilation and gains through emissions [44,45]. Supporting calculations can be found in the Supporting Information (SI 1).

2.1.6. Removal strategies

When formaldehyde originates from merchandise offered by the store, removal of the source is not a viable option. Exposure to formaldehyde may be mitigated through air cleaning (filtration), emission control (humidity control), and targeted dilution (local ventilation). All three options are considered in this paper.

2.1.6.1. Filtration

A review of published formaldehyde control technologies is provided in the Supporting Information (SI 1). None of the technologies presented are mature or widely accepted for removal of formaldehyde. Control technologies marketed for formaldehyde removal are limited, and products provide no guarantee of efficiency; technical specifications are not readily available for any products. For these reasons, the theoretical impact of filtration on indoor formaldehyde concentrations is modeled in the current study through generic efficiencies of 20%, 60% and 100% using Equation 3.

$$C_{operating} = \frac{\frac{\alpha_{RH} \cdot E \cdot A}{V} + \left(1-\eta_f\right)\lambda_v C_{out} + \lambda_i C_{out}}{\eta_f \lambda_r + \lambda_v + \lambda_i} \qquad \text{(Eq. 3)}$$

Where α_{RH} is the RH impact factor (-) (next section), and all other variables are as defined previously. We assume that the HVAC system operates on reduced airflows when the store is closed, and the indoor formaldehyde concentration C_{closed} can be calculated by setting λ_v and λ_i to their lowest value (Table 22) in Equation 3.

2.1.6.2. Humidity control

Many researchers have investigated the impact of temperature and relative humidity (RH) on formaldehyde emissions [31,46]}. As temperature is set for comfort in commercial environments, we only consider controlling RH as a way to control formaldehyde emissions. The impact of RH can be modeled following the rationale for classical adsorption isotherms and transport coefficients [31,46]. Chamber experiments have been conducted on formaldehyde emissions from wallboard, carpet [46], pressed-wood products [47-50], and other building materials [51]. A recent test of benchseats and cabinetry extracted from temporary housing units suggested that increasing RH from 50% to 85% leads to a 1.8 to 2.6-fold increase in formaldehyde [52]. However, the changes in release rates reported in these chamber studies are specific to the material tested and the two levels of RH selected. The Berge equation (Equation 4) can be used to standardize the effect of temperature and relative humidity on formaldehyde release test results [53].

$$C_x = \frac{C}{[1+A(RH-RH_0)]e^{-R(\frac{1}{T}-\frac{1}{T_0})}} \qquad \text{(Eq. 4)}$$

Where C_x is the corrected concentration (mg/m^3), C the test concentration (mg/m^3), R the coefficient of temperature (9799), T the test temperature (K), T_0 the standardized temperature (K), A the coefficient of humidity (0.0175), RH the test relative humidity (%), and RH_0 the standardized relative humidity (%). The Berge equation is based on emissions from two types of particleboard in a large well-mixed climate chamber in which the air exchange rate was varied from 0.2 to 1 h^{-1}, and loading rates from 0.4 to 1.6 m^2/m^3. The validity of this equation was verified by Godish and Rouch [54] in their study involving climate control as a way to control formaldehyde in residences. Through a simple mass balance, we use this equation maintaining all parameters as constant but RH to calculate an RH impact factor, α_{RH}, calculated as the ratio of C_x to C (Table 23).

Table 23: Definition of RH cases.

Parameters	Cases			
	vlow	low	normal	high
RH_{in} [%]	30	40	50	60
α_{RH} [-]	0.65	0.83	1	1.18

Variations in RH_{in} are limited here to the range typically recommended for the comfort of the building occupants (30% to 60%), even though a field investigation of fourteen U.S. retail stores measured RH_{in} ranging from 20% to 60% [40]. In retail stores, humidity is typically controlled around refrigerated cases (rated at 55%), which is a major energy consumer.

2.1.6.3. Local ventilation

In order to reduce the amount of fresh air required to dilute indoor formaldehyde, we investigated the potential to partition the store into two zones, providing increased ventilation locally to the zone containing the formaldehyde sources. The majority of formaldehyde-emitting products (e.g. the furniture section) would be grouped in a small part of the store (Zone 1) and kept separate from the rest of the store (Zone 2) by an air curtain or a physical partition (Figure 20).

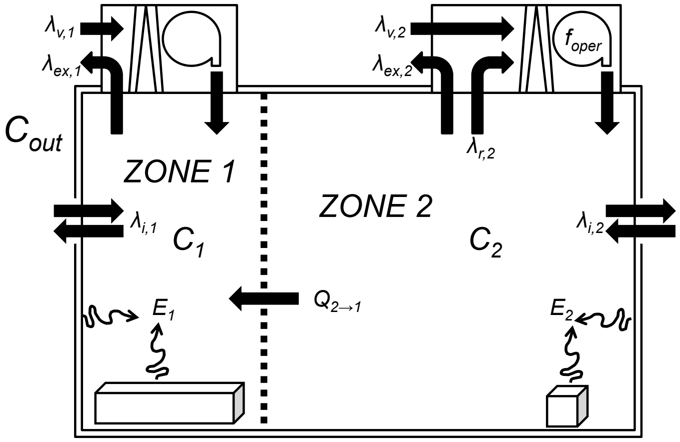

Figure 20: Schematic for 2-zone modeling of indoor formaldehyde concentration in retail stores when investigating the use of local ventilation as a removal strategy. Block arrows represent airflows.

In Figure 20, C_1 is the indoor formaldehyde concentration in Zone 1 (μg/m^3), C_2 is the indoor formaldehyde concentration in Zone 2 (μg/m^3), E_1 is the formaldehyde emission rate in Zone 1 (μg/m^2.h), E_2 is the formaldehyde emission rate in Zone 2 (μg/m^2.h), $\lambda_{v,1}$ is the ventilation rate at which outdoor air is introduced into Zone 1 by the Zone 1-HVAC system (h^{-1}), $\lambda_{v,2}$ is the ventilation rate at which outdoor air is introduced into Zone 2 by the Zone 2-HVAC system (h^{-1}), $\lambda_{ex,1}$ is the exhaust rate in Zone 1 (h^{-1}), $\lambda_{ex,2}$ is the exhaust rate in Zone 2 (h^{-1}), $\lambda_{r,2}$ is the recirculation rate in Zone 2 (h^{-1}), $\lambda_{i,1}$ is the infiltration rate at which air enters and exits Zone 1 through the building envelope (h^{-1}), $\lambda_{i,2}$ is the infiltration rate at which air enters and exits Zone 2 through the building envelope (h^{-1}), $Q_{2\rightarrow 1}$ is the interzonal airflow leaving Zone 2 and entering Zone 1 (m^3/h), and f_{oper} is the fraction of time the HVAC system in Zone 2 is running on operating hours mode (-).

We assume that 80% of the emissions can be restricted to 20% of the store. Airflows at the scale of the entire store are balanced, but Zone 1 is assumed to be negatively-pressurized and Zone 2 positively-pressurized to avoid contamination from Zone 1 to Zone 2. To this intent, exhaust, ventilation and interzonal flows in Zones 1 and 2 are related as shown in Equations 5 and 6.

$$Q_{ex,2} = Q_{v,2} - Q_{2\to1} \tag{Eq. 5}$$

$$Q_{ex,1} = Q_{v,1} + Q_{2\to1} \tag{Eq. 6}$$

Where $Q_{ex,2}$ is the exhaust airflow in Zone 2 (m^3/h) defined as the product of $\lambda_{ex,2}$ and V_2, $Q_{v,2}$ is the make-up ventilation airflow coming into Zone 2 (m^3/h) defined as the product of $\lambda_{v,2}$ and V_2, $Q_{ex,1}$ is the exhaust airflow in Zone 1 (m^3/h) defined as the product of $\lambda_{ex,1}$ and V_1, and $Q_{v,1}$ is the make-up ventilation airflow coming into Zone 1 (m^3/h) defined as the product of $\lambda_{v,1}$ and V_1. The introduction of air from Zone 2 to Zone 1 would likely create some backflow from Zone 1 to Zone 2 around the partition, and locally challenge the well-mixed assumption for both zones. Considering the scope of this analysis, we neglect these effects. Flowrates in Zone 2 ($\lambda_{v,2}$, $\lambda_{r,2}$, and $\lambda_{i,2}$) are taken to be similar to those introduced in Table 22 during operating hours. During closed hours, we assume that $\lambda_{v,2}$, $\lambda_{r,2}$, and $\lambda_{i,2}$ are reduced to their lowest respective value in their recirculation mode (Table 22). The Zone 1-HVAC system is assumed to run continuously at its set flowrate. This setting is likely to be unrealistic, but necessary in this modeling effort to maintain a unidirectional flow from Zone 2 to Zone 1. The parameter controlling the local ventilation scenario is the Zone 1 exhaust airflow: $\lambda_{ex,1}$ is initially set to the high level previously chosen for make-up ventilation rates, and infiltration in Zone 1 is set to the corresponding high value (Table 22). In order to estimate the impact of increasing air flowing through Zone 1, the exhaust airflow in Zone 1 is doubled to obtain medium, high, and very high levels, but infiltration is kept constant at its initial value. The interzonal airflow $Q_{2\rightarrow 1}$ is computed as the minimum of $Q_{ex,1}$ and $Q_{v,2}$, and corresponding values for $Q_{ex,2}$ and $Q_{v,1}$ are then computed using Equations 5 and 6. Table 24 summarizes all airflow parameters used in this part of the modeling effort. We recognize that this set of conditions is a small subset of possible conditions, and use them here simply to illustrate a reasonable range of parameters.

Table 24: Definition of airflow cases for removal strategy LV. Base case are shown in bold (following section).

Parameters	**Cases**
Zone 2	
Airflows	40RA low, 40RA med, 40RA high, 65RA low, **65RA med**, 65RA high, 90RA low, 90RA med, 90RA high
Zone 1	
$\lambda_{ex,1}$ [h^{-1}]	0.75, **1.5**, 3, 6
$\lambda_{i,1}$ [h^{-1}]	**0.30**

Two mass balances must be simultaneously solved to calculate the impact of local ventilation on formaldehyde concentrations in the two zones of the partitioned store (Equations 7 & 8). In each case we simplify by assuming time-averaged conditions for each zone.

$$C_2 = \frac{\frac{\alpha_{RH} \cdot E_2 \cdot A_2}{V_2} + \lambda_{i,2} C_{out} + \lambda_{v,2} C_{out}}{\lambda_{v,2} + \lambda_{i,2}} \qquad \text{(Eq. 7)}$$

$$C_1 = \frac{\frac{\alpha_{RH} \cdot E_1 \cdot A_1}{V_1} + \frac{Q_{2\rightarrow 1}}{V_1} C_2 + \lambda_{i,1} C_{out} + \frac{Q_{v,1}}{V_1} C_{out}}{\lambda_{i,1} + \lambda_{ex,1}} \qquad \text{(Eq. 8)}$$

Where V_1 is the volume of Zone 1 (m^3), V_2 is the volume of Zone 2 (m^3), A_1 is the floor area of the retail space in Zone 1 (m^2) and A_2 is the floor area of the retail space in Zone 2 (m^2). All other variables are as described above.

2.2. Modeling the energy consumed by controlling indoor formaldehyde

The removal strategies previously introduced are associated with an energy penalty characterized as one or a combination of the following: (1) heating, (2) cooling, (3) fan use, (4) humidification, or (5) dehumidification.

2.2.1. Heating and cooling energy

For all of the removal strategies investigated, the amount of power required for heating additional outdoor air is calculated using Equation 9. Heating is assumed to be provided by a gas furnace following the recommendations of the U.S. EPA Exposure Factor Handbook for commercial buildings [36]:

$$W_{heating} = \Delta Q_v \rho_{air} C_{p,air} |T_{out} - T_{sa}| \quad \text{(Eq. 9)}$$

Where $W_{heating}$ is the required rate of heat energy used (kJ/h), ΔQ_v is the additional outdoor airflow to be conditioned (m^3/h), ϱ_{air} is the density of air (kg/m^3), $C_{p,air}$ is the specific heat capacity of air at atmospheric conditions (kJ/kg. °C), T_{out} is the temperature of outdoor air (°C) and T_{sa} is the temperature of supply air (°C). The corresponding monthly or annual energy requirement can be estimated by Equation 10.

$$E_{heating} = \frac{W_{heating} \cdot t_{heat}}{\eta_{heating}} \quad \text{(Eq. 10)}$$

Where $E_{heating}$ is the required heating energy (kWh), $\eta_{heating}$ is the furnace efficiency (-), and t_{heat} is the time when heating was performed during the period considered (h).

We assume air handling units are equipped with a cooling coil operating under the minimum requirement for electrically operated unitary AC units of ASHRAE Standard 90.1[55]. The required cooling power $W_{cooling}$ is calculated similarly to Equation 9, and the corresponding energy according to Equation 11.

$$E_{cooling} = \frac{W_{cooling} \cdot t_{cool}}{SEER} \qquad \text{(Eq. 11)}$$

Where $E_{cooling}$ is the required cooling energy (kWh), *SEER* is the seasonal energy efficiency ratio of the air conditioner (BTU/Wh), and t_{cool} is the time when cooling was performed during the period considered (h).

2.2.2. Additional fan energy

The electric energy required for HVAC fans to overcome the additional pressure drop due to the presence of formaldehyde filters is calculated with Equation 12.

$$E_{fan,additional} = \frac{(\lambda_v + \lambda_r) V \cdot \Delta P_f}{\eta_{fan} \cdot \eta_{motor}} t_{ope} \qquad \text{(Eq. 12)}$$

Where $E_{fan,additional}$ is the required additional fan energy (kWh), η_{fan} is the fan efficiency (-), η_{motor} is the motor efficiency (-), ΔP_f is the additional pressure drop due to formaldehyde filters (Pa), and t_{ope} is the time when the HVAC system is running (h). In the absence of published information on the pressure drop caused by formaldehyde filters of varying efficiencies, we assume low, base, and high levels (4 Pa, 20 Pa, and 100 Pa, respectively) as explained in the Supporting Information (SI 1) to evaluate the impact of pressure drop on fan energy consumption.

A field investigation of fourteen U.S. retail stores suggests that most stores are most commonly equipped with fans without speed control [40,56]. However for simplicity in this analysis, we assume that units were equipped with fans with speed control that could maintain a constant airflow. Based on recent measurements in air-handling units in retail stores, the total fan efficiency was assumed to be 23% [56].

2.2.3. Humidification and dehumidification energy

The energy penalty associated with the use of humidity control as a removal strategy is that of humidification and dehumidification. If the moisture content of the outdoor air, based on its temperature and relative humidity, is higher than that of the desired supply air, the outdoor air is first cooled to its dew point (associated energy calculated similarly to Equation 11), dehumidified to reach the water content of the supply air (Equation 13), and finally reheated from its dew point temperature to the desired supply temperature (Equation 10).

$$W_{dehum} = \lambda_v V \rho_{air} \Delta h_v |w_{out} - w_{sa}| \qquad \text{(Eq. 13)}$$

Where W_{dehum} is the required heat for evaporation (kJ/h), Δh_v is the latent heat of vaporization for water (assumed constant) (kJ/kg), w_{sa} is the humidity ratio of the supply air (kg/kg), w_{out} is the humidity ratio of outdoor air (kg/kg). The dehumidification process can be considered as further cooling, and the associated electric energy is calculated with Equation 11.

If the outdoor air does not contain enough moisture, the air is first heated or cooled to the supply temperature desired. Water droplets are then injected into the air stream with a steam humidifier. The power required for the humidification process is calculated similarly to Equation 13. The corresponding monthly or annual energy requirement can be estimated by Equation 14.

$$E_{hum} = \frac{W_{hum} \cdot t_{hum}}{\eta_{humidifier}} \qquad \text{(Eq. 10)}$$

Where E_{hum} is the required humidifying energy (kWh), $\eta_{humidifier}$ is the efficiency for a gas-fired steam humidifier (obtained from manufacturer specifications) (-), and t_{hum} is the time when humidification was performed during the period considered (h).

2.3. Estimating the costs of controlling indoor formaldehyde

Annual cost can serve as a common denominator to compare removal strategies. In the absence of information on formaldehyde filters and to avoid making further assumptions on the equipment required, the analysis is restricted to energy costs. Therefore, acquisition and maintenance costs for the additional equipment required by every removal strategy are not taken into account. For simplicity, spatial variations in the cost of electricity and natural gas are not taken into consideration. Natural gas prices were assumed constant at the average 2012 Henry Hub natural gas spot price [57], and electricity at the average U.S. electricity price for commercial consumption in December 2013 [1]. All quantities used for energy and energy cost calculations are summarized in Table 25.

Table 25: Selected quantities for energy and energy cost calculations.

Quantity	Value	Source
Number of days in a month	30	assumed
Density of air [kg/m^3]	1.2	ASHRAE Handbook [58]
Specific heat capacity of air [kJ/kg.C]	1	ASHRAE Handbook [58]
Latent heat of vaporization for water [kJ/kg]	2257	ASHRAE Handbook [58]
Supply temperature [C]	21	assumed
Fan efficiency [-]	0.23	Zaatari et al. [56]
Furnace efficiency [-]	0.8	Deru et al. [37]
Steam humidifier efficiency [-]	0.9	engineering judgment
SEER of cooling equipment [BTU/Wh]	13	ASHRAE Standard 90.1 [55]
Natural gas cost [$/million BTU]	2.75	U.S. EIA [57]
Electricity cost [$/kWh]	0.0998	U.S. EIA [1]

3. Methods

3.1. General framework

The model described above is used to investigate the impact of filtration (F), humidity control (HC), and local ventilation (LV) on indoor formaldehyde concentrations on a broad scale. Each removal strategy is associated with a defining parameter, as introduced in the previous sections. Filtration is defined for three filter efficiencies: 20%, 60%, and 100%. Humidity control is defined for four levels of RH_{in}: 30%, 40%, 50%, and 60%. Local ventilation is defined for four levels of Zone 1-exhaust flowrate: 0.75 h^{-1}, 1.5 h^{-1}, 3 h^{-1}, and 6 h^{-1}. Parameters defining the modeled buildings and ambient conditions are also varied in three levels. Parameters selected for modeling of indoor formaldehyde concentrations are summarized in Table 26.

Table 26: Summary of varied parameters. Base values are shown in bold (next section).

Parameters	**Strategy**	**Cases**
Emission rate [μg/m^2.h]	F, HC, LV	24.7, **61.0**, 91.0
C_{out} [μg/m^3]	F, HC, LV	0, **2.1**, 4.2
T_{out} [°C]	F, HC, LV	0, **15**, 35
RH_{out} [-]	F, HC, LV	30%, **50%**, 75%
HVAC operation	F, HC	**continuous**, night-time reduction
	LV	**continuous**, night-time reduction in Zone 2
Volume [m^3]	F, HC, LV	510, **3310**, 6116
Airflows	F, HC	40RA low, 40RA med, 40RA high, 65RA low, **65RA med**, 65RA high, 90RA low, 90RA med, 90RA high [a]
	LV	*(see Table 24)*
RH_{in}	F, LV	**normal** [b]
	HC	vlow, low, **normal**, high [b]
Filter efficiency	F	20%, **60%**, 100%
	LV, HC	**0%**

[a] See Table 22

[b] See Table 23

A scenario is defined as a unique combination of parameters. Every combination of parameters was modeled, which amounted to 4,374 scenarios for the no removal case (NR), 13,122 scenarios for the filtration strategy (F), 17,486 scenarios for the humidity control strategy (HC), and 17,496 scenarios for the local ventilation strategy (LV).

Many organizations set guidelines for indoor formaldehyde concentration. While the World Health Organization recommends a 30-minute guideline set at 100 μg/m^3 to prevent both sensory irritations and cancer effects [59], the California Office of Environmental Health Hazard Assessment (OEHHA) sets much stricter reference exposure levels (RELs) at 9 μg/m^3 (chronic and 8-hour exposure) and 55 μg/m^3 (acute exposure)[17]. The National Institute for Occupational Safety and Health (NIOSH) and the Federal Emergency Management Agency (FEMA) both recommend to limit 8-hour formaldehyde exposures to 19.6 μg/m^3. The Leadership in Energy & Environmental Design (LEED) rating system for green buildings includes indoor environmental quality credits, and recently developed a compliance alternative path (EQpc68) establishing minimum standards for indoor air quality set at 33 $\mu g/m^3$ for formaldehyde [60]. Results obtained with this model are compared to the three strictest concentration limits: OEHHA chREL, NIOSH REL, and LEED EQpc68.

Following the same framework, we modeled the additional energy required to implement the three removal strategies across all parameters shown in Table 27. Changes in energy consumption are calculated over a fictional month during which all parameters are assumed to remain constant.

3.2. Sensitivity analysis

A sensitivity analysis on modeled indoor formaldehyde concentrations was completed by varying the parameters presented in Table 26 from their base values (in bold) to their low and high values. Baselines are defined for every removal strategy. The filtration baseline consists of a filter efficiency of 60%. The humidity control baseline consists of a relative humidity of 50%. The local ventilation baseline consists of $\lambda_{ex,1}$ set at 1.5 h^{-1}.

3.3. Case study

To help in the comparison of filtration, humidity control, and local ventilation as removal strategies, the analysis is restricted to a case study. Filtration is modeled for a 60% efficient filter. Humidity control is modeled for an indoor relative humidity of 30%. Local ventilation is modeled with a Zone 1-exhaust flowrate of 6 h^{-1}. A traditional ventilation strategy (whole-building ventilation) where the make-up ventilation flowrate for the whole building is raised to 6 h^{-1} is also considered as a basis for comparison. Concentrations, energy, and energy costs are estimated in three buildings of low, medium and high volume. Each building is simulated in three cities: Austin, TX (hot and humid climate); Seattle, WA (cold and humid climate); and Phoenix, AZ (hot and dry climate). Variations in electricity prices and billing schemes amongst the three cities would likely influence the results of this analysis, but are deemed out of the scope of this illustrative case study. Calculations are run over a year using TMY3 hourly weather data files [61]. Outputs are first generated for a reference case (NR - no removal), then for each of the removal strategies with parameters defined in Table 27.

Table 27: Summary of parameters used in the case study.

Parameter	**Strategy**[a]	**Value**
RH_{in} [-]	NR, V, F, LV	50%
	HC	30%
T_{out}, RH_{out}	NR, V, F, LV, HC	Austin, Seattle & Phoenix
T_{sa} [°C]	NR, V, F, LV, HC	21
λ_v [h^{-1}]	NR, F, HC, LV ($\lambda_{v,2}$)	0.43
	V	6
λ_i [h^{-1}]	NR, F, HC, V	0.17
	LV ($\lambda_{i,1}$; $\lambda_{i,2}$)	0.3; 0.17
λ_r [h^{-1}]	NR, F, HC, V	3.87
E [μg/m^{2}h]	NR, V, F, LV, HC	61
C_{out} [μg/m^3]	NR, V, F, LV, HC	2.1
f_{oper} [-]	NR, V, F, LV (Zone 1), HC	0.7
η_f [-]	NR, V, LV, HC	0%
	F	60%
α_{RH} [-]	NR, V, F, LV	1
	HC	0.65
$\lambda_{ex,1}$ [h^{-1}]	NR, V, F, HC	N/A
	LV	6

[a] NR refers to the reference (no-removal) case, V refers to whole-building ventilation, F to filtration, LV to local ventilation, and HC to humidity control.

The ratio of dollar per μg/m^3 of formaldehyde removed is introduced to facilitate the comparison of all removal strategies investigated in this case study.

4. Results and Discussion

4.1. Indoor formaldehyde concentrations

4.1.1. Overview of results

Indoor formaldehyde concentrations varied widely across parameters, as represented by the box plots in Figure 21. The bottom of the box indicates the 25th percentile; the horizontal line indicates the median and the top of the box the 75th percentile of model simulations. The whiskers indicate the data ranging within 1.5 times the interquartile range of the 25th and 75th percentile. Filled circles are outliers. Concentrations are presented for various values of all parameters defining the removal strategies investigated. In the case of local ventilation, the output consists of two boxes that represent the formaldehyde concentrations in Zone 1 (light gray) and Zone 2 (dark gray).

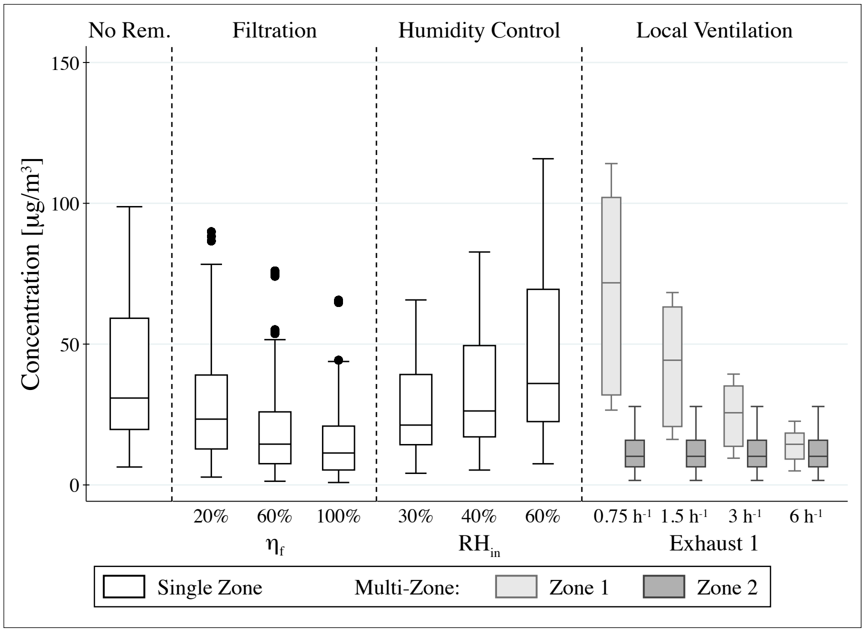

Figure 21: Impact of removal strategies and their defining parameters on modeled indoor formaldehyde concentrations. Parameter codes are defined in Table 26. "No Rem." indicates formaldehyde concentrations modeled without any removal strategy.

The first (leftmost) box summarizes indoor concentrations when no removal (NR) is intended and all other parameters varying as a basis for comparison. NR concentrations ranged from 6.4 to 99 µg/m^3, with a median of 31 µg/m^3. These results are consistent with measured concentrations of formaldehyde sampled in fourteen U.S. retail stores, that ranged from 5.6 to 82 µg/m^3 [16], which confirms that the input parameters selected in this modeling study are representative of actual retail buildings. When filtration was introduced, the overall range of concentrations remained similar to the no removal case (0.9 – 90 µg/m^3), but the median was halved to 16 µg/m^3. A significant decrease in median concentration was observed with increasing filter efficiency, from 23 µg/m^3 for a low efficiency filter, to 15 µg/m^3 for a 60% efficient filter, and 11 µg/m^3 for a perfect (100% efficient) filter. The effectiveness of filtration is limited not only by single-pass removal efficiency, but also by the fraction of time that air recirculated through the filter (cycling frequency).

The humidity control (HC) case investigates the impact of relative humidity on indoor concentrations. When set to its high value (RH_{in}=60%), HC does not act as a removal strategy, but induces an increase in emission rate. For this reason, the maximum concentration obtained in this strategy was higher than concentrations obtained in the no removal scenario, reaching as high as 116 $\mu g/m^3$. Decreasing indoor RH below the base value (50%) led to slight decreases in median concentrations to 26 $\mu g/m^3$ (RH=40%) and 21 $\mu g/m^3$ (RH=30%).

Indoor concentrations obtained when modeling the use of local ventilation (LV) were overall the lowest for Zone 2. Concentrations in Zone 1 ranged from 5.0 to 114 $\mu g/m^3$, with a median of 28 $\mu g/m^3$, while concentrations in Zone 2 were relatively low in comparison, ranging from 1.6 to 27.9 $\mu g/m^3$, with a median of 10.2 $\mu g/m^3$. Increasing exhaust rates in Zone 1 led to consistent decreases on Zone 1 concentrations, but had no impact on Zone 2 concentrations. Although the median Zone 1 concentration was higher than the NR median concentration for low (72 $\mu g/m^3$) and base (44 $\mu g/m^3$) values of $\lambda_{ex,1}$, high and very high values of $\lambda_{ex,1}$ resulted in median concentrations lower in Zone 1 than in the NR case (26 $\mu g/m^3$ and 14 $\mu g/m^3$, respectively, vs. 31 $\mu g/m^3$).

4.1.2. Comparison with concentration limits

The percentages of scenarios that generated concentrations lower than specific concentration limits are shown in Tables 28-30. Results are presented for each level of every parameter. As a basis for comparison, results for the no removal case are shown in italics. Cells with a light grey background indicate combinations of parameters that lead to 50 to 75% of scenarios in attainment with specific concentration limits. Cells with a dark grey background indicate combinations of parameters that lead to more than 75% of scenarios in attainment.

Table 28: Summary of the performance of filtration control strategies.

Parameters	**Cases**		**% scenarios meeting OEHHA**				**% scenarios meeting NIOSH**				**% scenarios meeting LEED**			
			NR	**20%**	**60%**	**100%**	***NR***	**20%**	**60%**	**100%**	***NR***	**20%**	**60%**	**100%**
Emission		low	11	33	59	70	67	78	89	100	100	100	100	100
		base	0	6	24	39	11	33	56	67	44	70	78	89
		high	0	0	11	22	0	13	31	52	17	35	63	72
C_{out}		low	6	15	35	44	28	43	59	74	56	70	81	87
		base	6	13	30	44	28	41	59	72	56	69	81	87
		high	0	11	30	43	22	41	57	72	50	67	78	87
HVAC Operation		reduced@night	0	7	23	40	22	33	52	64	41	62	77	85
		continuous	7	19	40	48	30	49	65	81	67	75	84	89
Airflow	40RA	low flow	0	0	0	0	0	0	0	33	33	33	33	33
		medium flow	0	0	6	17	33	33	33	50	50	50	78	83
		high flow	11	11	17	28	44	50	61	67	78	83	83	100
	65RA	low flow	0	0	0	0	0	0	33	33	33	33	33	67
		medium flow	0	6	22	33	33	33	50	83	50	67	94	100
		high flow	11	17	39	50	44	56	83	89	78	83	100	100
	90RA	low flow	0	0	33	67	0	33	67	100	33	67	100	100
		medium flow	0	33	83	100	33	83	100	100	50	100	100	100
		high flow	11	50	83	100	44	83	100	100	78	100	100	100
	Overall		4	13	31	44	26	41	59	73	54	69	80	87

If the airflow was set to low with limited recirculation (40RA_low), little to no differences were seen with the implementation of filtration since little air goes through the filter. A low-efficiency filter led to significant changes (>50% scenarios modeled achieving the NIOSH guideline) only if recirculation was at its maximum (90RA_med and 90RA_high) or emissions were low.

Concentrations under the LEED EQpc68 limits were guaranteed if the recirculation rate was set to its maximum. If the recirculation was at its maximum and airflows were medium or high (90RA_med and 90RA_high), more than 83% of scenarios modeled were below the NIOSH guideline and the LEED reference limit. Such a combination of parameters with a perfect filter (100% efficiency) even guaranteed all scenarios to achieve all guidelines considered.

The limited extent to which humidity control reduces indoor formaldehyde concentrations is shown in Table 29. The percentage of scenarios leading to various concentration limits is shown for indoor relative humidity set to very low, low and high levels, and compared to the non-removal case, which corresponds to RH_{in} of 50%.

Table 29: Summary of the performance of humidity control strategies.

Parameters	**Cases**	**% scenarios meeting OEHHA**				**% scenarios meeting NIOSH**				**% scenarios meeting LEED**			
		NR	**30%**	**40%**	**60%**	***NR***	**30%**	**40%**	**60%**	***NR***	**30%**	**40%**	**60%**
Emission	low	*11*	28	11	6	*67*	89	67	56	*100*	100	100	89
	base	*0*	0	0	0	*11*	28	17	6	*44*	67	56	22
	high	*0*	0	0	0	*0*	17	6	0	*17*	44	17	17
C_{out}	low	*6*	17	6	6	*28*	56	33	28	*56*	72	61	50
	base	*6*	6	6	0	*28*	44	28	17	*56*	72	56	44
	high	*0*	6	0	0	*22*	33	28	17	*50*	67	56	33
HVAC Operation	reduced@night	*0*	4	0	0	*22*	33	22	15	*41*	63	48	30
	continuous	*7*	15	7	4	*30*	56	37	26	*67*	78	67	56
Airflow[a]	low flow	*0*	0	0	0	*0*	22	0	0	*33*	33	33	22
	medium flow	*0*	6	0	0	*33*	39	33	22	*50*	83	56	39
	high flow	*11*	22	11	6	*44*	72	56	39	*78*	94	83	67
Overall		*4*	9	4	2	*26*	44	30	20	*54*	70	57	43

[a] The fraction of recirculation does not impact the results: "low flow" stands for "40RA_low", "65RA_low", and "90RA_low", "medium flow" stands for "40RA_med", "65RA_med", and "90RA_med", and "high flow" stands for "40RA_high", "65RA_high", and "90RA_high".

Results for the high level of RH_{in} were expectedly worse than the NR case, and demonstrate how high levels of uncontrolled RH_{in} negatively affect formaldehyde concentrations. If RH_{in} was as high as 60%, more than 67% of scenarios modeled could only be in attainment with respect to the LEED EQpc68 limits if all flowrates were set to high or emission rates are low.

Humidity control does not appear to be an appropriate strategy for stores trying the achieve the OEHHA chREL, as never more than 28% of the scenarios modeled led to concentrations under the OEHHA guideline. However, decreasing RH_{in} to 30% led to twice as many stores being in attainment than the non-removal case if either the emission rate or the ambient formaldehyde concentration was low, the HVAC system was continuously on, or the flowrates (λ_v, λ_i , λ_r) set to medium or high. Such an impact was not observed when considering attainment with the LEED EQpc68 limits, where the level of the other parameter considered (low emission, high flow, HVAC operation) seemed to determine whether or not a store was in attainment.

Humidity control had a positive impact on the percent of scenarios reaching the NIOSH chREL if a RH_{in} of 30% was combined with either a low emission rate, low ambient concentration, high flowrates (λ_v, λ_i , λ_r), or a HVAC continuously running. The limited impact of humidity control may be partially due to the limited range of its defining input parameter. Indoor relative humidity is traditionally set within 30% to 60% to assure occupant comfort [62].

The extent to which local ventilation reduced formaldehyde concentrations to levels meeting health standards is shown in Table 30. Results for Zone 1 are presented by level of $\lambda_{ex,1}$ but not results for Zone 2 since concentrations in Zone 2 are not dependent upon $\lambda_{ex,1}$.

Table 30: Summary of the performance of the local ventilation control strategies. Results for Zone 1 are presented by level of $\lambda_{ex,1}$.

Parameters	Cases	% scenarios meeting OEHHA					% scenarios meeting NIOSH					% scenarios meeting LEED				
		Zone 1				Zone 2	Zone 1				Zone 2	Zone 1				Zone 2
		low	base	high	vhigh		low	base	high	vhigh		low	base	high	vhigh	
Emission	low	0	0	0	67	89	0	67	100	100	100	89	100	100	100	100
	base	0	0	0	0	33	0	0	0	100	89	0	0	100	100	100
	high	0	0	0	0	11	0	0	0	33	67	0	0	0	100	100
C_{out}	low	0	0	0	33	56	0	33	33	100	89	33	33	67	100	100
	base	0	0	0	33	50	0	33	33	67	89	33	33	67	100	100
	high	0	0	0	0	28	0	0	33	67	78	22	33	67	100	100
HVAC Zone 2 Operation	reduced@night	0	0	0	22	33	0	22	33	78	85	30	33	67	100	100
	continuous	0	0	0	22	56	0	22	33	78	85	30	33	67	100	100
Airflow Zone 2[a]	low flow	0	0	0	22	22	0	22	33	78	56	22	33	67	100	100
	medium flow	0	0	0	22	44	0	22	33	78	100	33	33	67	100	100
	high flow	0	0	0	22	67	0	22	33	78	100	33	33	67	100	100
Overall		0	0	0	22	44	0	22	33	78	85	30	33	67	100	100

[a] The fraction of recirculation in Zone 2 does not impact the results: "low flow" stands for "40RA_low", "65RA_low", and "90RA_low", "medium flow" stands for "40RA_med", "65RA_med", and "90RA_med", and "high flow" stands for "40RA_high", "65RA_high", and "90RA_high".

Partitioning the store ensured that formaldehyde never was a contaminant of concern in the major part of a store (Zone 2) according to the LEED EQpc68 concentration limit. Local ventilation also led to more than 75% of modeled scenarios to achieve the NIOSH REL in Zone 2, unless the emission rate was high (67%) or airflows in Zone 2 ($\lambda_{v,2}$, $\lambda_{i,2}$, $\lambda_{r,2}$) low (56%). Local ventilation with high airflows ($\lambda_{v,2}$, $\lambda_{i,2}$, $\lambda_{r,2}$) and low emission rates even led to more than 67% of modeled scenarios achieving the strict OEHHA guideline in Zone 2. However, the OEHHA reference level could not be achieved in Zone 1 in any scenario using local ventilation if $\lambda_{ex,1}$ was at a low, base or high level. A majority of scenarios achieved the OEHHA guidelines in Zone 1 only if $\lambda_{ex,1}$ was set a its very high level and emissions were low.

Low and base levels of Zone 1 exhaust rates generally did not result in satisfying indoor concentrations in Zone 1 with regards to OEHHA and NIOSH guidelines. However, a very high $\lambda_{ex,1}$ guaranteed that the store would achieve the LEED EQpc68 level over all parameters, and that more than 67% of modeled scenarios would achieve the NIOSH level if emissions were not high. The high level of Zone 1 exhaust rate was generally sufficient in most cases for more than 67% of scenarios modeled to result in concentrations below the LEED EQpc68 concentration limit.

Overall, local ventilation resulted in the most uniform improvements to indoor formaldehyde concentrations across building characteristics, while the impact of humidity control appeared limited. The use of filtration could also help many retail stores to achieve NIOSH and LEED EQpc68 concentration limits, especially if the clean air delivery rate is maximized (high flow, high filter efficiency). To further investigate and separate the impact of individual parameters, a sensitivity analysis was conducted.

4.1.3. Sensitivity analysis

In this section, we explore the relative effects of changes in parameters on formaldehyde concentrations. Figure 22 contains three bar graphs representing the three removal strategies investigated filtration (F), humidity control (HC), and local ventilation (LV). Every graph shows the change in formaldehyde concentration due to a single parameter (one bar) changing from its base value to it high (dark grey) and low (light grey) value, with all other parameters remaining constant at base value. Selected concentration limits are displayed with dashed lines for comparison with the modeled concentrations.

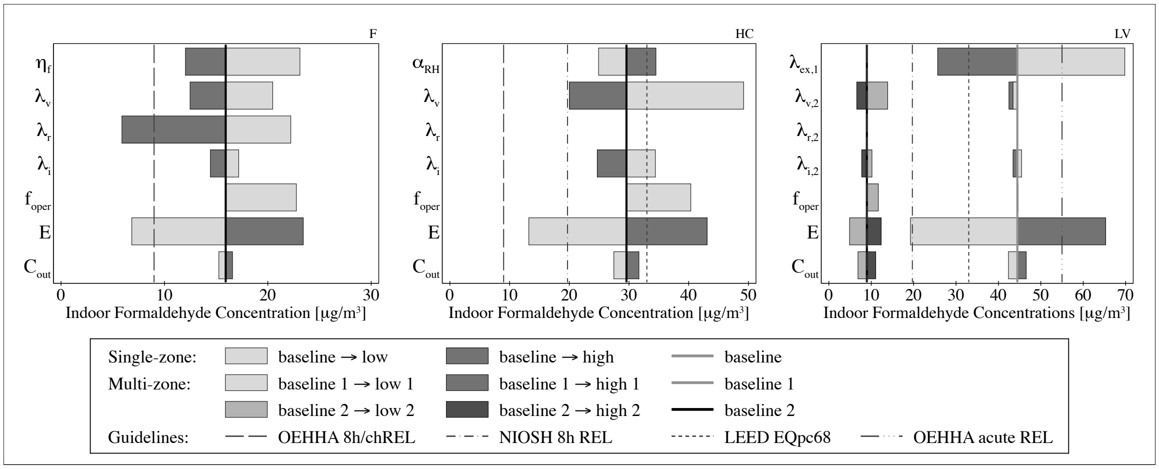

Figure 22: Sensitivity analysis on indoor formaldehyde concentrations after use of filtration (F), humidity control (HC), and local ventilation (LV) as removal strategies.

The defining parameter of each removal strategy is investigated first (top of the graphs). For the filtration strategy, η_f had a significant impact on indoor formaldehyde concentrations comparable to that of the recirculation rate, the emission rate, and the HVAC operation. Setting the recirculation rate to its highest level decreased the concentration under the OEHHA guideline. A similar decrease in concentration was obtained by setting the emission rate to its lowest level.

For the humidity control strategy, the make-up ventilation rate was the parameter influencing indoor concentrations the most. Although it would potentially lead to drastic savings in terms of energy consumed, setting a low ventilation rate raised the formaldehyde concentration far above the LEED EQpc68 concentration limit. The emission rate and the HVAC operation also had a significant impact on concentrations. Relative to other parameters, RH had a small impact on indoor concentrations. However, increasing RH_{in} (shown as α_{RH}) to its high value raised the indoor concentration above the LEED EQpc68 concentration limit.

The impact of changing various parameters on formaldehyde concentrations in both Zone 1 (that contains most of the sources) and Zone 2 of the partitioned store are shown in the third graph of Figure 22. None of the parameters investigated but $\lambda_{v,2}$ led to major changes in the predicted formaldehyde concentration in Zone 2, with Zone 2 concentrations remaining under the NIOSH guideline. Furthermore, none of the Zone 2 airflow parameters led to a major change in the concentration in Zone 1. The Zone 1-exhaust flowrate had amongst the greatest impact on concentrations in Zone 1 with emission rate, but had no impact on concentrations in Zone 2.

4.2. Energy consumption

The monthly energy penalty due to the implementation of filtration, humidity control, and local ventilation varied widely across parameters and amongst removal strategies, as represented by the box plots in Figures 23, 24, and 25, respectively. The bottom of the box indicates the 25th percentile; the horizontal line indicates the median and the top of the box the 75th percentile of model simulations. The whiskers indicate the data ranging within 1.5 times the interquartile range of the 25th and 75th percentile. Filled circles are outliers.

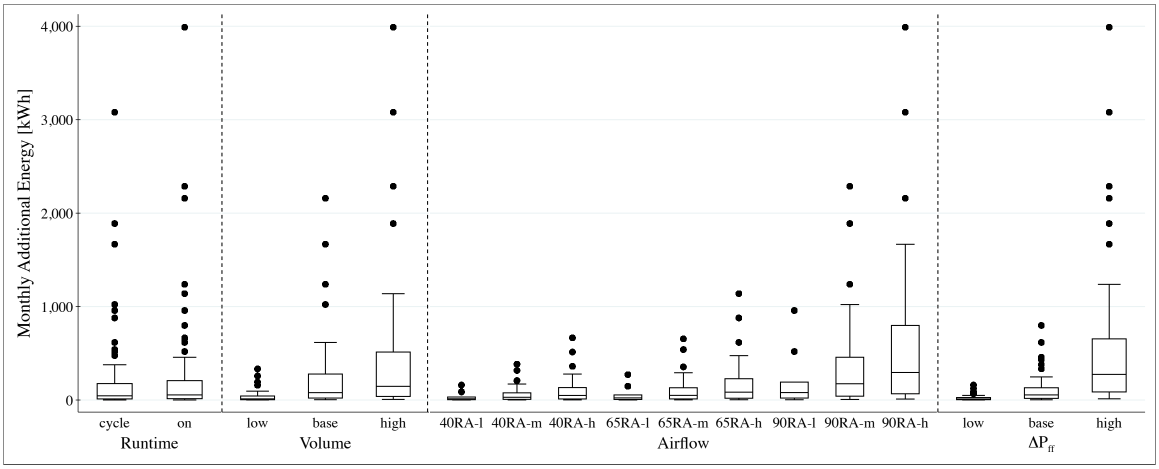

Figure 23: Impact of various parameters on modeled monthly additional energy required for the use of filtration as a removal strategy. Parameter codes are defined in Table 26.

Implementing filtration as a measure to reduce formaldehyde concentrations led to increases in monthly energy consumption ranging from 0.5 kWh to 3990 kWh, with a median of 53 kWh in all scenarios modeled. Whether the HVAC system switched to provide reduced airflows at night or not did not visibly impact the energy consumed. Considering the impact of this parameter on indoor formaldehyde concentrations reported in sections 2.1.1. and 2.1.3., this finding suggests that under most situations cycling may not be worth-while. Most notable increases in monthly energy consumed followed increased recirculation. Logically, the highest energy penalties were observed when the air going through the filter was maximized (90RA_high). Not surprisingly, increased pressure drops, which are artificially set to amount to increased filter efficiency in this modeling study, significantly influenced the modeled monthly energy penalty, with medians raising from 11 kWh (low case) to 55 kWh (base case), and finally 275 kWh (high case).

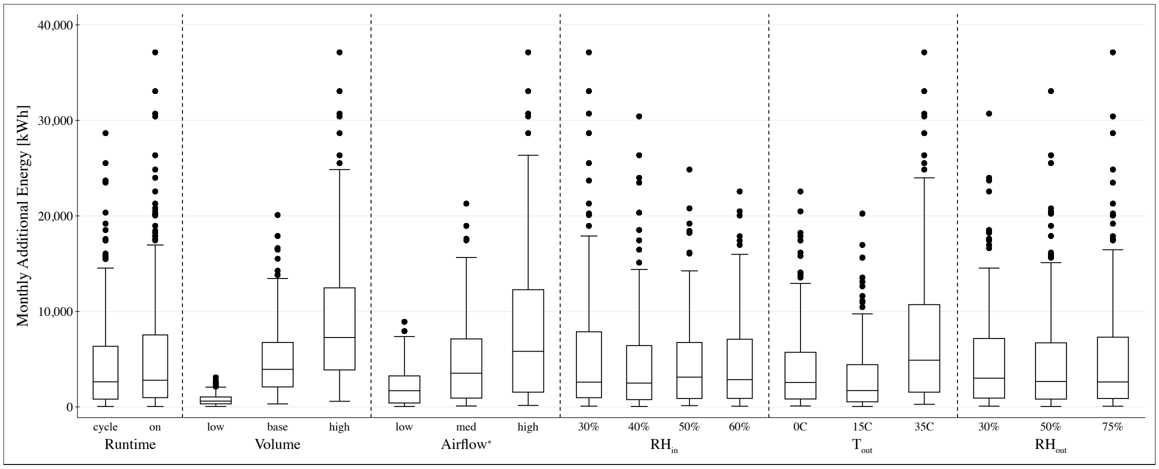

Figure 24: Impact of various parameters on modeled monthly additional energy required for the use of humidity control as a removal strategy. Parameter codes are defined in Table 26.

The energy penalties associated with the use of humidity control are due to heating, cooling, humidification, and dehumidification. Overall, the implementation of humidity control led to monthly energy increases ranging from 49 kWh to 37 000 kWh, with a median of 2667 kWh. Variations in building volume, and therefore in the amount of air brought in through the HVAC system to condition, had the greatest impact on energy consumption. Changes in relative humidity, indoors or outdoors, had a relatively small influence on the energy consumed. However, notable changes were observed for variations of outdoor temperature, with medians of 2563 kWh for 0°C, 1711 kWh for 15°C, and 4890 kWh for 35°C. The energy consumed was significantly higher at high T_{out} than at low or medium T_{out} because of the need for dehumidification and subsequent re-heating.

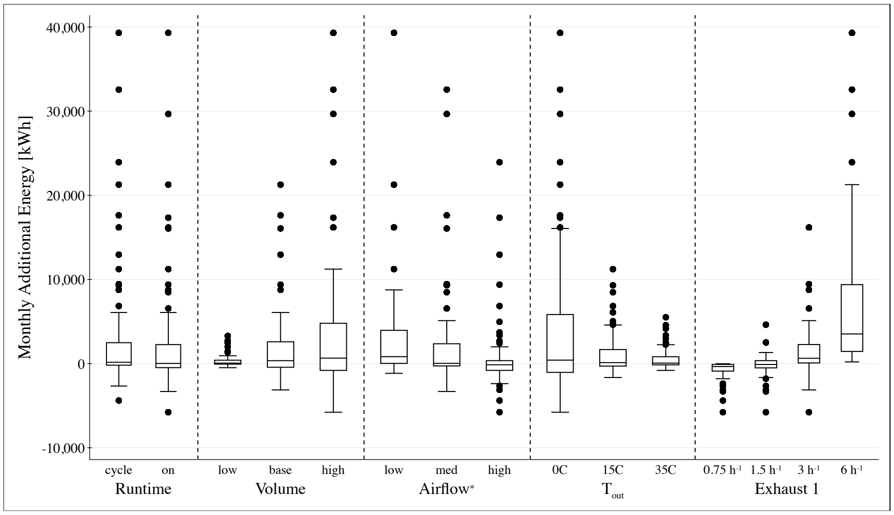

Figure 25: Impact of various parameters on modeled monthly additional energy required for the use of local ventilation as a removal strategy. Parameter codes are defined in Table 26.

Local ventilation is the only removal strategy considered in this study to have the potential to decrease the amount of energy used monthly. Decreases in energy relative to a non-removal reference case were possible when the total airflow entering through the HVAC systems in Zones 1 and 2 of the partitioned store was lower than that of a corresponding single-zone store. In these modeled scenarios that resulted in energy savings, the corresponding formaldehyde concentrations were always achieving the LEED reference limit in Zone 2, and in 34% of the time for Zone 1. These findings suggest that local ventilation has the potential to lead to acceptable formaldehyde concentrations while using less energy.

Overall, the energy associated with implementing local ventilation ranged from -5800 kWh to 39 300 kWh, with a median of 110 kWh. In terms of medians, increased exhaust flowrates in Zone 1 led to great increases in the energy consumed, with medians indicative of energy savings for the low and base case (-350 kWh and -104 kWh, respectively), to 630 kWh (high $\lambda_{ex,1}$) and 3525 kWh (very high $\lambda_{ex,1}$). Counter-intuitively, the energy consumed decreased with increasing airflows ($\lambda_{v,2}$, $\lambda_{i,2}$, $\lambda_{r,2}$), with medians from 826 kWh (low) to 33 kWh (base), and finally -138 kWh for high flowrates ($\lambda_{v,2}$, $\lambda_{i,2}$, $\lambda_{r,2}$).

Overall, filtration was the solution with the potential to consume the least energy across parameters. Local ventilation resulted to the minimum and the maximum energy consumed, and showed the potential to decrease energy consumption. Humidity control was generally associated with a large energy penalty. Since the model used to obtain these results is strongly influenced by the assumptions made when defining the removal strategies, these findings serve mostly to illustrate trends and to highlight promising strategies to remove formaldehyde in retail buildings. Moreover, the energy results should be considered as an upper bound on what actual energy consumption might be. The energy consumption could be decreased if, for instance, stores were equipped with more efficient equipment (humidifiers, dehumidifiers, fans [63]), or if heat from the exhaust airflows was recovered [64]. For the humidity control strategy, energy calculations also don't take into account the heat added to the airstream by the fan, although it has been shown to alter humidity control [65]. In the local ventilation removal strategy, we further neglected the energy penalty associated with the operation of an air curtain [66].

The energy penalty associated with filtration is assumed to be fully consumed as electricity (fan energy), while humidity control and local ventilation use both electricity (cooling energy and dehumidification energy) and gas (heating energy and humidification energy). Since the price of gas is much lower than that of electricity (Table 25), monthly energy costs associated with each removal strategies would not have the same profiles as energy penalties. Such considerations are illustrated by the following case study.

4.3. Estimation of costs: a case study

To illustrate the tradeoffs of formaldehyde removal, energy consumption and energy costs for each removal strategy in a more realistic setting, three buildings (low, medium and high volume) were modeled over a year for three cities: Austin, TX; Seattle, WA, and Phoenix, AZ.

Modeled indoor concentrations were assumed to be independent of volume. As such, a formaldehyde concentration of 40 $\mu g/m^3$ was found in the base case (no removal) scenario for all store sizes. Results for the small store and the medium store can be found in Supporting Information (SI 2). Table 31 shows the decreases in concentrations (ΔC) and increases in yearly energy consumption (ΔE) and energy cost (ΔEC) relative to the base case caused by the use of filtration, humidity control, and local ventilation for the medium-sized store in the three cities. A simple increase in air exchange rate for the entire store, referred to as "whole-building ventilation" here, was also modeled as a basis to assess the performance of the three removal strategies investigated in this study.

Table 31: Predicted performance and annual energy cost for the three alternative removal strategies investigated in a medium retail building in three U.S. cities, as compared to the use of whole-building ventilation (in italics).

Removal Strategy	**ΔC [μg/m^3]**	**Austin**			**Seattle**			**Phoenix**		
		ΔE [kWh/year]	**ΔEC [$/year]**	**R [$/(μg/m^3)/year]**	**ΔE [kWh/year]**	**ΔEC [$/year]**	**R [$/(μg/m^3)/year]**	**ΔE [kWh/year]**	**ΔEC [$/year]**	**R [$/(μg/m^3)/year]**
Filtration	32[a]	2501	250	7.8	2501	250	7.8	2501	250	7.8
Humidity control	13	78 990	2199	166	51 895	1224	92	44 436	1072	81
Local ventilation	26[a]	41 819	923	36	46 389	1391	54	103 580	1006	39
Whole-building ventilation	*18*	*172 519*	*4961*	*282*	*192 808*	*7401*	*421*	*435 565*	*4333*	*247*

[a] The formaldehyde concentration reached met the NIOSH REL.

Whole-building ventilation is the removal strategy most commonly recommended to reduce exposure to indoor pollutants such as formaldehyde [25]. In the case study modeled here, whole-building ventilation led to a decrease in formaldehyde close to half that caused by the use of filtration, but was seventeen to thirty as expensive in terms of annual energy cost. Not only was whole-building ventilation the most expensive and energy-intensive removal strategy across cities, it was amongst the most cost-intensive solutions. In the hot and humid climate of Austin, both whole-building ventilation and humidity control had annual costs per unit of formaldehyde removed one to two orders of magnitude higher than filtration or local ventilation. In drier climates, humidity control was still the second most cost-intensive strategy but by a lesser margin.

Increased ventilation, when provided locally to areas of the store containing most formaldehyde sources, led to greater reductions in formaldehyde concentrations and cost four to five times less than ventilation raised uniformly for the whole store. Local ventilation as well as filtration caused formaldehyde concentrations to drop under the NIOSH exposure limit. In Phoenix, local ventilation was associated with a larger energy penalty than humidity control and filtration. However, local ventilation was the second least cost-intensive solution in all cities. Filtration was the strategy with the cheapest yearly operational energy costs ($250 USD across cities), and was the most cost-effective strategy with a mere $7.8/(μg/m^3)/year. However, it should be noted that these metrics only take into consideration energy costs, and different conclusions may have been reached if the filter acquisition and maintenance costs were included in the analysis.

5. Limitations

The results of this analysis suggest that local ventilation would be the second most efficient and cost-effective strategy for removal of formaldehyde in many retail stores. However, this strategy was designed to condense 80% of the store's sources to 20% of the retail floor area. Such a concentration of sources may only be possible for specific types of retail stores, such as large general merchandise or office supply stores that have a relatively small furniture section, or furniture stores that carry a small selection of pressed wood items within a larger collection of solid wood products.

The sensitivity analyses conducted for humidity control and filtration suggest that increased infiltration rates would reduce indoor formaldehyde, at no cost. This finding is misleading, and comes from our choice not to explicitly model thermal and sensible loads in the stores. The introduction of unconditioned air would actually affect the temperature and moisture content of the air in the store, and the recirculated air would require conditioning.

The modeling framework developed here was based on parameters varying independently. However, formaldehyde emissions would likely be affected by changes in air exchange rates, as surface air movement has been shown to have a non-negligible impact on material emissions[67].

In the future, cost analyses should be refined by adding more realistic parameters as they become available, notably for filtration, and by expanding the simulation to more climate zones. Future analyses could also investigate the impact of transient effects on concentrations that would occur as the HVAC system changes operating mode.

Finally, it should be noted that if European health guidelines had been considered, formaldehyde control strategies would have been unnecessary in the vast majority of scenarios considered in this paper.

6. Conclusions

The results of an effort to model the impact of various parameters on the concentration of formaldehyde in retail stores were presented in this paper. Removal strategies were introduced and optimized to reduce exposure to formaldehyde with a minimal energy penalty. Local ventilation and filtration were found to have the largest potentials to reduce indoor concentrations. The extent to which humidity control reduced exposure to formaldehyde was very limited, but the analysis brought to light the negative impacts of high indoor relative humidity on formaldehyde concentrations.

This work identified critical parameters according to their impacts on concentration and energy consumption, and should help designers as they consider formaldehyde removal strategies. Local ventilation was the only removal strategy to have the potential to decrease the amount of energy used monthly and maintain formaldehyde concentrations under the LEED reference limit. A case study revealed that filtration was the most promising strategy in terms of energy cost-to-unit of formaldehyde removed.

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References

[1] Monthly Energy Review. US Energy Information Administration; 2014.

[2] U.S. Energy Information Administration. Table B11. Selected Principal Building Activity: Part 1, Number of Buildings for Non-Mall Buildings, 2003. WwwEiaGov 2008.

[3] U.S. Energy Information Administration. Table B7. Building Size, Floorspace for Non-Mall Buildings, 2003. WwwEiaGov 2008.

[4] U.S. Energy Information Administration. Table E1. Major Fuel Consumption (Btu) by End Use for Non-Mall Buildings, 2003. WwwEiaGov 2008.

[5] U.S. Department of Labor. Industries at a Glance - Retail Trade: NAICS 44-45. WwwBlsGov 2014.

[6] U.S. Department of Labor. ATUS Latest Numbers: Purchasing Goods and Services. WwwBlsGov 2013.

[7] U.S. Census Bureau. Historical Adjusted Monthly Sales - Retail Total (excl. food services). WwwCensusGov 2014.

[8] Spangenberg EA, Crowley AE, Henderson PW. Improving the store environment: do olfactory cues affect evaluations and behaviors? Journal of Marketing 1996;60:67–80.

[9] Douce L, Janssens W. The Presence of a Pleasant Ambient Scent in a Fashion Store: The Moderating Role of Shopping Motivation and Affect Intensity. Environment and Behavior 2013;45:215–38.

[10] Salthammer T, Mentese S, Marutzky R. Formaldehyde in the Indoor Environment. Chem Rev 2010;110:2536–72.

[11] Hotchi T, Hodgson AT, Fisk WJ. Indoor air quality impacts of a peak load shedding strategy for a large retail building. LBNL Report 2006;59293.

[12] Loh MM, Houseman EA, Gray GM, Levy JI, Spengler JD, Bennett DH. Measured Concentrations of VOCs in Several Non-Residential Microenvironments in the United States. Environ Sci Technol 2006;40:6903–11.

[13] Wu XM, Apte MG, Maddalena R, Bennett DH. Volatile Organic Compounds in Small- and Medium-Sized Commercial Buildings in California. Environ Sci Technol 2011;45:9075–83.

[14] Grimsrud DT, Carlson N, Bridges B, Springman T, Williams S. Investigation of appropriate ventilation rates for retail stores. Indoor Air, 2011, pp. 1–6.

[15] Dutton SM, Chan WR, Mendell MJ, Barrios M, Parthasarathy S, Sidheswaran M, et al. Evaluation of the Indoor Air Quality Procedure for Use in Retail Buildings 2013.

[16] Nirlo EL, Crain N, Corsi RL, Siegel JA. Volatile organic compounds in fourteen U.S. retail stores. Indoor Air 2014:n/a–n/a.

[17] Salmon AG, Marthy MA, Alexeef GV. Technical support document for the derivation of noncancer reference exposure levels. California Environmental Protection Agency; 2008.

[18] Nielsen GD, Hougaard KS, Larsen ST, Hammer M, Wolkoff P, Clausen PA, et al. Acute airway effects of formaldehyde and ozone in BALB/c mice. Human & Experimental Toxicology 1999;18:400–9.

[19] Wolkoff P. Indoor air pollutants in office environments: Assessment of comfort, health, and performance. International Journal of Hygiene and Environmental Health 2013;216:371–94.

[20] Krzyzanowski M, Quackenboss JJ, Lebowitz MD. Chronic respiratory effects of indoor formaldehyde exposure. Environmental Research 1990;52:117–25.

[21] Wolkoff P, Nielsen GD. Non-cancer effects of formaldehyde and relevance for setting an indoor air guideline. Environment International 2010;36:788–99.

[22] Nielsen GD, Larsen ST, Wolkoff P. Recent trend in risk assessment of formaldehyde exposures from indoor air. Arch Toxicol 2013;87:73–98.

[23] U.S. Environmental Protection Agency. Formaldehyde (CASRN 50-00-0) - IRIS. WwwEpaGov 2012.

[24] World Health Organization. International Agency for Research on Cancer Monographs on the Evaluation of Carcinogenic Risks to Human, Volume 88: Formaldehyde, 2-Butoxyethanol and 1-tert-Butoxy-2-propanol, World Health Organization, Lyon; 2006.

[25] ASHRAE. *ASHRAE Standard 62.1-2013 Ventilation for Acceptable Indoor Air Quality*. Atlanta: American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc 2013.

[26] Turner WJN, Logue JM, Wray CP. A combined energy and IAQ assessment of the potential value of commissioning residential mechanical ventilation systems. Building and Environment 2013;60:194–201.

[27] U.S. Environmental Protection Agency. Energy Cost and IAQ Performance of Ventilation Systems and Controls. U.S. Environmental Protection Agency; 2000.

[28] Apte MG, Mendell MJ, Sohn MD, Dutton SM, Berkeley PM, Spears M. Balancing energy conservation and occupant needs in ventilation rate standards for Big Box stores in California: predicted indoor air quality and energy consumption using a matrix of ventilation scenarios. Lawrence Berkeley National Laboratory; 2013.

[29] Ng LC, Persily AK, Emmerich SJ, Teichman KY. The IAQ and Energy Impacts of Reducing Formaldehyde Emissions in Commercial Buildings. ASHRAE IAQ 2013 Proceedings: Environmental Health in Low Energy Buildings., 2013, pp. 1–8.

[30] Riley WJ, McKone TE, Lai ACK, Nazaroff WW. Indoor Particulate Matter of Outdoor Origin: Importance of Size-Dependent Removal Mechanisms. Environ Sci Technol 2002;36:200–7.

[31] Hawthorne AR, Matthews TG. Models for estimating organic emissions from building materials: Formaldehyde example. Atmospheric Environment (1967) 1987;21:419–24.

[32] Salthammer T. Formaldehyde in the ambient atmosphere: from an indoor pollutant to an outdoor pollutant? Angewandte Chemie International Edition 2013;52:3320–7.

[33] Guven BB, Olaguer EP. Ambient formaldehyde source attribution in Houston during TexAQS II and TRAMP. Atmospheric Environment 2011;45:4272–80.

[34] Grosjean D, Grosjean E, Moreira LFR. Speciated Ambient Carbonyls in Rio de Janeiro, Brazil. Environ Sci Technol 2002;36:1389–95.

[35] Weisel CP, Zhang J, Turpin BJ, Morandi MT, Colome S, Stock TH, et al. Relationships of Indoor, Outdoor, and Personal Air (RIOPA). Part I. Collection methods and descriptive analyses. Research Report (Health Effects Institute) 2005:1–107–discussion109–27.

[36] U.S. Environmental Protection Agency. *Chapter 19—Building Characteristics. Exposure Factors Handbook*, U.S. Environmental Protection Agency; 2011, pp. 1–58.

[37] Deru M, Field K, Studer D, Benne K, Griffith B, Torcellini P, et al. US Department of Energy commercial reference building models of the national building stock. National Renewable Energy Laboratory; 2011.

[38] Zaatari M, Nirlo EL, Jareemit D, Crain N, Srebric J, Siegel JA. Ventilation and indoor air quality in retail stores: A critical review (RP-1596). HVAC&R Research 2014;20:276–94.

[39] Turk BH, Geisling-Sobatka K, Froelich DA, Grimsrud DT, Harrison J, Koonce JF, et al. Indoor Air Quality and Ventilation Measurements in 38 Pacific

Northwest Commercial Buildings -Volume 1: Measurement Results and Interpretation. Berkeley, CA: Lawrence Berkeley Laboratory; 1987.

[40] Siegel JA, Srebric J, Crain N, Nirlo EL, Zaatari M, Hoisington A, et al. Ventilation and indoor air quality in retail stores. ASHRAE; 2013.

[41] Bennett DH, Fisk WJ, Apte MG, Wu XM, Trout A, Faulkner D, et al. Ventilation, temperature, and HVAC characteristics in small and medium commercial buildings in California. Indoor Air 2012;22:309–20.

[42] Won D, Corsi RL, Rynes M. Sorptive interactions between VOCs and indoor materials. Indoor Air 2001;11:246–56.

[43] Plaisance H, Blondel A, Desauziers V, Mocho P. Field investigation on the removal of formaldehyde in indoor air. Building and Environment 2013;70:277–83.

[44] Weschler CJ. Ozone in indoor environments: concentration and chemistry. Indoor Air 2000;10:269–88.

[45] Weschler CJ, Shields HC. Production of the hydroxyl radical in indoor air. Environ Sci Technol 1996;30:3250–8.

[46] Xu J, Zhang JS, Liu X, Gao Z. Determination of partition and diffusion coefficients of formaldehyde in selected building materials and impact of relative humidity. Journal of the Air & Waste Management Association 2012;62:671–9.

[47] Andersen IB, Lundqvist GR, Mølhave L. Indoor air pollution due to chipboard used as a construction material. Atmospheric Environment 1975;9:1121–7.

[48] Pickrell JA, Griffis LC, Mokler BV, Kanapilly GM, Hobbs CH. Formaldehyde release from selected consumer products: influence of chamber loading, multiple products, relative humidity, and temperature. Environ Sci Technol 1984;18:682–6.

[49] Myers GE. The effects of temperature and humidity on formaldehyde emission from UF-bonded boards: a literature critique. Forest Products Journal 1985;35:20–31.

[50] Frihart CR, Wescott JM, Chaffee TL, Gonner KM. Formaldehyde Emissions from Urea-Formaldehyde-and No-Added-Formaldehyde-Bonded Particleboard as Influenced by Temperature and Relative Humidity. Forest Products Journal 2012;62.

[51] van Netten C, Shirtliffe C, Svec J. Temperature and humidity dependence of formaldehyde release from selected building materials. Bulletin of Environmental Contamination and Toxicology 1989;42:558–65.

[52] Parthasarathy S, Maddalena RL, Russell ML, Apte MG. Effect of Temperature and Humidity on Formaldehyde Emissions in Temporary Housing Units. Journal of the Air & Waste Management Association 2011;61:689–95.

[53] Berge A, Mellegaard B, Hanetho P, Ormstad EB. Formaldehyde release from particleboard—evaluation of a mathematical model. Holz Als Roh-Und Werkstoff 1980;38:251–5.

[54] Godish T, Rouch J. An Assessment of the Berge Equation Applied to Formaldehyde Measurements under Controlled Conditions of Temperature and Humidity in a Mobile Home. Journal of the Air Pollution Control Association 1985;35:1186–7.

[55] Energy Standard for Buildings Except Low-Rise Residential Buildings. ASHRAE; 2013.

[56] Zaatari M, Novoselac A, Siegel JA. The relationship between filter pressure drop, indoor air quality, and energy consumption in rooftop HVAC units. Building and Environment 2014;73:151–61.

[57] U.S. Energy Information Administration. Henry Hub Natural Gas Spot Price (Dollars per Million Btu). WwwEiaGov 2014.

[58] ASHRAE. Psychrometrics. ASHRAE Handbook - Fundamentals, Atlanta, GA: American Society of Heating, Refrigerating, and Air Conditioning Engineers, Inc; 2012, pp. 1–1.

[59] WHO European Centre for Environment and Health, WHO Regional Office for Europe. WHO Guidelines for Indoor Air Quality: Selected Pollutants. Copenhagen, Denmark: World Health Organization; 2010.

[60] U S Green Building Council. Indoor air quality procedure - alternative compliance path: EQpc68. WwwUsgbcorg 2014.

[61] TMY3 - Austin, TX; Phoenix, AZ; Seattle, WA 2014.

[62] Wolkoff P, Nojgaard JK, Franck C, Skov P. The modern office environment desiccates the eyes? Indoor Air 2006;16:258–65.

[63] Chua KJ, Chou SK, Yang WM, Yan J. Achieving better energy-efficient air conditioning : A review of technologies and strategies. Applied Energy 2013;104:87–104.

[64] Genest F, Minea V. High-Performance Retail Store with Integrated HVAC Systems. ASHRAE Transactions 2006;112.

[65] Witte MJ, Henninger RH. Evaluating the Ability of Unitary Equipment to Maintain Adequate Space Humidity Levels. ASHRAE Transactions 2010;116.

[66] Gil-Lopez T, Galvez-Huerta MA, Castejon-Navas J, Gomez-Garcia V. Experimental analysis of energy savings and hygrothermal conditions

improvement by means of air curtains in stores with intensive pedestrian traffic. Energy & Buildings 2013;67:608–15.

[67] Knudsen HN, Kjaer UD, Nielsen PA, Wolkoff P. Sensory and chemical characterization of VOC emissions from building products: impact of concentration and air velocity. Atmospheric Environment 1999;33:1217–30.

Supporting Information

SI 1: Expanded Discussion on Selected Input Parameters

1. Homogeneous reactions

Formaldehyde can be consumed by reactions with highly reactive species such as hydroxyl radicals and ozone [1]. Typical indoor hydroxyl radical concentrations are estimated at 1.7×10^{5} molecules/cm^{3} [2]. Since the reaction rate constant of hydroxyl radicals with formaldehyde is equal to 9.37×10^{-12} cm^{3}/molecules/s [3], the rate of removal for a reasonable formaldehyde concentration can be estimated to be $5\text{-}10\times10^{-3}$ h^{-1}, negligible compared to losses by ventilation. Formaldehyde can also be formed as ozone reacts with unsaturated volatile organic compounds [4]. Although limited, data on ozone concentrations encountered in retail stores [5] suggests that ozone concentrations are too low to significantly impact indoor formaldehyde concentrations. For these reasons, gains and losses of formaldehyde by homogenous reactions are neglected in this analysis.

2. Formaldehyde removal

In this section, the various technologies that have been investigated to remove formaldehyde from an airstream are summarized, and whether these solutions could be used as a control device for removal of formaldehyde under typical indoor conditions is indicated.

Photocatalytic oxidation. Many studies have investigated the photodegradation of formaldehyde by TiO_2 (or titania) [6-9]. This process requires contact between the photocatalyst and the pollutant, and the presence of light (or UV). The titania can be placed on a glass plate reactor [10,11] to simulate coated windows, on lighted textile

[12], on meso-porous materials [13], or in paints [14]. Reported downsides include the price and low efficiency of the photocatalytic oxidation process, issues with deactivation and competitive conversion in gas mixtures [15,16], and the formation of by-products [17]. No study reported clean air delivery rates (CADR = flow times efficiency).

Adsorption. Formaldehyde can be captured by activated carbon (AC) filters if the AC is chemically enhanced with metal oxides (copper [18], manganese [19,20]). Other options include silica materials functionalized with amino-propyl groups [21], scallop shell nanoparticles [22], or the addition of nano-size carbon colloids onto a filter [23]. Stromm and Gesser [24] tested coating air filters with polymeric amines and glycerol to capture aldehydes, and reported initial single pass efficiencies of 40% for acetaldehyde. Only one study [18] reported removal efficiencies and clean air delivery rates for a copper-enhanced AC filter, although the CADRs (0.098-0.154 m^3/h) were extremely low.

Combination filters. A common combination is that of AC filters, generally in a honeycomb rotor, and photocatalytic reactors [25-27]. Sekine et al. [28] developed an air cleaner that combines a photocatalyst filter, an AC filter, and a MnO_2 filter, recommended for formaldehyde and toluene. The reported CADR ranged from 20 to 35 m^3/h for an input formaldehyde concentration of 10 mg/m^3.

Biotechnologies. Lu et al. [29,30] investigated the performance of four bacterial strains to remove formaldehyde in a biotrickling filter. For input formaldehyde concentrations in air as low as 222 $\mu g/m^3$, the filters had efficiencies ranging from 69 to 94%, for a pressure drop of 120 Pa under an airflow of 1.5 L/min.

3. Fan energy: pressure drop associated with a formaldehyde filter.

We estimate a minimum additional pressure drop from Equation 1, developed for 2" activated carbon filters [31], using medium airflows and volume values as determined in sections 2.1.3 and 2.1.4.4.

$$\Delta P_{ff} = 0.0142\times\left(\frac{(\lambda_v+\lambda_r)V}{n_{filter}}\right) - 25.145 \qquad \text{(Eq. 1)}$$

Where n_{filter} is the number of filters required (-), determined by first calculating the area of filtration required to maintain a face velocity of 2.5 m/s [32] on the filters under medium airflows, and dividing this area by that of an individual filter. Pressure drop will be varied from this minimum value to medium and high levels (obtained by applying factors of 5) to evaluate its impact on fan energy consumption.

References

[1] Salthammer T, Mentese S, Marutzky R. Formaldehyde in the Indoor Environment. Chem Rev 2010;110:2536–72.

[2] Weschler CJ, Shields HC. Production of the hydroxyl radical in indoor air. Environ Sci Technol 1996;30:3250–8.

[3] Atkinson R. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. Chem Rev 1985;85:69–201.

[4] Weschler CJ. Ozone in indoor environments: concentration and chemistry. Indoor Air 2000;10:269–88.

[5] Siegel JA, Srebric J, Crain N, Nirlo EL, Zaatari M, Hoisington A, et al. Ventilation and indoor air quality in retail stores. ASHRAE RP-1596; 2013.

[6] Noguchi T, Fujishima A, Sawunyama P, Hashimoto K. Photocatalytic Degradation of Gaseous Formaldehyde Using TiO 2Film. Environ Sci Technol 1998;32:3831–3.

[7] Zhang Y, Yang R, Zhao R. A model for analyzing the performance of photocatalytic air cleaner in removing volatile organic compounds. Atmospheric Environment 2003;37:3395–9.

[8] Wang S, Ang HM, Tade MO. Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art. Environment International 2007;33:694–705.

[9] Yu K-P, Lee GW-M, Huang W-M, Wu C-C, Lou C-L, Yang S. Effectiveness of

Photocatalytic Filter for Removing Volatile Organic Compounds in the Heating, Ventilation, and Air Conditioning System. Journal of the Air & Waste Management Association 2006;56:666–74.

[10] Obee TN. Photooxidation of sub-parts-per-million toluene and formaldehyde levels on titania using a glass-plate reactor. Environ Sci Technol 1996;30:3578–84.

[11] Ching WH, Leung M, Leung DYC. Solar photocatalytic degradation of gaseous formaldehyde by sol–gel TiO2 thin film for enhancement of indoor air quality. Solar Energy 2004;77:129–35.

[12] Bourgeois P-A, Puzenat E, Peruchon L, Simonet F, Chevalier D, Deflin E, et al. Characterization of a new photocatalytic textile for formaldehyde removal from indoor air. Applied Catalysis B: Environmental 2012;128:171–8.

[13] Saadoun L, Ayllon JA, Jimenez-Becerril J, Peral J, Domenech X, Rodrıguez-Clemente R. Synthesis and photocatalytic activity of mesoporous anatase prepared from tetrabutylammonium-titania composites. Materials Research Bulletin 2000;35:193–202.

[14] Kibanova D, Sleiman M, Cervini-Silva J, Destaillats H. Adsorption and photocatalytic oxidation of formaldehyde on a clay-TiO2 composite. Journal of Hazardous Materials 2012;211-212:233–9.

[15] Ao CH, Lee SC, Yu JZ, Xu JH. Photodegradation of formaldehyde by photocatalyst TiO2: effects on the presences of NO, SO2 and VOCs. Applied Catalysis B: Environmental 2004;54:41–50.

[16] Obee TN, Brown RT. TiO2 photocatalysis for indoor air applications: effects of humidity and trace contaminant levels on the oxidation rates of formaldehyde, toluene, and 1, 3-butadiene. Environ Sci Technol 1995;29:1223–31.

[17] Destaillats H, Sleiman M, Sullivan DP, Jacquiod C, Sablayrolles J, Molins L. Key parameters influencing the performance of photocatalytic oxidation (PCO) air purification under realistic indoor conditions. Applied Catalysis B: Environmental 2012;128:159–70.

[18] Huang Y-C, Luo C-H, Yang S, Lin Y-C, Chuang C-Y. Improved Removal of Indoor Volatile Organic Compounds by Activated Carbon Fiber Filters Calcined with Copper Oxide Catalyst. Clean Soil Air Water 2010;38:993–7.

[19] Sekine Y, Nishimura A. Removal of formaldehyde from indoor air by passive type air-cleaning materials. Atmospheric Environment 2001;35.

[20] Sekine Y. Oxidative decomposition of formaldehyde by metal oxides at room temperature. Atmospheric Environment 2002;36:5543–7.

[21] Ewlad-Ahmed AM, Morris MA, Patwardhan SV, Gibson LT. Removal of Formaldehyde from Air Using Functionalized Silica Supports. Environ Sci Technol 2012;46:13354–60.

[22] Yamanaka S, Suzuma A, Fujimoto T, Kuga Y. Production of scallop shell nanoparticles by mechanical grinding as a formaldehyde adsorbent. J Nanopart Res 2013;15:1573.

[23] Kim H-J, Han B, Kim Y-J, Yoon Y-H, Oda T. Efficient test method for

evaluating gas removal performance of room air cleaners using FTIR measurement and CADR calculation. Building and Environment 2012;47:385–93.

[24] Strommen M, Gesser HD. The trapping of indoor air contaminants. Central European Journal of Chemistry 2011;9:404–9.

[25] Chin P, Yang LP, Ollis DF. Formaldehyde removal from air via a rotating adsorbent combined with a photocatalyst reactor: Kinetic modeling. Journal of Catalysis 2006;237:29–37.

[26] Ao CH, Lee SC. Indoor air purification by photocatalyst TiO 2 immobilized on an activated carbon filter installed in an air cleaner. Chemical Engineering Science 2005;60:103–9.

[27] Shiraishi F, Yamaguchi S, Ohbuchi Y. A rapid treatment of formaldehyde in a highly tight room using a photocatalytic reactor combined with a continuous adsorption and desorption apparatus. Chemical Engineering Science 2003;58:929–34.

[28] Sekine Y, Fukuda M, Takao Y, Ozano T, Sakuramoto H, Wang KW. Simultaneous removal of formaldehyde and benzene in indoor air with a combination of sorption-and decomposition-type air filters. Environmental Technology 2011;32:1983–9.

[29] Lu Y, Liu J, Lu B, Jiang A, Wan C. Study on the removal of indoor VOCs using biotechnology. Journal of Hazardous Materials 2010;182:204–9.

[30] Lu N, Pei J, Zhao Y, Qi R, Liu J. Performance of a biological degradation method for indoor formaldehyde removal. Building and Environment 2012;57:253–8.

[31] Corsi RL, Aldred J, Darling E, Siegel JA, Morrison GC. *Literature and Product Review and Cost Benefit Analysis of Commercially Available Ozone Air Cleaning for HVAC Systems*. ASHRAE RP-1491; to be published in 2014.

[32] Bekö G, Clausen G, Weschler CJ. Is the use of particle air filtration justified? Costs and benefits of filtration with regard to health effects, building cleaning and occupant productivity. Building and Environment 2008;43:1647–57.

SI 2: Case study - results for the small and the large stores.

Table 32 shows the decreases in concentrations (ΔC) and increases in yearly energy consumption (ΔE) and energy cost (ΔEC) relative to the base case caused by the use of filtration, humidity control, and local ventilation for the small-sized store in the three cities. A simple increase in air exchange rate for the entire store, referred to as "whole-building ventilation" here, was also modeled as a basis to assess the performance of the three removal strategies investigated in this study. Table 33 shows the results for the large modeled store.

Table 32: Predicted performance and annual energy cost for the three alternative removal strategies investigated in a small retail building in three U.S. cities, as compared to the use of whole-building ventilation (in italics).

Removal Strategy	**ΔC [µg/m^3]**	**Austin**			**Seattle**			**Phoenix**		
		ΔE [kWh/year]	**ΔEC [$/year]**	**R [$/(µg/m^3)/year]**	**ΔE [kWh/year]**	**ΔEC [$/year]**	**R [$/(µg/m^3)/year]**	**ΔE [kWh/year]**	**ΔEC [$/year]**	**R [$/(µg/m^3)/year]**
Filtration	32[a]	385	38	1.2	385	38	1.2	385	38	1.2
Humidity control	13	12 171	339	25.5	7996	189	14.2	6847	165	12.4
Local ventilation	26[a]	6443	142	5.6	7148	214	8.4	15 959	155	6.0
Whole-building ventilation	*18*	*26 582*	*764*	*43.5*	*29 708*	*1140*	*64.9*	*67 111*	*668*	*38.0*

[a] The formaldehyde concentration reached met the NIOSH REL.

Table 33: Predicted performance and annual energy cost for the three alternative removal strategies investigated in a large retail building in three U.S. cities, as compared to the use of whole-building ventilation (in italics).

Removal Strategy	**ΔC [µg/m^3]**	**Austin**			**Seattle**			**Phoenix**		
		ΔE [kWh/year]	**ΔEC [$/year]**	**R [$/(µg/m^3)/year]**	**ΔE [kWh/year]**	**ΔEC [$/year]**	**R [$/(µg/m^3)/year]**	**ΔE [kWh/year]**	**ΔEC [$/year]**	**R [$/(µg/m^3)/year]**
Filtration	32[a]	4621	461	14.5	4621	461	14.5	4621	461	14.5
Humidity control	13	145 953	4064	306	95 889	2261	170	82 105	1980	149
Local ventilation	26[a]	77 270	1706	66.6	85 715	2570	100	191 389	1859	72.5
Whole-building ventilation	*18*	*318 770*	*9166*	*522*	*356 259*	*13676*	*778*	*804 808*	*8006*	*456*

[a] The formaldehyde concentration reached met the NIOSH REL.

APPENDIX D: VENTILATION AND INDOOR AIR QUALITY IN RETAIL STORES: A CRITICAL REVIEW (RP-1596).

VENTILATION AND INDOOR AIR QUALITY IN RETAIL STORES: A CRITICAL REVIEW (RP-1596)

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Abstract

Identifying air pollutants that pose potential adverse health exposures in retail stores will facilitate exposure mitigation. Assessing the role of ventilation in mitigating this exposure is important to understand the energy implications of maintaining acceptable indoor air quality. In this work, we summarize results from 28 papers that report ventilation rates and/or pollutant concentrations in retail stores. These results were compared to available standards as well as data collected in non-retail environments. The findings of this review are: (1) half of the stores tested met/exceeded ASHRAE Standard 62.1-2010 (or California Code of Regulations Title 24-2010) for ventilation; (2) $PM_{2.5}$, acrolein, formaldehyde, and acetaldehyde exceeded their established most conservative

limits/reference exposures for a few of the stores tested in the U.S.; outside the U.S., researchers reported PM_{10}, benzene and trichloroethylene as additional pollutants found at concentrations that exceeded their limits; (3) alternative control methods would be more effective and possibly more economical than ventilation, (4) meeting or exceeding the ventilation requirements does not necessarily negate the presence of pollutants above their suggested limits; and (5) using disability-adjusted-life-year (DALY) as a metric of disease burden, two pollutants were identified as priority hazards in retail stores: $PM_{2.5}$ and acrolein. Control strategies should focus on decreasing exposure of retail employees to these pollutants generated indoors or infiltrated from outdoors.

Introduction

Among commercial buildings, retail buildings rank second in energy consumption and greenhouse gas emissions, after office buildings (Zhang et al., 2011, Kennedy et al., 2012). Within retail stores, HVAC systems have been identified as one of the largest energy users, accounting for 28% to 48% of the total building energy use (Alhafi, 2012). The retail sector employs 15 million workers, approximately 10% of the U.S. workforce (NRF, 2010), making the indoor air quality (IAQ) of retail buildings an important occupational exposure consideration. Additionally, the average American above the age of fifteen spends 0.48 hours per day purchasing goods and groceries (ATUS, 2011), further highlighting the importance of IAQ in these environments. Ventilation is generally regarded as the most effective measure to improve IAQ when source control is not an option. However, there is a tradeoff between increasing ventilation to improve

IAQ and saving fan and conditioning energy associated with ventilation. A sustainable approach to retail environment ventilation must also consider the occupant perceptions and health exposures for retail workers and customers.

Despite the importance of retail buildings, there have been no published reviews focusing on contaminants of concern in retail buildings, and whether ventilation can be used to control these contaminants below their reference or regulatory limits. Specifically this literature review addresses the following questions:

1. How do ventilation rates measured in retail stores compare to standards?
2. What are the dominant pollutants in different types of retail spaces?
3. How do different ventilation measurement methods affect the reported results?
4. What are the associations between ventilation and IAQ?
5. What are the contaminants of concern from an exposure perspective?

This paper addresses these questions by summarizing ventilation rates and pollutants concentrations reported in the relevant literature. These data are also compared to the available standards and guidelines as well as data collected in non-retail environments. The reported concentrations are contextualized with information about sampling and analysis approaches where possible. Furthermore, this investigation also discusses the available data linking ventilation and measured pollutant concentrations, and finally evaluates contaminants of concern found in retail environments through a disability-adjusted-life-years (DALYs) loss assessment. The central objective of this approach is to provide baseline data for comparison of results from the ASHRAE RP-1596 project conducted between 2011 and 2013 (Siegel et al., 2013). The goal of the RP-1596 project was to characterize the ventilation, indoor air quality, and occupant perception in 14 retail stores located in Texas and Pennsylvania and this literature review serves as background to that investigation.

Methodology and search criteria

The literature review systematically searched the following online databases: the ISI Web of science, Compendex, ScienceDirect, government reports, and Google Scholar. The keywords used to guide the search included various combinations of ‘energy’, ‘ventilation’, ‘infiltration’, ‘air exchange rate’, ‘outdoor air rate’, ‘IAQ’, multiple pollutants (i.e. ‘VOCs’, ‘SVOC’, ‘aldehydes’, ‘particulate matter’, ‘bacteria’, ‘fungi’, ‘radon’, ‘carbon monoxide’, ‘nitrogen dioxide’, ‘sulfur dioxide’) with ‘retail’, ‘mall’, ‘supermarket’, “store”, “shopping”, and ‘commercial building’. Other types of buildings were also included in the search for comparison purposes. Excluding those references included from other building types, papers had to report measured ventilation, indoor air quality, and/or occupant survey results for retail buildings. Records for approximately 118 papers were deemed to be the most relevant to the research questions of interest, and of those 28 publications specifically reported measurements in retail spaces. After the articles were selected they were sorted into one of the following categories: (i) Ventilation; (ii) Particulate matter; (iii) VOCs; and (iv) Other pollutants (i.e. Ozone, SVOCs, microbiological contaminants, radon, CO, NO_X, and SO_X).

Summary of literature review

The existing studies with reported ventilation raters and/or IAQ measurements provide data for retail ventilation rates, particulate matter, VOCs, and other pollutant concentrations. Some of the studies included investigations that considered the impact of ventilation on these concentrations. The studies that reported ventilation and/or pollutant concentrations in retail stores are categorized and summarized in Table 34.

Table 34: Summary of measurement studies in retail stores.

Study	N	Store Type[1]	Ventilation/ Pollutant	Sampling Method	Location
Shaw 1981	10	9 Supermarket 1 Shopping mall	Infiltration	Pressure difference	
Yu et al. 1996	10	Malls	Radon	Tsivoglou procedure (TN-WL-MS filter)	Hong Kong
Grimsrud et al. 1999	1	General merchandise	$PM_{2.5}$	Continuous particle counting (Atcor APC)	Minnesota, U.S.
Marley 2000	1	General merchandise	Radon	Continuous radon level (NITON Rad 7)	Northampton-shire, UK
Chao and Chan 2001	2	Computer	Air exchange rate	Tracer gas decay (SF_6)	Hong Kong
			43 VOCs	4-hr canister sample	
Kim et al. 2001	5	2 Department 3 Perfume	15 VOCs	2-hr sorbent tubes	Birmingham, U.S.
Li et al. 2001	9	Malls	PM_{10}	Continuous particle mass (TSI Dusttrak)	Hong Kong
			CO	Non-dispersive infrared (Thermo Electron Model 48 Analyzer)	
			Bacteria	Culturing	
Rea et al. 2001	1	Retail (unspecified)	$PM_{2.5}$	Integrated gravimetric particle mass (PEM, MSP)	Baltimore, U.S.
Sakai et al. 2002	1	Department	PM_{10}, PPAH	Continuous particle mass (TSI Dusttrak, AQM)	Tokyo, Japan

Hartman et al. 2004	5	2 Furniture 3 Electronics	SVOC	Polyurethane foam (PUF) plugs	Zurich, Switzerland
Wang et al. 2004	8	Supermarket/office	Radon	Passive detector (SSNTD of CR-39) Active detector-continuous radon level (SNC 1027)	China
Wargocki et al. 2004	1	Department	Air exchange rate	Outdoor air duct pressure differential	Germany
Liu et al. 2004	5	General merchandise	PM_{10}, $PM_{2.5}$, PM_1	Continuous particle mass (Dustmate)	Beijing, China
Tang et al. 2005	7	2 Supermarkets 4 Department 1 Book	11 VOCs	30-min sorbent tubes	Guangzhou, China
Hotchi et al. 2006	1	General merchandise	Air exchange rate	Tracer gas decay (PMCH)	San Francisco, U.S.
			34 VOCs	30-min sorbent and DNPH tubes	
Loh et al. 2006	113	17 Hardware 12 Multipurpose 16 Grocery 8 Drugstores 14 Sporting goods 11 Furniture 16 Houseware 10 Department 9 Electronics	16 VOCs	1 to 3-hr composite sorbent and DNPH tubes	Boston, U.S.
Lee and Hsu 2007	12	Photocopy	$PM_{2.5}$, ultrafine particles (<0.1 μm)	Continuous particle mass (Dusttrak), particle sizer (SMPS/CPC Model 3025A & APS)	Taiwan
			5 VOCs	2-hr sorbent tubes	
			Ozone	Ecotech ML9810B	
Bruno et al. 2008	4	2 Supermarkets 2 Pharmacies	15 VOCs	24-hr diffusive samplers	Bari, Italy
Eklund et al. 2008	4	1 Jeweler 1 Clothing rental 1 Optician 1 Video rental	28 VOCs	8-hr canister	New Jersey, U.S.
Tringe et al. 2008	2	Malls	Bacteria	DNA sequencing and cloning	Singapore
Caselli et al. 2009	2	Printing	23 VOCs	24-hr diffusive samplers	Bari, Italy

Maskey et al. 2011	1	Mall	Chemical analysis of particles 1–2.5 µm and 2.5–10 µm	X-ray Microanalysis (low-Z particle Electron probe)	Korea
Bennett et al. 2011	10	2 Grocery 1 Florist 1 Cabinet 1 Water filters 1 Art supplies 1 Bookstore 2 Sporting goods 1 Convenience/gas station	Air exchange rate	Tracer gas decay (SF_6) Steady-state PFT CO_2 equilibrium	California, U.S.
			PM_{10}, $PM_{2.5}$, sub-3micron particles (<3 μm)	Integrated gravimetric particle mass (Harvard cascade impactors), Continuous particle counting (Met One Model 237B, TSI CPC Model 3781)	
Grimsrud et al. 2011	3	General merchandise	Air exchange rate	Tracer gas decay (CO_2)	Minnesota, Florida, Maryland, U.S.
			20 VOCs	48-hr formaldehyde and passive organic vapor badges	
Wu et al. 2011	9	2 Grocery 7 Retail (unspecified)	Air exchange rate	Tracer gas decay (SF_6)	California, U.S.
			30 VOCs	4-hr sorbent and DNPH tubes	
			SVOC (DEP)	Sorbent tubes	
Brown et al. 2012	2	1 Bookstore 1 Grocery	$PM_{2.5}$, submicron particles (<1 μm)	Continuous particle mass (TSI Dusttrak) number (TSI P-Trak Model 8525)	Atlanta, U.S.
Chan et al. 2012	5	2 Grocery 3 Furniture	Air exchange rate	Tracer gas decay (SF_6)	California, U.S.
			PM_{10}, $PM_{2.5}$	Integrated gravimetric particle mass (SKC PEM)	
			46 VOCs	1&2-hr sorbent, DNPH and PFP tubes	
			Ozone	2B Tech Model 205	
Bennett et al., 2012	10	2 Grocery 1 Florist 1 Cabinet 1 Water filters 1 Art supplies 1 Bookstore 2 Sporting goods 1 Convenience/gas station	Air exchange rate, mechanical air exchange rate	Tracer gas decay (SF_6), calibrated variable speed fan with integral airflow meter	California, U.S.

Dong et al. 2013	1	General merchandise	$PM_{2.5}$	Integrated gravimetric particle mass (TH-16A)	Jinan, China

[1] As characterized by the authors.

1. Ventilation

The ventilation parameters measured in retail stores, comparisons with standards and non-retail environments, and potential implications of sampling approaches are discussed below.

1.1 Ventilation: measurements in retail stores

The studies that reported ventilation rates in retail stores typically measured the total outdoor air exchange rates (Chao and Chan 2001; Wargocki et al. 2004; Hotchi et al. 2006; Lee and Hsu 2007; Bennett et al. 2011, 2012; Chan et al. 2012). In addition, two studies measured the components of total outdoor air exchange rate: mechanical ventilation rate supplied by the roof top units (RTUs) (Bennett et al. 2011, 2012), and the infiltration rate through retail entrance doors (Shaw 1981). Table 34 includes the summary on these two studies that examined ventilation rates in more details.

Total outdoor air exchange rates (AER). The required minimum ventilation rates provided in the ASHRAE standard 62.1 are determined based on space type, and occupancy density. Consequently, the standard separates minimum ventilation rate for grocery stores from retail since the building activity, and function of grocery stores that offer mostly food products have a different type of potential internal contaminant sources than the potential sources in other retail stores. Six studies have measured AER in retail stores in the U.S., Europe and Asia. Two of these studies investigated the impact of changing AER on measured indoor pollutant concentrations and/or environmental perceptions (Wargocki et al. 2004; Hotchi et al. 2006). The number of existing studies is limited, so the current AER findings are limited to specific case studies. The average ventilation rate found in grocery stores was 1.6 ± 1.3 $L/s \cdot m^2_{floor}$ (0.32 ± 0.26 cfm/ft^2_{floor}) (Bennett et al. 2011; Chan et al. 2012). The average ventilation rate found in retail stores other than groceries was 1.45 ± 1.3 $L/s \cdot m^2_{floor}$ (0.29 ± 0.26 cfm/ft^2_{floor}) (Chao and Chan 2001; Wargocki et al. 2004; Hotchi et al. 2006; Bennett et al. 2012; Chan et al. 2012). Most of these studies used tracer gas measurements to establish time-averaged AERs, and, therefore, the relatively high standard AER deviations can indicate a relatively large temporal AER variability. A detailed description of the individual studies is provided below.

Currently, the most comprehensive study to report AER in retail stores examined typical U.S. commercial buildings in California (Bennett et al. 2012). The study included a total of 37 buildings; ten of which were retail establishments. Bennett et al. (2012) used SF_6 as the tracer gas. The average of the measured retail AERs was 1/h ± 0.7/h, which corresponds to 1 ± 0.5 $L/s \cdot m^2_{floor}$ (0.2 ± 0.11 cfm/ft^2_{floor}). The highest air exchange rate (2.33/h) was measured at a retail store that sold water filtration supplies. According to the authors, the infiltration rates were high since the doors were open most of the time, and contributed to the high air exchange rate observed.

In a recent pilot study that aimed to quantify the contaminant emission rates in retail stores, the outdoor air exchange rates were measured in two grocery stores and three furniture stores in northern California using SF_6 as the tracer gas (Chan et al. 2012). In the two-day-long measurement, one grocery store showed an average AER of 0.6 - 0.7/h (1.4 $L/s{\cdot}m^2_{floor}$, 0.28 cfm/ft^2_{floor}) while the other grocery store showed a higher average AER of 1.8/h - 2.0/h (3.5 $L/s{\cdot}m^2_{floor}$, 0.7 cfm/ft^2_{floor}). The furniture stores were naturally ventilated and their air exchange rate ranged from 0.3 to 3.9/h (0.4-1.3 $L/s{\cdot}m^2_{floor}$, 0.08-0.26 cfm/ft^2_{floor}). The doors in furniture stores were kept open most of the time and the entrance and loading doors in one of these stores had a large opening area.

Another study evaluated the impact of reduced ventilation rates on indoor air quality to develop a peak load shedding strategy for a general merchandise store located in California (Hotchi et al. 2006). The study measured the ventilation rate during regular operation before shutting down a certain number of RTUs. Their study used perfluoromethylcyclohexane (PMCH) as the tracer gas. The AERs were 0.71/h and 0.95/h measured in two separate experiments on two different days.

A European study examined the relationship between AERs and occupant perception of air quality in seven buildings, one of which was a department store (Wargocki et al. 2004). In their study, the ventilation measurements were conducted under constant air volume (CAV) operation of the air handling unit. AERs were determined from the pressure differential in the outdoor air supply duct under the assumption that the building was positively pressurized, so the potential infiltration rates were neglected. The total air exchange rates or floor area were not reported. The measured AER normalized by the floor area was 3.5 $L/s{\cdot}m^2_{floor}$ (0.7 cfm/ft^2_{floor}), and constituted 50% of the total airflow supplied to the building.

Chao and Chan (2001) investigated the relationship between typical AERs and VOCs concentrations in a total of 20 buildings in Hong Kong; of which two were computer shopping centers in two different shopping malls. The study used the SF_6 tracer gas decay method to measure the AER. The two computer shopping centers had the same AER of 0.9/h, which corresponds to 0.5 $L/s{\cdot}m^2_{floor}$ (0.1 cfm/ft^2_{floor}). The reported AER was lower than the AERs in offices (1.69/h) and public buildings (2.17/h) measured by the same study.

Lee and Hsu (2007) reported the air exchange rates for 12 photocopy centers located in Taiwan, which had an average AER of 7.34/h. The study did not mention how the air exchange rate was measured.

Mechanical system ventilation rates. Only one study measured the mechanical ventilation rates in retail stores (Bennett et al. 2012). Bennett et al. (2012) reported that on average 71% of total AER was supplied mechanically. This averaged percentage for mechanically supplied air included buildings with 100% of outdoor air brought in through the HVAC system and excluding buildings with doors open most of the time and the buildings that have no mechanical ventilation. Therefore, their study indicated that even in the fully mechanically ventilated buildings, unintentional ventilation, such as infiltration, makes a significant contribution to the total AERs.

Infiltration rates through entrance doors. Retail stores are usually assumed to have a tight building envelope. However, Shaw (1981) tested air leakage in ten retail stores and found that the range of infiltration rates in these stores was greater than other building types: double the infiltration rates measured in school and quadruple the infiltration rate measured in high-rise office buildings. Although, retail ventilation systems are often designed to minimize air infiltration by pressurizing the building interior, air infiltration through door usage in entrance/exit lobbies and loading docks make a significant contribution to the whole building air leakage rate (McGowan et al. 2006). The infiltration rates through entrance doors in standalone retail and strip mall buildings have been identified as one of the significant contributors to the total energy use. For example, Bennett et al. (2012) found that buildings with the doors kept open had an average air exchange rate of 2/h, which was significantly greater than the rate of 1/h that was found when the doors were closed. To decrease infiltration through entrance doors, ASHRAE Standard 90.1-2010 requires the use of vestibules. For a prototype well-sealed standalone retail building, Cho et al. (2010) estimated that the infiltration rate for peak hours was 3,375 m^3/h (1,986 cfm) and for off-peak hours was 442 m^3/h (260 cfm) through doors with vestibules. The infiltration rate was 1.5 times the rates observed for doors without vestibules. Cho et al. (2010) also estimated potential national weighted-average site energy saving from the use of vestibules to be 2.4% and 5.6% for standalone retail and strip mall buildings respectively, higher than any other type of commercial buildings except restaurants.

1.2 Ventilation: comparison to standards

Recommended outdoor ventilation rates for different building types are provided in several standards including the American Society of Heating, Refrigerating, and Air Conditioning (ASHRAE) Standard 62.1-2010, the European Standard CEN CR 1752-

1998, and the California Code of Regulations Title 24-2010. ASHRAE Standard 62.1-2010 and CEN CR 1752-1998 define two required ventilation components. One ventilation component is based on the occupancy rates and the other is based on the floor area. The differentiation between the occupancy and the area requirements provide flexibility when using occupancy-based control, such as demand control ventilation with CO_2 sensors. While the California Code of Regulations Title 24-2010 recommends outdoor airflow rate no less than the larger of the ventilation rate per conditioned of floor area or 15 cfm per person. Table 35 contains a summary of the required outdoor ventilation rate for the different standards.

Table 35: Comparison of ventilation standards requirements for retail stores and supermarkets.

Standards	**People Outdoor Air Rate, $L/s\cdot m^2_{floor}$ (cfm/ft^2_{floor})**	**Area Outdoor Air Rate, $L/s\cdot m^2_{floor}$ (cfm/ft^2_{floor})**	**Combined outdoor air rate, $L/s\cdot m^2_{floor}$ (cfm/ft^2_{floor})**
ASHRAE 62.1 (2010)			
Retail sales	**0.57[1](0.11)**	**0.6(0.12)**	**1.2[1](0.23)**
Supermarket	**0.3[1](0.06)**	**0.3(0.06)**	**0.6[1](0.12)**
CEN CR 1752 (1998)			
Low polluted building			
Type A[2]	**2.1(0.4)**	**2(0.38)**	**4.1(0.78)**
Type B[2]	**1.5(0.29)**	**1.4(0.27)**	**2.9(0.55)**
Type C[2]	**0.9(0.17)**	**0.8(0.15)**	**1.7(0.32)**
Non-low polluted building			
Type A[2]	**2.1(0.4)**	**3(0.57)**	**5.1(0.97)**
Type B[2]	**1.5(0.29)**	**2.1(0.4)**	**3.6(0.69)**
Type C[2]	**0.9(0.17)**	**1.2(0.23)**	**2.1(0.4)**
California Code of Regulations Title 24 (2010)	**2.6[3](0.5)**	**1(0.2)**	**Max(people rate , conditioned area rate)[4]**

[1] To make a comparison of total outdoor air rate requirements, these values are multiplied by the occupancy density per floor area (retail 15 people/ 100m^2, supermarket 8 people/ 100m^2) provided in ASHRAE Standard 62.1-2010.

[2] Type A corresponds to 15% of occupants dissatisfied; Type B corresponds to 20% of occupants dissatisfied; Type C corresponds to 30% occupants dissatisfied.

[3] From Section 1004 Occupant Load in 2010 California Building Code Title 24, Part 2, the space with a design occupant density is 60 ft^2/ person. Since the space is without fixed seating, the default occupant density will be one half of the maximum occupant load that is 30 ft^2 /person.

[4] California Title 24 recommends the outdoor air rate to be no less than the larger of people outdoor rate and area outdoor rate.

Table 35 shows that ASHRAE Standard 62.1-2010 recommends a combined design ventilation rate for general retail sales double of that required for grocery stores. The European Standard CEN CR 1752-1998 differentiates between low polluted buildings and non-low polluted buildings. For both cases, the European Standard requires higher outdoor ventilation rates than the ventilation rates required by ASHRAE Standard 62.1-2010. In the California Code of Regulations Title 24-2010, the recommended ventilation rate based on the floor area is between the values recommended by ASHRAE for retail non-grocery stores and grocery stores; however, when considering the ventilation rate based on the occupancy rates, the standard Title 24-2010 requires higher outdoor ventilation rate than the rates required by ASHRAE Standard 62.1-2010.

For grocery stores, the range of ventilation rates in the stores reported by Chan et al. (2012) and Bennett et al. (2011) met the minimum performance required by the ASHRAE Standard 62.1-2010 and the per floor area requirement in California Code of Regulations Title 24-2010. For the non-grocery stores, two of the eight retail stores measured by Bennett et al. (2011) and two of the three retail stores measured by Chan et al. (2012) and the store measured by Hotchi et al. (2006) met both ASHRAE Standard 62.1-2010 and the floor area minimum required in Title 24 standard. One retail store measured by Chan et al. (2012) met the ventilation rate per floor area recommended in Title 24 standard. For the retail stores measured outside the U.S., measurement reported by Wargocki et al. (2004) met both standards requirements for the U.S. and the European Standard for type C buildings (30% of occupants dissatisfied). The measurements reported by Chao and Chan (2001) in Hong Kong did not meet the requirements of both U.S. standards.

1.3 Ventilation: comparison to other environments

In order to put retail environments in context, Figure 26 shows a summary of air exchange rates found in literature for various environments. As in all similar plots in this paper, the bottom of the box indicates the 25th percentile; the horizontal line indicates the median and the top of the box the 75th percentile. The whiskers indicate the data range within 1.5 times the interquartile range of the 25th and 75th percentile. If present, any filled circles are outliers.

These investigations showed that the ventilation rates in retail stores are generally less than bars/restaurants and healthcare facilities and comparable to other environments (i.e. fitness centers, residences, offices, and schools). The high ventilation rates found in bars and restaurants may be driven by the use of kitchen exhaust fans. This finding is expected since the outdoor airflow required by area for restaurants in ASHRAE Standard 62.1-2010 is higher than the requirement of outdoor air flow by area required for retail and grocery stores. Also, the healthcare category shown in Figure 26 encompasses both treatment rooms for dentists as well as rooms for surgery and critical care. The requirements for surgery and critical care in ASHRAE Standard 170-2008 are significantly higher than other environments. The published studies demonstrated that the ventilation rates within a single category varied widely. The wide range of ventilation rates is influenced by the building envelope leakage, operation of ventilation control systems, and the approach used to calculate the ventilation rate. Commercial buildings that have a relatively large envelope area and frequently used entrance doors tend to have high ventilation rates due to infiltration.

1.4 Ventilation: implications of sampling approaches

The studies cited above used a variety of different tracer gas techniques to measure ventilation. Several studies evaluated sources of uncertainties when conducting tracer gas measurements. Axley (1991) found that the significant uncertainty of tracer gas measurements came from incomplete air mixing and unsteady airflow rates. Sandberg (1989) investigated the effect of airflow rates on the measurement errors for both constant concentration, and the decay methods and demonstrated a good agreement between the two tested methods. Sandberg (1989) also concluded that the measurement errors resulting from the changes in airflow rates during the experimental time period could generally be neglected when compared to the large errors due to poor air mixing in the tested environments. Poor mixing was estimated to contribute an error of 12%-18% .

Previous studies demonstrated a good correlation between the tracer gas constant injection and decay methods (Kumar et al. 1979; Sandberg 1989; Axley 1991; Heidt and Werner 1986) and between constant concentration and decay methods when the measurement was conducted for fixed airflow rates (Kumar et al. 1979). However, various analytical approaches might provide different ventilation rates and uncertainties. Sherman (1990) reported that each analytical approach provided strong results at specific environmental conditions. The study compared many different approaches including regression, integral, averaging, and transient techniques with various measurement time intervals and airflow rates. The averaging decay method presented high uncertainties when the measurement time interval increased because the tracer gas concentrations tended to be low and variable at the end of the experiment. The regression and integral decay methods reduced the errors found in the averaging decay method, and both methods had the same level of uncertainty. The constant concentration requires preparations of the system controls for real time tracer gas injection to maintain the concentration at the same level. The uncertainties from this technique depended on the measurement time interval and the accuracy of system controls, but not on the changes in the airflow rates.

Due to high instrumentation expenses and/or labor intensity in measuring AERs with the typical tracer gas decay method using SF_6 and the fact that SF_6 is potent greenhouse gas, there is an interest in understanding CO_2-based ventilation rate measurements. One particular area of interest is the use of metabolic CO_2 as the tracer for continuous ventilation rate measurements. The CO_2 generation rate per occupant is correlated with the metabolic rate, respiration quotient and body surface area that depend on factors such as occupant activity type and physical condition. If the occupancy rates are known, the CO_2 generation rate can be calculated, and measurements of CO_2 levels can be used to calculate AER and percentage of AER supplied mechanically.

The successful application of CO_2 as the tracer gas has been demonstrated in residential and commercial buildings (Aglan 2003; Asadi et al. 2011; Grimsrud et al. 2011). In general, these studies are performed in single zone settings with easily determined occupancy rates. While the single zone assumption could be used for well-mixed retail floors, the difficulty in using CO_2 as a tracer in retail buildings comes from transient and difficult-to-account-for occupancy rates.

Grimsrud et al., 2011 measured ventilation rates in three large retail stores located in three climate regions of the U.S. (MN, FL, and MD) using the CO_2 decay method. Hourly occupancy data for 48-hour periods, including employees, were used together with continuous CO_2 measurements taken in 6 to 12 locations in the stores to determine the hourly ventilation rates. Results agreed with SF_6 tracer-decay measurements and measurement results for the rooftop ventilation systems with an uncertainty of 10%.

Instead of using CO_2 decay method to measure the ventilation rate, Bennett et al. (2011) used the CO_2 equilibrium (steady-state) method and showed that the findings from this method are unreliable. In some of the test sites, the CO_2 concentrations never reached steady-state. In other buildings, the occupancy profiles were not consistent and in other buildings the difference between the indoor and outdoor CO_2 concentrations was small and caused large uncertainties. The authors recommended the use of the tracer decay method instead of the CO_2 steady-state method for future studies. Besides using CO_2 equilibrium to measure ventilation rates, Bennett et al. (2011) also used SF_6 decay method and PFT steady-state method. The R^2 value for the correlation between the SF_6 decay method and the PFT method was 0.76, between the PFT and CO_2 equilibrium was 0.84, and between the SF_6 and the CO_2 equilibrium was 0.74. According to the authors, the air exchange rate measured by steady state PFT was lower than the air exchange rate determined by SF_6 decay, probably because the steady state is influenced by the nighttime period, which tends to have lower ventilation rates than during the day. Another reason is related to the poor mixing in some buildings. The poor mixing lead to higher ventilation rates determined by SF_6 decay as the SF_6 sampling was done in areas in the building with significant airflow. Nonetheless, the SF_6 decay method was considered as the most accurate method to measure ventilation rates in retail stores.

2. IAQ

The following sections summarize the literature on contaminants measured in retail stores: particulate matter, VOCs, and other pollutants (i.e. ozone, SVOCs, microbiological contaminants, radon, and carbon monoxide). For each contaminant, the average observed concentration, comparisons to standards, non-retail environments as well as the implications of collection methods is summarized below.

2.1 Particulate matter

There is reason to believe that certain retail environments have particulate matter sources that is of indoor origin. Many groceries, general merchandise, and malls include food preparation areas or food courts. Cooking events can generate fine and ultrafine particles (e.g. Abt et al. 2000; Wallace et al. 2004). Other retail sites sell new clothing, which can be a source for textile particles (Maskey et al. 2011). Additionally, retail environments usually have high foot traffic areas, which contribute to indoor particles through movement of people, transport of outdoor dust, and resuspension of previously deposited particles (e.g. Abt et al. 2000; Lee et al. 2002). Frequent cleaning and other activities, such as the use of forklifts to move merchandise or propane-powered floor burnisher, may also contribute to elevated particle concentrations (e.g. Abt et al. 2000; Grimsrud et al., 1999).

Although short in duration, non-occupational exposures occurring during time spent in retail buildings can be significant contributors to 24-h personal exposures (Chang et al. 2000; Rea et al. 2001). Rea et al. (2001) suggested that up to 35% of particle exposure takes place in microenvironments (primarily retail buildings, restaurants, and coffee shops) where people spend only 4-13% of their time. Exposure to particulate matter has been associated with serious health effects (e.g. lung cancer, cardiovascular morbidity and mortality, ischemic heart disease mortality, non-fatal myocardial infarction, heart rate variability and systemic inflammation) in several epidemiological studies (e.g., Dockery et al. 1993; Pope et al. 2003; Pope and Dockery 2006; Weichenthal et al. 2008; Brook et al. 2010). The U.S. Environmental Protection Agency (EPA) considers both PM_{10} and

$PM_{2.5}$ as Criteria Pollutants, which can cause serious health effects. The WHO air quality guideline asserts there is no threshold below which particulate matter is not associated with adverse health effects (WHO 2005). It should be noted that PM standards/guidelines are established for outdoor concentrations. In the absence of indoor air quality standards, we assume that ambient standard/guidelines also apply to indoor concentrations. The comparisons between indoor concentrations and outdoor standards are used for reference only. The average particulate matter concentrations found in retail stores, possible indoor sources, comparisons with standards and other environments, and implications of sampling approaches are discussed below.

2.1.1 Particulate matter: measurements in retail stores

Indoor particulate matter concentrations in retail spaces have been reported in 11 articles. Of those studies, five studies reported PM_{10}, eight studies reported $PM_{2.5}$, one study reported PM_1, and one study reported particle with attached polycyclic aromatic hydrocarbons (PPAH) mass concentrations. Additionally, three literature studies reported ultrafine or a proxy for ultrafine (submicron, sub-3 μm) number concentrations. Also, one study reported chemical analysis of fine and coarse particles. Among these studies, only three (Lee and Hsu 2007; Bennett et al. 2011; and Chan et al. 2012) also reported the ventilation rates of the retail spaces. Figure 27 summarizes PM_{10}, $PM_{2.5}$, and submicron particle concentrations from these studies. In addition to the figure features described above, the dotted line represents the mean concentration and the short-dash line represents the mean concentration reported only by U.S. studies.

PM_{10} and $PM_{2.5}$. Median PM_{10}, shown in Figure 27, is dominated by studies conducted in Hong Kong, Taiwan, Japan and China where the outdoor air was an important contributor to indoor PM_{10} (Li et al. 2001; Lee and Hsu 2007; Dong et al. 2013). Bennett et al. (2011) and Chan et al. (2012) are the only studies that reported PM_{10} concentrations in U.S. retail stores. These two studies reported an average PM_{10} mass concentration for the 15 retail stores of 24.3 $\mu g/m^3$. Using data from Grimsrud et al., (1999); Rea et al., (2001); Bennett et al. (2011); Brown et al., (2012); and Chan et al. (2012) the average $PM_{2.5}$ mass concentration calculated for U.S. retail sites is 11.6 $\mu g/m^3$. Approximately half of all the stores tested had indoor-to-outdoor (I/O) ratio larger or equal to 1 and the rest had I/O ratio less than 1. This suggests that indoor PM_{10} and $PM_{2.5}$ can originate either indoors, outdoors, or both. The reported indoor sources include: cleaning (Grimsrud et al. 1999), cooking (Li et al. 2001; Bennett et al. 2011; Brown et al. 2012), and smoking (Li et al. 2001). Additionally, there is evidence that grocery stores exhibit higher particle concentrations than other types of stores: $PM_{2.5}$ mean concentration recorded in grocery stores measured in the U.S. was 31.7 $\mu g/m^3$ with a maximum concentration of 90 $\mu g/m^3$ (Bennett et al. 2011; Brown et al. 2012; Chan et al. 2012). The main contributor to elevated concentrations in these grocery stores is cooking events. Besides grocery stores, the data available for U.S. sites is insufficient to draw conclusions about specific indoor particle sources for different store types.

Submicron particles. Figure 27 contains a graph showing the submicron particle number concentrations reported by two studies conducted in the U.S. (Bennett et al. 2011; Brown et al. 2012). The average submicron concentration was 17,000/cm^3

($481 \cdot 10^6/\text{ft}^3$). It is worth noting that the submicron concentration measured in these studies is a good proxy for ultrafine particles since the particle number concentration is typically dominated by small particles. Another non-U.S. study reported only the highest ultrafine number concentrations observed during photocopying of $10^8/\text{cm}^3$ ($3{,}000\ 10^9/\text{ft}^3$, Lee and Hsu 2007); thus the number reported in Lee and Hsu (2007) is not included in the figure. These investigations associated submicron particle number concentrations with in store cooking, cleaning, photocopying, and specific activities (presence of silk screening area) (Lee and Hsu 2007; Bennett et al. 2011; Brown et al. 2012).

PPAH. Sakai et al. (2002) measured particles of diameter under 1 μm with attached polycyclic aromatic hydrocarbons (PPAH), and reported an indoor average concentration of 3.5 ng/m^3 and an outdoor average concentration of 45.2 ng/m^3 in the parking lot of the store. Sakai et al. (2002) reported that the average concentration of PPAH in the department store was low compared to levels measured by their study in restaurants, near garages, and in smoking rooms.

Chemical analysis of coarse and fine particles. Maskey et al. (2011) reviewed the chemical make-up of 7900 particles in 1–2.5 μm and 2.5–10 μm diameter bins in an underground mall in Korea. Maskey et al. (2011) reported that soil derived particles were the most common, followed in order by, primary soil-derived, carbonaceous, iron-containing, secondary soil derived, and secondary sea-salt particles. Given the proximity of the underground mall to subway terminals, their results for iron-containing particles correspond well with other studies in subway terminals (e.g., Aarnio et al. 2005). A significant baseline concentration of larger, thread-like textile particles with the chemical constituents of carbon, nitrogen, and oxygen were also observed in some of the samples.

2.1.2 Particulate matter: comparison to outdoor standards

Comparison of the measurements reported in the literature to the standards and guidelines is difficult, owing to the difference of averaging periods (1-year average or 24-hour average for regulatory/reference levels versus 8 hours or less reported in literature studies), location (ambient versus indoors), and different measurement methods. Given these limitations, comparison with the National Ambient Air Quality Standards (NAAQS) limit (24-hour PM_{10} limit =35 $\mu g/m^3$, and annual $PM_{2.5}$ limit = 12 $\mu g/m^3$) reveals that both PM_{10} and $PM_{2.5}$ mean mass concentrations measured in retail stores in the U.S. were below outdoor regulatory levels. However, the mean concentration measured in grocery stores in the U.S. for $PM_{2.5}$ mass concentration was 31.7 $\mu g/m^3$, which is 2.6 times higher than the NAAQS value.

2.1.3 Particulate matter: comparison to non-retail environments

PM_{10} and $PM_{2.5}$. Figure 28 shows a summary of PM_{10}, and $PM_{2.5}$ mass concentrations found in literature for various environments, none of which included (legal) smoking activities. Considering other environments, PM mass concentrations measured in retail stores in the U.S. are comparable to offices, religious buildings, healthcare facilities, and residences, and generally less than restaurants and classrooms. The wide range of values is largely the result of differences in averaging periods, ventilation rates, source strengths, outdoor concentrations, and sampling techniques used in the studies.

Submicron particles. Submicron number concentrations reported in retail environments were lower than concentrations (average>50,000/cm^3 (>10^9/ft^3)) observed in restaurants or residences during cooking events (Buonanno et al. 2010; Wallace and Ott 2011; and Bennett et al. 2011), in photocopy centers (Lee and Hsu 2007; and Morawska et al. 2009), and near freeways or busy roads (Zhu et al. 2002; Kaur et al. 2005; and Zhu et al. 2008). Other environments where the submicron concentrations were lower than values reported for retail stores include residences measured overnight or with no cooking events, and classrooms (Zhu et al. 2005; Weichenthal et al. 2008; Mullen et al. 2011).

2.1.4 Particulate matter: implications of sampling approaches

Broadly, the sampling techniques used to measure particle mass concentrations can be divided into two categories: filter-based integrated gravimetric methods, and real-time methods.

For the ten studies found in the literature, four studies used a gravimetric technique, three studies used a laser photometric instrument combined with gravimetric technique for calibration, and three studies used a photometric instrument without any calibration. Since gravimetric methods directly measure the mass of particles accumulated during a sampling period, it is considered the most reliable method. However, there are many difficulties in conducting this type of measurement. Bennett et al. (2011) reported issues that arose during sampling such as the filter ripped during sampling and poor seal of the impactor. Bennett et al. (2011) also reported differences between results obtained when sampling $PM_{2.5}$ and PM_{10} directly through one impactor compared to summing PM masses through multiple stages of impactors.

For the studies that used laser photometer instruments with no calibration, their reported concentrations are less accurate than the studies that used gravimetric technique. Laser photometers are generally calibrated at the factory against a gravimetric reference using a specific test dust. Aerosols with different physical/optical properties compared to the calibration dust can produce photometer responses differing by as much as a factor of 3 (Jiang et al., 2011). Ramachandran et al. (2000) demonstrated that the readings of TSI DustTrak (see Table 34) could exceed the true $PM_{2.5}$ values by a factor of 5 to 10. In addition to the calibration issue, the studies that employed a real-time particle counter and then converted the particle concentration to a mass concentration must assume a particle density, which increases the uncertainty.

Ultrafine particle measurements were monitored using condensation particle counters (CPCs): TSI ultrafine particle counters Model 3781 (0.006 – 3 μm; Bennett et al. 2011), Model 3025A (0.003 – 3 μm; Lee and Hsu 2007), and Model 8525 (0.02 - 1 μm; Brown et al. 2012). Given the differences in particle size range and instrument responses to environmental conditions and aerosol composition used in these studies, we would expect different results from these instruments if used in the same space.

2.2 Volatile organic compounds (VOCs)

Volatile organic compounds (VOCs) are a broad class of chemicals ubiquitous in the indoor environment. Concentrations of VOCs have the potential to be elevated in retail spaces as VOCS are emitted by a large range of products and activities. VOCs can be emitted by the retail merchandise (e.g. textiles, furniture containing pressed wood, etc.), produced during typical building operational procedures such as cooking or cleaning, and by building materials and displays present in the space. There is little evidence of harmful health effects caused by the majority of VOCs, at concentrations typically found non-industrial indoor environments (Molhave 2002). The average VOC concentrations found in retail stores, possible indoor sources, comparisons with standards and other environments, and implications of sampling approaches are discussed below.

2.2.1 VOCs: measurements in retail stores

Indoor VOC concentrations in retail spaces have been reported in 12 journal articles. The investigators found a total of 60 different VOCs in over 160 retail spaces using a variety of collection techniques. For the purpose of this paper, the VOCs were divided into eight categories. The VOC categories were developed by combining compounds that exhibit similar chemical behaviors and/or potential exposure characteristics. Table 36 lists the individual compounds in each category.

Table 36: VOC categories and constituting compounds.

Name of Category	N*	Compounds
Aromatic compounds	11	Xylene and isomers, 1-ethyl-2-methylbenzene, 1-ethyl-3-methylbenzene, benzene, ethylbenzene, naphthalene, phenol, propylbenzene, styrene, toluene, benzothiazole, butylated hydroxytoluene
Halogenated compounds	8	Carbon tetrachloride, chloroform, freon 11, freon 113, methylene chloride, tetrachloroethylene, trichloroethylene, 1,4-dichlorobenzene
Terpenoids	6	Limonene, pinene, p-cymene
Alkanes	6	Cyclohexane, decane, dodecane, heptane, hexane, nonane, undecane
Alcohols	6	1-Butanol, 1-methanol-3-cyclohexene, 2-butoxyethanol, 2-ethyl-1-hexanol, ethanol, isopropyl alcohol, cyclohexanol
Carbonyls	6	2-Butanone, 4-methyl-2-pentanone, acetone, benzaldehyde, butyl ester acetic acid, decanal hexanal, nonanal, octanal, pentanal, acrolein
C_1-C_2 aldehydes	5	Acetaldehyde, formaldehyde
Remaining VOCs	9	1-(2-Methoxypropoxy)-2-propanol, decamethylcyclopentasiloxane, TMPD-MIB, TMPD-DIB, 1,3-butadiene, methyl tert-butyl ether, diethyl phthalate

* Number of studies investigating the category considered. Note that not all studies provided concentrations we could use for further analysis.

Eight of the papers in Table 34 (Kim et al. 2001; Tang et al. 2005; Hotchi et al. 2006; Lee and Hsu 2007; Bruno et al. 2008; Caselli et al. 2009; Wu et al. 2011; Chan et al. 2012) provided information that allowed for further analysis of the reported VOCs using this categorization. A summary of these results, converted to molar concentrations, is presented in Figure 29. Concentrations are weighted by the number of stores sampled when reported as an average of a store type.

Aromatic compounds. The concentration of aromatic compounds averaged 15 ± 41 ppb (mean ± standard deviation), with a maximum concentration of 195 ppb measured for toluene in photocopy centers (Lee and Hsu 2007). The BTEXS group (benzene, toluene, ethylbenzene, xylenes, styrene) were found to have the highest concentrations in retail stores investigated in seven of the eight studies. Identified sources, particularly of toluene, include motor vehicle exhaust (Chao et al. 2001; Kim et al. 2001), newspaper ink in printing shops (Caselli et al. 2009) and photocopy centers (Lee and Hsu 2007), and building materials in pharmacies (Bruno et al. 2008) and shopping malls (Tang et al. 2005).

Halogenated compounds. The concentrations for this category averaged 1 ± 1 ppb, with a maximum concentration of 6 ppb measured for trichloroethylene in a department store (Tang et al. 2005). Tang et al. (2005) identified halogenated compounds as contaminants of concern in a shopping mall in South China, mainly due to chlorinated cleaning agents, deodorizers, and domestic electrical appliances.

Terpenoids. The mean concentration of the terpenoids category was 5 ± 5 ppb, with a maximum of 17 ppb for limonene. Limonene, emitted by household cleaning products, was the primary pollutant in two supermarkets (Bruno et al., 2008).

C_1-C_2 Aldehydes. Three studies reported acetaldehyde and formaldehyde concentrations across a variety of store types, and all suggested formaldehyde was the primary contaminant of concern. C_1-C_2 aldehydes concentrations averaged 13 ± 10 ppb, with formaldehyde reaching a maximum of 26 ppb, and acetaldehyde concentrations as high as 15 ppb. Identified formaldehyde sources included pressed wood products (Hotchi et al. 2006; Loh et al. 2006), and carpet (Wu et al. 2011). Acetaldehyde is typically emitted during baking processes, and is naturally present in ripe fruits.

Carbonyls. The mean concentration of the carbonyls category was 3 ± 4 ppb. The highest concentration (14 ppb) was measured for acetone in the retail stores sampled by Wu et al. (2011), where it was likely emitted by medical and cosmetics products. Due to proximity to a nail salon, acetone was the primary contaminant of concern in the stores of a strip mall center (Eklund et al. 2008).

Alkanes, alcohols, and other VOCs. Compounds from the alkanes, alcohols and remaining VOCs categories were not considered pollutants of concern by any study. They were found in retail spaces at mean concentrations of 5 ± 4 ppb, 5 ± 15 ppb and 1 ± 3 ppb respectively. Specific sources were not identified. Four studies reported concentrations of non–halogenated C_6-C_{12} alkanes, which are typically emitted by fuels, paints, sealants and grease. Compounds from the alcohol category are typically generated by solvent-containing products and baking activities.

Overall individual VOC concentrations were low, with a mean under 10 ppb and a median under 2 ppb across all compounds and all studies. It remains unclear if the variability between store types explained the variation in VOC concentrations. Studies in which samples were collected in different store types can help to answer this question. Loh et al. (2006) reported higher toluene concentrations in multipurpose store, higher formaldehyde concentrations in houseware and furniture stores, and higher acetaldehyde concentrations in grocery stores. Chan et al. (2012) conducted measurement in two grocery stores and three furniture stores, and reported similar trends in formaldehyde and acetaldehyde concentrations.

In addition to individual VOC concentrations, three studies reported TVOC concentrations averaging 439 ± 313 μg/m^3. Tang et al. (2005) computed the TVOC by adding the concentrations as indicated by the peak area in total ion chromatography of all species together, while Bruno et al. (2008) and Caselli et al. (2009) summed all reported VOC concentrations. Bruno et al. (2008) observed the minimum TVOC concentration (188 μg/m^3) in a supermarket, and the maximum concentration (1,393 μg/m^3) in a pharmacy.

Figure 30 contains a comparison of categorized VOC and TVOC concentrations by store type. Considering the limitations in sample size, number of compounds per category and the presence of confounding factors across studies, there are insufficient data to draw definitive conclusions about differences between store type and VOC category concentrations.

2.2.2 VOCs: comparison to exposure guidelines

Little is known regarding the health impacts from exposure to mixtures VOCs. For this reason, in this section we consider the health impacts of individual VOCs. Comparison of VOC concentrations to exposure guidelines is difficult as many organizations recommend different concentrations limits for specific compounds. We will consider here the most conservative reference limits published. Moreover, most chronic health guidelines assume either a continuous exposure, or an eight average period; while the duration of measurements conducted in the studies reviewed ranged from 30 minutes to 24 hours. Given the assumption that the samples collected in these studies were representative of typical concentrations, a comparison to heath guidelines can be used in assessing exposure to VOCs. Six of the reviewed studies mentioned concerns about exposure of retail workers (Tang et al. 2005; Hotchi et al. 2006; Loh et al. 2006; Lee et al. 2007; Wu et al. 2011; Chan et al. 2012).

Across all studies, four compounds were reported as exceeding the most conservative exposure guidelines published. Formaldehyde concentrations (average concentrations across all the studies 20 ± 8 ppb) exceeded the California Office for Environmental Health and Hazard Assessment chronic recommended exposure limit (CA OEHHA chronic REL = 7 ppb) in most of the stores measured. In general merchandise stores (Hotchi et al. 2006; Chan et al. 2012), acetaldehyde concentrations were above the inhalation reference concentrations (RfC) set by the U.S. Environmental Protection Agency at 5 ppb. It should also be noted that the RfC is defined as "an estimate with uncertainty spanning perhaps an order of magnitude", that assumes a continuous exposure over a lifetime. Tang et al. (2005) reported benzene concentrations above the Hong-Kong IAQ objective of 5 ppb. Acrolein was only measured by Chan et al. (2012), and concentrations exceeded the U.S. EPA RfC of 0.009 ppb.

Out of the 160 compounds detected across all studies, several are considered potentially carcinogenic by the U.S. EPA. For instance carbon tetrachloride, chloroform, and tetrachloroethylene were detected at several sites, but at concentrations lower than their U.S. EPA RfCs. However, trichloroethylene concentrations averaged 1.1 ± 1.8 ppb, above its RfC of 0.4 ppb. This result is dominated by the concentrations found in a shopping mall in South China (Tang et al., 2005).

2.2.3 VOCs: comparison to non-retail environments

Two of the reviewed studies investigated multiple micro-environments. These studies allow for direct comparisons between VOC concentrations and eliminate potential confounding factors such as sampling techniques. Unfortunately, the findings are inconsistent, especially for VOCs generated outdoors, for which the location of the space is the decisive factor. For instance Loh et al. (2006) reported higher average concentrations of aromatic compounds in retail stores than in transportation microenvironments, while Kim et al. (2001) reached the opposite conclusion. Residences and offices are two significant indoor environments, both in terms of occupancy and published investigations. The relationship of indoor, outdoor, and personal air (RIOPA) study was conducted in 100 residences from 1999 to 2001 in three American cities (Weisel et al. 2005). Logue et al. (2011) reviewed 77 published studies that reported measurements of chemical pollutants in residences from 2001-2008 (newer homes than in the RIOPA study) in the United States and in countries with similar lifestyles. The building assessment survey and evaluation (BASE) study involved 100 office buildings across the U.S. (Apte and Erdmann 2002). The mean categorized VOC concentrations in retail stores presented in Figure 29 were generally similar, or slightly lower, compared to the results reported in the BASE and the RIOPA studies. However, some of the contaminants found in retail stores were much lower than the mean concentration reported by Logue et al. (2011). For instance, formaldehyde averaged 20 ± 8 ppb in retail stores, 21 ± 11 ppb in residences-RIOPA, 56 ± 25 ppb in residences-Logue et al. (2011), and 13 ± 7 ppb in offices. The concentrations in retail spaces are also in general agreement with averaged concentrations found in residences in North America in the 1990s, as reported by Hodgson and Levin (2003). Notable exceptions are acetone and toluene, which are on average 10 times higher in retail environments when compared to residences.

2.2.4 VOC: implications of sampling approaches

While all samples of C_1-C_2 aldehydes were obtained using 2,4-dinitrophenylhydrazine (DNPH) cartridges, the sampling approach for all other VOCs differed amongst studies (cf. Table 34). VOCs were measured using stainless steel canisters (Summa canisters) in two studies, passive organic badges in three studies, and sorbent tubes in seven studies. The sorbents used by these seven studies also differed: four used tubes packed with Tenax TA, one with Tenax GR, and two with multiple sorbents.

Each sampling approach is associated with characteristic issues that can affect the identification and quantification of VOCs. For example, Summa canisters have been reported to show low recovery of alcohols (Ochiai et al. 2002), as well as aldehydes and terpenes (Batterman et al. 1998). Compounds with fewer than four carbon atoms and relatively high vapor pressures such as acetone, ethanol and isopropanol, are not readily sorbed by Tenax (Harper et al. 2000). In addition to the use of different collection methods, variations in the duration of sampling from 30 minutes to 24 hours might confound comparisons. Loh et al. (2006) also mentioned the potential differences in concentrations arising from mobile/personal versus stationary sampling, as the space might not be perfectly mixed.

Few field studies have investigated the differences in the concentrations obtained by various sampling techniques used simultaneously, and quantified these biases for the specific compounds collected. Depending on the compound sampled, organic vapor monitors have been reported to underestimate (Stock et al. 1999) or overestimate (Pratt et al. 2005) concentrations when compared to canisters. Dobos et al. (2000) reported that styrene concentrations measured by organic vapor monitors were 31% higher than measurements from sorbent tubes.

2.3 Other Pollutants

Ozone. Ozone is a contaminant that is typically generated though photochemical reactions between nitrogen oxides and VOCs in the troposphere. Many epidemiological studies have documented the adverse health effects of ozone on the respiratory and cardiovascular systems, particularly the association between short-term exposure to ozone and daily mortality (Ito et al. 2005; Parodi et al. 2005; Bell et al. 2004; Levy et al. 2005; Gryparis et al. 2004; Zhang et al. 2006). Only two studies reported ozone concentrations in retail spaces. Lee and Hsu (2007) reported a maximum indoor ozone concentration of 70 ppb, measured when photocopying activities occurred, nearing the current U.S. EPA National Ambient Air Quality Standard (NAAQS) for ozone of 75 ppb. Indoor ozone concentrations before photocopying operations averaged about 4 ppb. Chan et al. (2012) presented the temporal profile of indoor and outdoor ozone concentrations for three stores over an afternoon. Average indoor concentrations ranged 10-25 ppb, while average outdoor concentrations range 29-37 ppb, both far below ozone health standards. The authors noted a positive relationship between ozone indoor-to-outdoor ratios and air exchange rates, moderated by potential losses to filters in mechanically ventilated spaces, further confirming the importance of outdoor air as a source of ozone.

Semivolatile organic compounds (SVOCs). SVOCs may be particularly important in the retail environment. Many stores have vinyl flooring, merchandise made of soft and hard plastics, foams and fabrics, all of which may contain plasticizers and flame-retardants. Also, cooking events, which occur in some retail environments, can release PAHs and pyrene (Weschler and Nazaroff 2008). Several SVOCs have been associated with adverse health effects and many SVOCs are endocrine-disrupting chemicals. Studies examining SVOC metabolites in blood and urine have provided direct evidence of widespread human exposure (Vonderheide et al. 2008; Heudorf et al. 2007; Weschler and Nazaroff 2008). Despite their health impact, SVOCs are understudied in indoor environments and there are relatively few standardized methods for their analysis. Only two studies have reported SVOC concentrations in retail environments (Hartmann et al. 2004; and Wu et al. 2011). Hartmann et al. (2004) used polyurethane foam (PUF) plugs to collect air samples and reported the concentrations of eight organophosphates in two furniture and three electronic stores in Zurich, Switzerland. Tributyl phosphate (TBP), tris (2-chloroethyl) phosphate (TCEP) and triphenyl phosphate (TPP) were found in all of sites. Tris(2-chloro-isopropyl)phosphate (TCPP), a flame retardant, was found in furniture stores, but not in electronics stores, and Tris(1,3-dichloroisopropyl) phosphate (TDCP) was not found in any of the locations studied. Wu et al. (2011) used multi-bed sorbent tubes with a primary bed of Tenax-TA sorbent backed with a section of Carbosieve III to capture air samples and measure diethyl phthalate (DEP), as well as several VOC concentrations in 37 small- and medium-sized commercial buildings distributed across different sizes, ages, uses, and regions of California. DEP, a plasticizer commonly found in cosmetics and food packaging, was found in all seven of the retail sites with mean concentration equal to 0.49 $\mu g/m^3$. This concentration is lower than the mean concentration found in residences (0.67 $\mu g/m^3$) by Rudel et al. (2003, 2010), Otake et al. (2004), and Fromme et al. (2004).

Fungi and bacteria. It is important to understand microbiological pollutants in the retail environment because of the high person density and potentially favorable conditions for which these pollutants can proliferate. There is some evidence that highly occupied environments that have to bring in large amounts of fresh air can increase the levels of indoor microbiological pollutants due to outdoor sources (Wu et al. 2005). The impacts of biological aerosol exposure on human health are considerable (e.g., Monto 2002; D'Amato et al. 2005). Only two studies investigated the presence of bacteria in shopping malls (Li et al. 2001; Tringe et al. 2008). Li et al. (2001) collected airborne bacteria and used culturing to estimate the amount of colony forming bacteria per cubic meter of air in nine shopping malls. Generally, they found an increased amount of bacteria on weekends, with increased occupant density, as assessed by carbon dioxide measurements. Tringe et al. (2008) characterized bacteria present on HVAC filters in two malls in Singapore through genomic DNA sequencing and large scale cloning processes. Tringe et al. (2008) also compared bacteria found on HVAC filter dust with water from an adjacent river, floor dust samples (inside and outside), soil samples near the mall, and human nasal swabs. The microbiome captured on the HVAC filter dust was significantly less diverse compared to the soil and water samples. Each of the two malls shared some abundant microorganisms, but overall phylotypes were diverse, suggesting the malls have different microbiomes. The DNA functional analysis showed genes participating in cell mobility and secretion were over-represented, compared to previously reported genes in other soil and oceanic studies. Currently, there are no threshold values suggested for any microbiological measurement in the indoor environment.

Radon. Radon comes from the natural (radioactive) decay of geological materials (e.g. uranium in soil, and rocks). According to EPA, radon is responsible of many thousands of deaths each year in the U.S. Thus, indoor radon is an important pollutant of concern, especially in underground stores or in locations with known high radon concentrations. Three studies have reported radon concentrations in retail spaces (Yu et al. 1997; Marley 2000; Wang et al. 2004). Yu et al. (1997) measured 10 underground shopping centers located in Hong Kong and found an average concentration of 29.2 Bq/m^3, comparable to the average of dwellings of 30.1 Bq/m^3 and lower than the concentration measured in underground railway stations of 41.6 Bq/m^3, sampled by the same author in Hong Kong. The average reported for the shopping malls is well below EPA recommended action limit for radon of 148 Bq/m^3. Marley (2000) tested radon in a general merchandise store located in Northamptonshire (UK), an area classified as a radon affected area. The affected area of the store was the basement. The average radon concentration reported before switching the AC On was 326 Bq/m^3, and the radon average after six hours from switching-on the AC was 22 Bq/m^3. The reported AER was 5 air exchange rates per hour. The study indicated that high radon concentrations can be mitigated using an appropriate ventilation strategy. Wang et al. (2004) measured 8 underground supermarket and office structures in China and reported a total average of 33.7 Bq/m^3. The reported average in supermarket/office was lower than the radon concentration found in underground parking lot, and in covered and uncovered tunnels measured by the same study.

Carbon monoxide (CO). The U.S. EPA considers CO as one of the Criteria Pollutants that can cause serious health effects, and reports that CO poisoning is responsible for five hundred deaths annually in the U.S. Some indoor activities such as cooking using gas stoves and outdoor activities such as stock loading and nearby traffic can elevate indoor CO levels inside retail buildings. Li et al. (2001) measured CO in nine shopping malls, and found an average between 890 and 5200 µg/m^3. According to the authors, heavy traffic near the shopping malls, cooking inside food courts, and in some malls the operation of the fuel-powered ice-resurfacing resulted in elevated indoor concentration of CO. Inside these malls, all the measured CO concentrations were below the Hong Kong Indoor Air Quality Objective (HKIAQO) and the NAAQS regulatoy limit of 10,000 µg/m^3 (8-hour average).

Other inorganic pollutants (NOx, SOx). The literature search did not reveal any studies that measured NOx, or SOx in retail environments.

Discussion

The following discussion focuses on the impact of ventilation on contaminants found in retail stores and the possible contaminants of concern for which control strategy should be prioritized.

1. Impact of ventilation rate on contaminant concentrations

Among all the reviewed studies, only four studies measured the impact of changing ventilation rates on pollutants concentrations or occupant's perception (VOCs: Hotchi et al. 2006; Grimsrud et al. 2011, Radon: Marley 2000, Occupant perception: Wargocki et al. 2004). In addition, Apte et al. (2011) modeled various ventilation scenarios (including scenarios that satisfy the ASHRAE 62.1 IAQ procedure) in California big box retail stores and estimated VOC concentrations and energy consequences.

Hotchi et al. (2006) reduced the ventilation rate by 30% (0.83/h to 0.57/h) in a general merchandise store in the U.S. and observed subsequent increases in VOCs concentrations ranging from 15% to 170%. In three general merchandise stores, Grimsrud et al. (2011) suggested that the ventilation rates could be lowered and still maintain an acceptable indoor air quality in accordance with ASHRAE standards in regards to TVOC and formaldehyde. Marley et al. (2000) suggested that an appropriate ventilation strategy is an effective solution to decrease radon concentrations in a general merchandise store located in a radon-affected area. Wargocki et al. (2004) found that the percent of panelists dissatisfied with indoor air quality increased from roughly 5% to 30% when the outdoor airflow rate decreased from 4 to 1 $L/s{\cdot}m^2_{floor}$ (0.8 to 0.2 cfm/ft^2_{floor}). To balance between energy consumption and air quality in retail stores, Apte et al. (2011) suggested alternative control strategies such as source removal, air cleaning, and local ventilation, combined with moderate ventilation rates.

The grocery stores investigated by Chan et al. (2012) exceeded both the minimum ventilation rate specified by ASHRAE Standard 62.1-2010 and California Code of Regulations Title 24-2010 and had acetaldehyde (12.7 ± 3.3 ppb) and acrolein (9.4 ± 8 ppb) concentrations above exposure guidelines (respectively 5 ppb and 0.009 ppb). For acrolein, both indoor and outdoor concentration exceeded the reference exposure level, limiting the value of ventilation to reduce exposure. In addition, one of the retail stores investigated by Bennett et al. (2011) met both ASHRAE Standard-2010 and California Code of Regulations Title 24-2010 ventilation requirements and had formaldehyde (11.3 ± 4.7 ppb) above the most conservative exposure guidelines (7 ppb). In addition, two of the tested stores by Bennett et al. (2011) also exceeded ventilation requirements but the measured $PM_{2.5}$ (60.2 $\mu g/m^3$, 21.4 $\mu g/m^3$) were above the NAAQS outdoor regulatory limit (12 $\mu g/m^3$). For both stores, $PM_{2.5}$ outdoor concentration also exceeded the NAAQS regulatory limit, limiting the value of ventilation to reduce exposure. These findings suggest that comparing ventilation rates in the tested store to ventilation requirements does not necessarily correlate to the air quality in the store. Depending on the pollutant and its source, alternative control methods such as filtration might be more effective and possibly more economical than ventilation.

2. Contaminants of concern

From the contaminants found in retail stores reported in the literature, there is evidence that some pollutants in some retail types are present at concentrations higher than their established limits. The established limits of some pollutants vary widely between different organizations. Thus, to evaluate contaminants of concern it is necessary to compare exposure to pollutants through a common metric of harm, such as disability-adjusted-life-year (DALY; Murray and Lopez 1996). This will allow prioritizing mitigation strategies, including energy efficiency measures that affect indoor air quality.

Two different approaches were used to estimate DALYs lost from exposure to contaminants: (1) intake-incidence-DALY (IND) approach based on epidemiology-based concentration-response (C-R) functions following the work of Logue et al. (2012); and (2) intake-DALY (ID) approach based on animal toxicity literature following the work of Huijbregts et al. (2005). The IND approach is a preferred health impact model than the ID approach since it does not require interspecies extrapolations; however, only information on C-R functions in humans are available for $PM_{2.5}$ and ozone. For the rest of pollutants, animal toxicity data was available in the literature to apply the ID approach.

$PM_{2.5}$ DALYs lost were calculated separately for total mortality, chronic bronchitis, and nonfatal stroke outcomes. For the rest of pollutants, the DALYs lost were calculated separately for the cancer and non-cancer outcomes taking into account the variations in susceptibilities of different age categories. For both methods, for each pollutant and each outcome, a Monte Carlo approach was used to quantify the central estimate and 95% confidence interval (CI) by sampling from uncertainty distributions of DALY factors.

Average concentrations for thirty pollutants (e.g. $PM_{2.5}$, acrolein, formaldehyde, acetaldehyde, trichloroethylene, toluene, benzene, xylene, styrene, carbon tetrachloride, chloroform, naphthalene, ozone, etc.) were included in the analysis. $PM_{2.5}$ concentrations are taken from: Grimsrud et al. 1999; Rea et al. 2001; Bennett et al., 2011; Brown et al. 2012; Chan et al. 2012; and Dong et al. 2013. VOCs concentrations are taken from: Kim et al. 2001; Tang et al. 2005; Hotchi et al. 2006; Loh et al., 2006; Lee and Hsu 2007; Bruno et al. 2008; Caselli et al. 2009; Bennett et al., 2011; Chan et al. 2012. Ozone concentrations are taken from Chan et al., 2012. These pollutants were chosen for their high potential health impacts at the concentrations found indoors, as well as the availability of damage factors to perform the calculations. Health impacts were determined using the damage per intake factors reported in Pope et al. (2003) and Huijbregts et al. (2005). For each pollutant, the average DALYs lost were estimated for customers and employees, assuming customers above the age of fifteen spend on average 0.48 hours of their daily time shopping, and employees work eight hours per week-day in the retail site.

The estimated average DALYs lost due to $PM_{2.5}$ exposure in retail stores in the U.S. contributed the largest to the annual health impacts, with an estimated 76 DALYs per 100,000 persons annually (95% CI: 7.9, 728.5). The average annual total DALYs from VOCs/ozone (29-pollutants) contributed an estimated 70 DALYs per 100,000 persons. Acrolein accounted for the vast majority of these losses, contributing an annual average of 60 DALYs lost per 100,000 persons (95% CI: 0.23, 15,609). It should be noted that the acrolein concentration used in the DALY analysis is largely based on two grocery stores from one study (Chan et al., 2012), and thus the results are highly uncertain and more testing is warranted to verify these concentrations. Both $PM_{2.5}$ and acrolein were mostly elevated in grocery stores with cooking activities, thus the DALYs lost presented herein may not apply to exposures in other store types. The total health burden was mainly attributed to the employees in retail stores. A figure showing the estimated number of DALYs lost due to indoor inhalation intake of $PM_{2.5}$, ozone, and selected VOCs and the corresponding pollutant concentrations is shown in the Supporting Information.

Comparing the findings from this investigation to DALYs lost reported by Logue et al. (2012) in residences provides further evidence that $PM_{2.5}$ and acrolein are two common contaminants of concern. In addition to $PM_{2.5}$ and acrolein, Logue et al. (2012) identified formaldehyde as a pollutant that accounts for annual DALYs lost comparable to acrolein. In these residences, the average concentration reported for formaldehyde was 69 $\mu g/m^3$. In retail buildings, the average formaldehyde reported by the three studies (Hotchi et al. 2006; Wu et al. 2011; and Chan et al. 2012) was 24.6 $\mu g/m^3$. It should be noted that these three studies took place in California, and therefore may not be representative of formaldehyde concentrations in retail stores in other states or countries. At this concentration formaldehyde accounts for 4 DALYs lost annually per 100,000 persons. DALYs lost from exposure to formaldehyde in retail buildings can be considered small even though the average concentration reported for formaldehyde in retail stores is 2.7 times the OEHHA chronic reference exposure for formaldehyde (9 $\mu g/m^3$).

Despite the large uncertainties associated with the toxicology data and the DALY approach, our analysis support the finding that mitigation strategies in retail stores, specifically the ones with cooking activities, should focus on decreasing exposure of employees to $PM_{2.5}$ and acrolein, with the caveat that more acrolein concentration data is needed to confirm this finding.

Conclusions

A review of ventilation measurements in retail stores found that half of the stores tested met/exceeded Standard 62.1-2010 or California Code of Regulations Title 24-2010; nonetheless, these ventilation rates were not sufficient to keep all pollutants below their most conservative limits, but this might not be true if we consider other authoritative limits. The work presented here reduced the number of pollutants found in retail environments (>70 pollutants) to a set of seven important pollutants that are found to exceed their established limits/reference exposures for a few of the stores tested ($PM_{2.5}$, acrolein, formaldehyde, acetaldehyde, trichloroethylene, benzene, and PM_{10}) and two priority pollutants ($PM_{2.5}$, acrolein) that contributed the largest to DALYs lost. Only a limited number of studies measured acrolein in retail stores, which suggests that further attention on this pollutant is warranted. Because of the lack of health guidelines for ultrafine particles and SVOCs, the concentrations of these pollutant categories could not be judged whether it is safe or unsafe, but it would also be prudent to also generate additional measurements of these compounds. Few pollutants, such as $PM_{2.5}$ and acrolein, had elevated concentrations both indoors and outdoors above their established limits.

Alternative ventilation strategies (i.e., nighttime flushes) for stores with high indoor concentrations and air cleaning approaches (i.e. particle filtration) might offer a more effective and less energy-intensive method to improve the air quality in retail stores. Generally, for the important pollutants identified above, there remains a need to perform additional testing in retail stores in an effort to determine sources of pollutant and potentially link them to activities in the store, as well as determine the importance of outdoor sources.

Illustrations

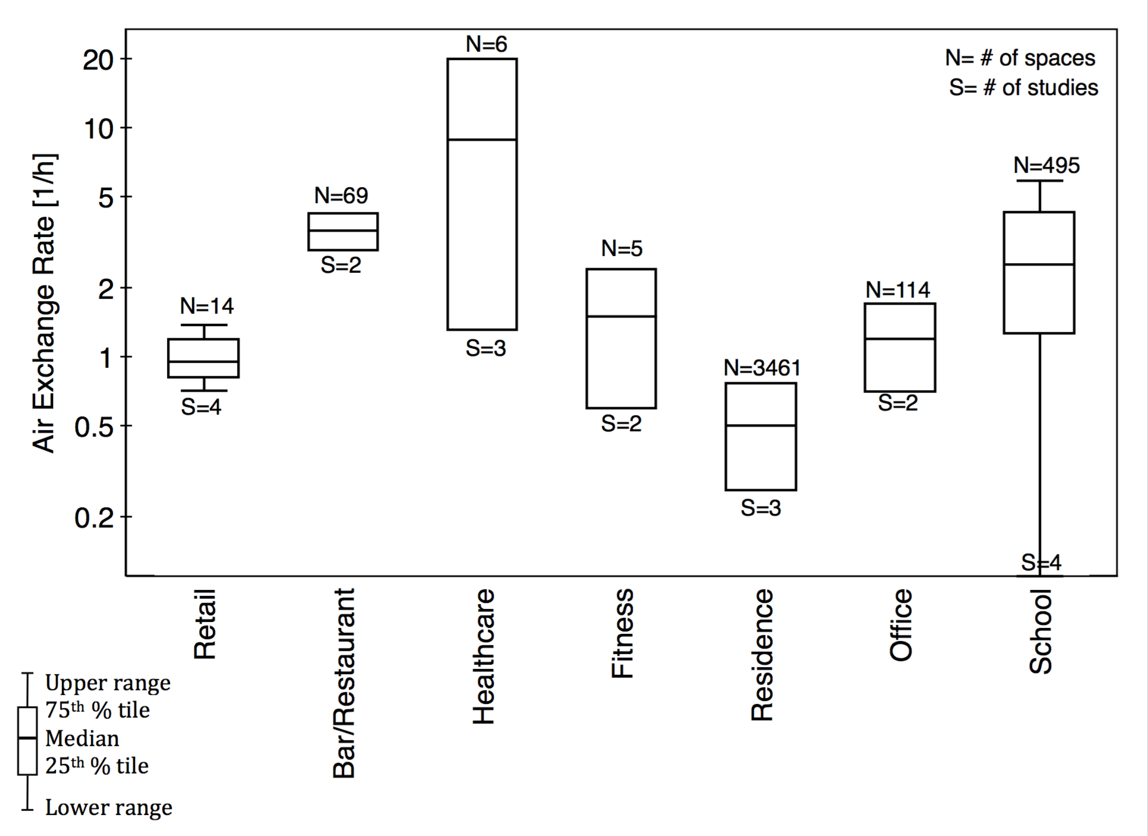

Figure 26: Summary of air exchange rate for different environments (N = number of spaces, S = number of studies). Data for retail stores from Chao and Chan (2001), Hotchi et al. (2006), Bennett et al. (2011), and Chan et al. (2012). Data for bars/restaurants from Bennett et al. (2011) and Bohac et al. (2012). Data for healthcare facilities from Qian et al. (2010), Bennett et al. (2011), and Knibbs et al. (2011). Data for fitness from Bennett et al. (2011) and Chao and Chan (2001). Data for residences from Mur- ray and Burmaster (1995), Offermann (2009), and Yamamoto et al. (2010). Data for offices from Chao and Chan (2001) and Parthasarathy et al. (2013; analyzed values from the BASE Study: Persily et al. 2005). Data for schools from Godwin and Batterman (2007), Apte et al. (2012; including results from two studies), and Ramalho et al. (2012).

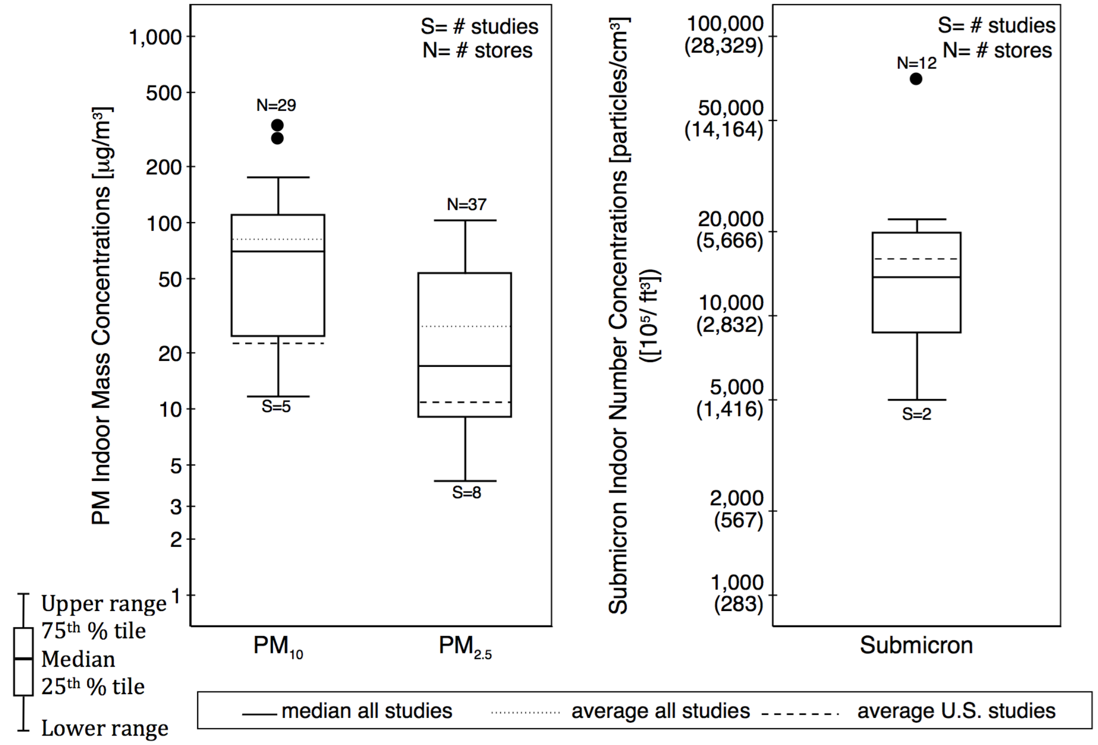

Figure 27: Summary of PM_{10}, $PM_{2.5}$ mass concentrations and sub- micron particle number concentrations. The horizontal line rep- resents the median concentration, the dotted line represents the mean concentration, and the short-dashed line represents the mean concentration reported only by U.S. studies. Data for PM_{10} from Li et al. (2001), Sakai et al. (2002), Liu et al. (2004), Ben- nett et al. (2011), and Chan et al. (2012). Data for $PM_{2.5}$ from Grimsrud et al. (1999), Rea et al. (2001), Liu et al. (2004), Lee and Hsu (2007), Bennett et al. (2011), Brown et al. (2012), Chan et al. (2012), and Dong et al. (2013). Data for submicron particles from Bennett et al. (2011) and Brown et al. (2012).

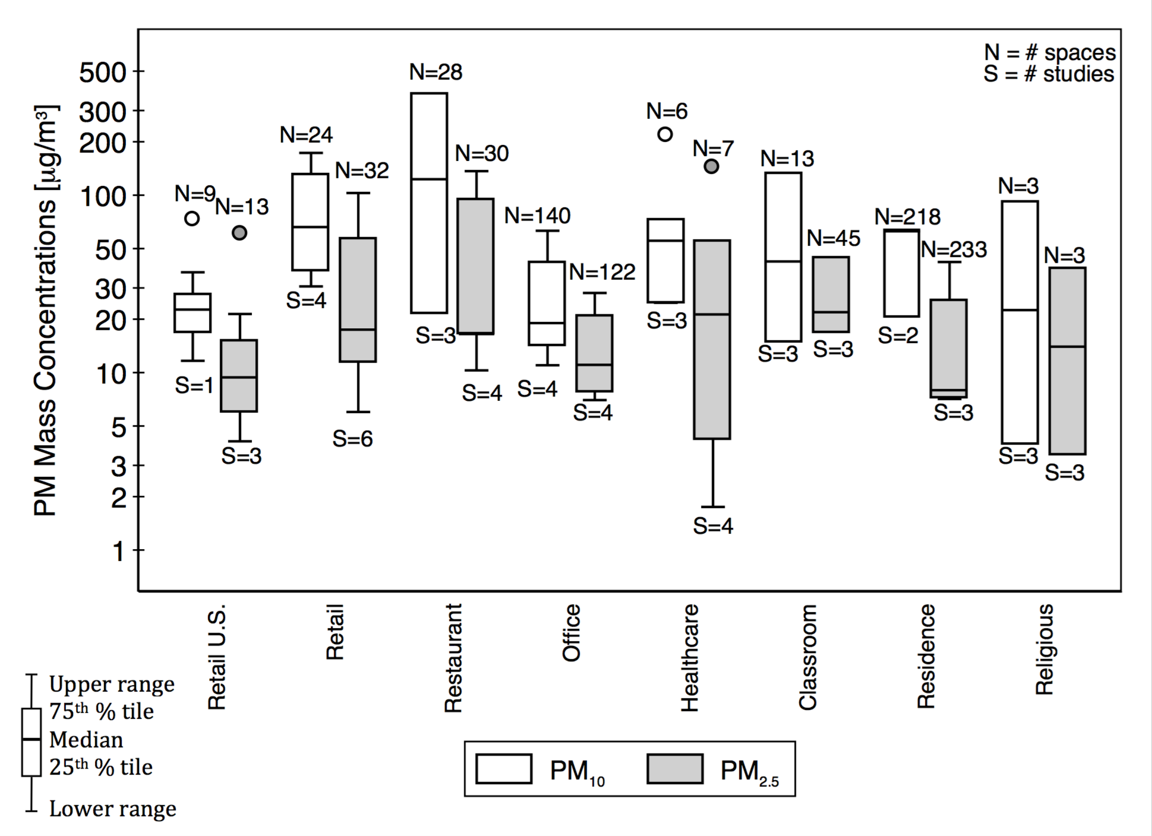

Figure 28: Summary of PM_{10}, $PM_{2.5}$ mass concentrations (N = num- ber of spaces, S = number of studies). Data for retail stores from Grimsrud et al. (1999), Li et al. (2001), Rea et al. (2001), Sakai et al. (2002), Liu et al. (2004), Lee and Hsu (2007), Bennett et al. (2011), Brown et al. (2012), Chan et al. (2012), and Dong et al. (2013). Data for restaurants from Liu et al. (2004), Buonanno et al. (2010), Bennett et al. (2011), and Brown et al. (2012). Data for offices from Turk et al. (1989), Burton et al. (2000), Liu et al. (2004), and Bennett et al. (2011). Data for healthcare facilities from Tsai et al. (2000), Helmis et al. (2007), Bennett et al. (2011), and Brown et al. (2012). Data for classrooms from Liu et al. (2004), Branis et al. (2005), and Weichenthal et al. (2008). Data for residences from Ozkaynak et al. (1997), Long et al. (2000), and Wheeler et al. (2011). Data for religious facilities from Bennett et al. (2011), Daher et al. (2011), and Chuang et al. (2012).

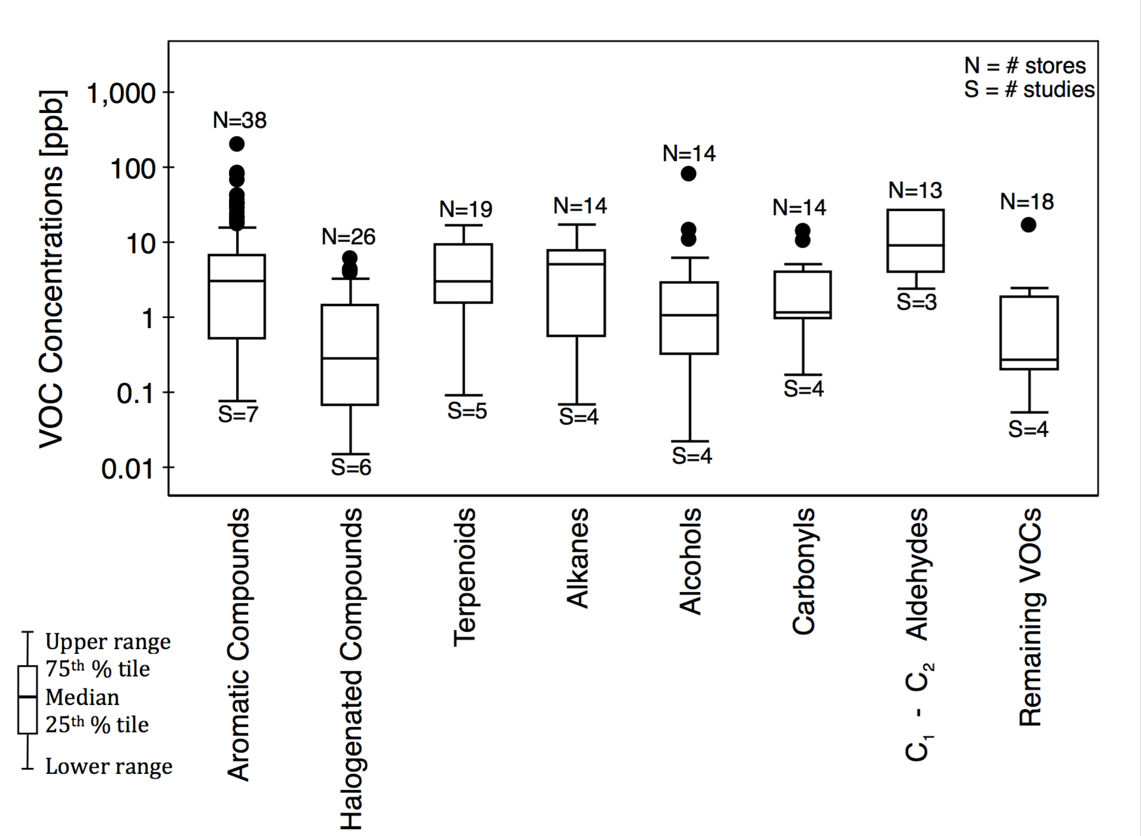

Figure 29: Summary of categorized VOC concentrations. Data for aromatic compounds from Kim et al. (2001), Tang et al. (2005), Hotchi et al. (2006), Lee and Hsu (2007), Bruno et al. (2008), Caselli et al. (2009), and Wu et al. (2011). Data for halogenated compounds from Kim et al. (2001), Tang et al. (2005), Hotchi et al. (2006), Bruno et al. (2008), Caselli et al. (2009), and Wu et al. (2011). Data for terpenoids from Kim et al. (2001), Hotchi et al. (2006), Bruno et al. (2008), Caselli et al. (2009), and Wu et al. (2011). Data for alkanes from Hotchi et al. (2006), Bruno et al. (2008), Caselli et al. (2009), and Wu et al. (2011). Data for alcohols from Hotchi et al. (2006), Bruno et al. (2008), Caselli et al. (2009), and Wu et al. (2011). Data for carbonyls from Hotchi et al. (2006), Bruno et al. (2008), Caselli et al. (2009), and Wu et al. (2011). Data for C_1-C_2 aldehydes from Hotchi et al. (2006), Wu et al. (2011), and Chan et al. (2012). Data for remaining VOCs from Kim et al. (2001), Hotchi et al. (2006), Wu et al. (2011), and Chan et al. (2012).

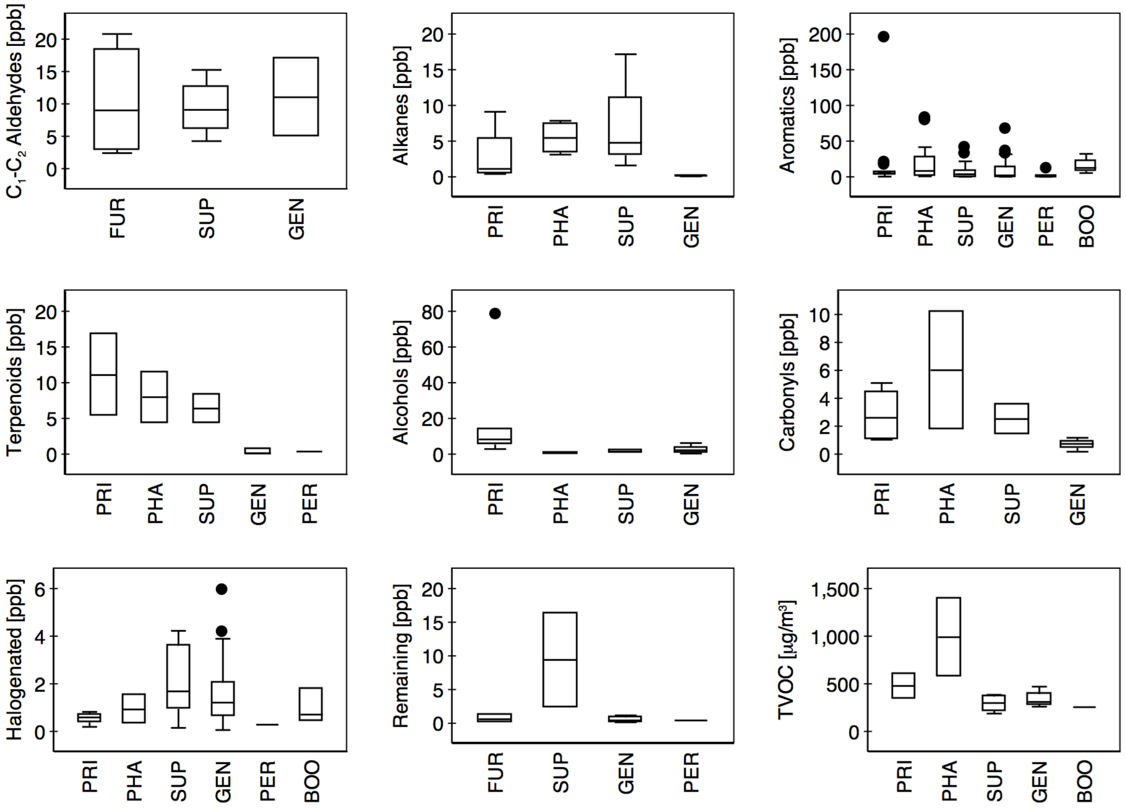

Figure 30: Comparison of categorized VOC and TVOC concentra- tions by store type. FUR = furniture store (3 stores, data from Chan et al. 2012), SUP = supermarket/grocery (6 stores, data from Tang et al. 2005; Bruno et al. 2008; Chan et al. 2012), GEN = general merchandise/department store (7 stores, data from Kim et al. 2001; Tang et al. 2005; Hotchi et al. 2006), PRI = printing shop/photocopying center (14 stores, data from Lee and Hsu 2007; Caselli et al. 2009), PHA = pharmacy (2 stores, data from Bruno et al. 2008), PER = perfume shop (3 stores, data from Kim et al. 2001), and BOO = bookstore (1 store, data from Tang et al. 2005).

References

Aarnio, P., Yli-Tuomi, T., Kousa, A., Mäkelä, T., Hirsikko, A., Hämeri, K., et al. 2005. The concentrations and composition of and exposure to fine particles ($PM_{2.5}$) in the Helsinki subway system. *Atmospheric Environment*, 39(28): 5059–5066.

Abt, E., Suh, H.H., Allen, G., and Koutrakis, P. 2000. Characterization of indoor particle sources: A study conducted in the metropolitan Boston area. *Environmental Health Perspectives*, 108(1): 35–44.

Aglan, H.A. 2003. Predictive model for CO_2 generation and decay in building envelopes. *Journal of Applied Physics*, 93(2): 1287–1290.

Alhafi Z, Shu S, Srebric J. 2012. Comparison of energy consumption depending on the indoor temperature settings for three retail buildings. In: Proceeding of the Second International Conference on Building Energy and Environment. Boulder, Colorado.

American Time Use Survey (ATUS). 2011. Purchasing goods and services on weekdays and weekend days in 2011. Available from: http://www.bls.gov/tus/current/purchasing.htm

Apte, M., and Erdmann, C. A. 2002. Indoor carbon dioxide concentrations and sick building syndrome symptoms in the BASE study revisited: Analyses of the 100 building dataset. Indoor Environment Department, Lawrence Berkeley National Laboratory, Berkeley, CA, LBNL-51570.

Apte, M.J., Mendell, M.J., Sohn, M.D., Berkeley, P.M., Dutton, S.M., and Spears, M. 2011. Balancing energy conservation and occupant needs in ventilation rate standards for “Big Box” stores in California: predicted indoor air quality and energy consumption using a matrix of ventilation scenarios. Lawrence Berkeley National Laboratory.

Apte, M.G., Bourassa, N., Faulkner, D., Hodgson, A.T., Hotchi, T., Spears, M., et al. 2012. Improving ventilation and saving energy: final report on indoor environmental quality and energy monitoring in sixteen relocatable classrooms. No. CEC-500-2012-075. Lawrence Berkeley National Laboratory.

Asadi, E., Costa, J.J., and Gameiro Da Silva, M. 2011. Indoor air quality audit implementation in a hotel building in Portugal. *Building and Environment*, 46(8): 1617–1623.

ASHRAE. 2008. *Ventilation Standard for Health Care Facilities-Standard 170*. Atlanta: American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc.

ASHRAE. 2010. *ASHRAE Standard 62.1-2010 Ventilation for Acceptable Indoor Air Quality*. Atlanta: American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc.

Axley, J. 1991. An integral mass balance formulation of the constant concentration tracer technique. Air Movement and Ventilation Control within Buildings. *Presented at the AIVC 12th Conference, Ottawa, Canada.*

Batterman, S. A., Zhang, G., and Baumann, M. 1998. Analysis and stability of aldehydes and terpenes in electropolished canisters. *Atmospheric Environment*, 32(10): 1647–1655.

Bell, M.L., McDermott, A., Zeger, S.L., Samet, J.M., and Dominici, F. 2004. Ozone and short-term mortality in 95 US urban communities, 1987-2000. *JAMA: The Journal of The American Medical Association*, 292(19): 2372–2378.

Bennett, D., Apte, M., Wu, X., Trout, A., Faulkner, D., and Sullivan, D. 2011. Indoor Environmental Quality and Heating, Ventilating, and Air Conditioning Survey of Small and Medium Size Commercial Buildings: Field Study. No. CEC-500-2011-043.

Bennett, D.H., Fisk, W., Apte, M. G., Wu, X., Trout, A., Faulkner, D., et al. 2012. Ventilation, temperature, and HVAC characteristics in small and medium commercial buildings in California. *Indoor Air*, 22(4): 309–320.

Bohac, D.L., Hewett, M.J., Kapphahn, K.I., and Grimsrud, D.T. 2012. Ventilation rate investigations in Minnesota bars and restaurants. *ASHRAE Transactions* 118(1): 847-852.

Branis M, Rezacova P, Domasova M. 2005. The effect of outdoor air and indoor human activity on mass concentrations of PM, PM, and PM in a classroom. *Environmental Research*, 99:143–149.

Brook, R.D., Rajagopalan, S., Pope, C.A., Brook, J.R., Bhatnagar, A., Diez-Roux, A.V., et al. 2010. Particulate matter air pollution and cardiovascular disease: An update to the scientific statement from the American heart association. *Circulation*, 121(21): 2331–2378.

Brown, K. W., Sarnat, J. A., and Koutrakis, P. 2012. Concentrations of $PM_{2.5}$ mass and components in residential and non-residential indoor microenvironments: The sources and composition of particulate exposures study. *Journal of Exposure Science and Environmental Epidemiology*, 22: 161–172.

Bruno, P., Caselli, M., de Gennaro, G., Iacobellis, S., and Tutino, M. 2008. Monitoring of volatile organic compounds in non-residential indoor environments. *Indoor Air*, 18(3): 250–256. Buonanno, G., Morawska, L., Stabile, L., and Viola, A. 2010. Exposure to particle number, surface area and PM concentrations in pizzerias. *Atmospheric Environment*, 44(32): 3963–3969.

Burton L.E, Girman J.G., Womble S.E. 2000. Airborne particulate matter within 100 randomly selected office buildings in the United States (BASE). In: Proceedings of Healthy Buildings. page 157–62.

California Energy Commission. 2010. Building Energy Efficiency Standards for Residential and Nonresidential Buildings. CEC-400-2008-001-CMF

Caselli, M., Allen, G., Saracino, M. R., and Tutino, M. 2009. Indoor contaminants from newspapers: VOCs emissions in newspaper stands. *Environmental Research*, 109(2): 149–157.

Chan, W., Sidheswaran, M., Sullivan, D., Cohn, S., and Fisk, W. 2012. Contaminant levels and source strengths in US retail stores-A pilot study. No. LBNL 5547E.

Chang, L.T., Koutrakis, P., Catalano, P.J., and Suh, H.H. 2000. Hourly personal exposures to fine particles and gaseous pollutants-results from Baltimore, Maryland. *Journal of the Air and Waste Management Association*, 50(7): 1223–1235.

Chao, C. Y., and Chan, G. Y. 2001. Quantification of indoor VOCs in twenty mechanically ventilated buildings in Hong Kong. *Atmospheric Environment*, 35(34): 5895–5913.

Cho, H., Gowri, K., and Liu, B. 2010. Energy saving impact of ASHRAE 90.1 vestibule requirements: modeling of air infiltration through door openings. A report for the U.S. Department of Energy No. PNNL-20026.

Chuang H.C., Jones T., BéruBé K. 2012. Combustion particles emitted during church services: Implications for human respiratory health. *Environment International*; 40:137–142.

D'Amato, G., Liccardi, G., D'Amato, M., and Holgate, S. 2005. Environmental risk factors and allergic bronchial asthma. *Clinical and Experimental Allergy*, 35(9): 1113–1124.

Daher N., Ruprecht A., Invernizzi G., De Marco C., Miller-Schulze J., Heo J.B., et al. 2011. Chemical Characterization and Source Apportionment of Fine and Coarse Particulate Matter Inside the Refectory of Santa Maria Delle Grazie Church, Home of Leonardo Da Vinci's "Last Supper". *Environmental Science & Technology*; 45: 10344–53.

Dobos, R. T. 2000. Field investigation comparing diffusion badge and charcoal tube monitoring for styrene. *Applied Occupational And Environmental Hygiene*, 15(9): 673–679.

Dockery, D. W., Pope, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., et al. 1993. An Association between Air-Pollution and Mortality in 6 United-States Cities. *The New England Journal of Medecine*, 329(24).

Dong, C., Yang, L., Yan, C., Yuan, Q., Yu, Y., and Wang, W. 2013. Particle size distributions, $PM_{2.5}$ concentrations and water-soluble inorganic ions in different public indoor environments: a case study in Jinan, China. *Frontiers of Environmental Science and Engineering*, 7(1): 55-65.

Eklund, B. M., Burkes, S., Morris, P., and Mosconi, L. 2008. Spatial and temporal variability in VOC levels within a commercial retail building. *Indoor Air*, 18(5): 365-374.

Fisk, W. J., Faulkner, D., and Sullivan, D. P. 2005. An evaluation of three commercially available technologies for real-time measurement of rates of outdoor airflow into hvac systems. *ASHRAE Transactions* 111: 443-455.

Fromme, H., Lahrz, T., Piloty, M., Gebhart, H., Oddoy, A., and Ruden, H. 2004. Occurrence of phthalates and musk fragrances in indoor air and dust from apartments and kindergartens in Berlin (Germany). *Indoor Air,* 14(3), 188–195.

Godwin C, Batterman S. 2007. Indoor air quality in Michigan schools. *Indoor Air*, 17(2),109–21.

Grimsrud, D., Carlson, N., Bridges, B., Springman, T., and Williams, S. A. 2011. Investigation of appropriate ventilation rates for retail stores. *Proceedings of Indoor Air*.

Grimsrud, D. T., Bridges, B. B., Carlson, N. G., and Hadlich, D. E. 1999. Ventilation requirements in a retail store. *Presented at the 20th AIVC Conference Ventilation and indoor air quality in buildings, the 8th International Conference on Indoor Air Quality and Climate, U.K.*

Gryparis, A. 2004. Acute effects of ozone on mortality from the “Air pollution and health: A European approach” project. *American Journal of Respiratory and Critical Care Medicine*, 170(10): 1080–1087.

Harper, M. 2000. Sorbent trapping of volatile organic compounds from air. *Journal of Chromatography*, 885(1): 129–151.

Hartmann, P. C., Bürgi, D., and Giger, W. 2004. Organophosphate flame retardants and plasticizers in indoor air. *Chemosphere*, 57(8): 781–787.

Helmis C.G., Tzoutzas J., Flocas H.A., Halios C.H., Stathopoulou O.I., Assimakopoulos V.D., et al. 2007. Indoor air quality in a dentistry clinic. *Science of The Total Environment*; 377:349–65.

Heidt, F. D., and Werner, H. 1986. Microcomputer-aided measurement of air change rates. *Energy and Buildings*, 9(4): 313–320.

Heudorf, U., Mersch-Sundermann, V., and Angerer, J. 2007. Phthalates: toxicology and exposure. *International Journal of Hygiene and Environmental Health*, 210(5): 623–634.

Hodgson, A. T., and Levin, H. 2003. Volatile organic compounds in indoor air: A review of concentrations measured in North America since 1990. Report LBNL-51715, Lawrence Berkeley National Laboratory, Berkeley, CA.

Hotchi, T., Hodgson, A. T., and Fisk, W. J. 2006. Indoor air quality impacts of a peak load shedding strategy for a large retail building. No. 59293. Lawrence Berkeley National Laboratory, Berkeley, CA.

Huijbregts, M., Rombouts, L., Ragas, A., and Van De Meent, D. 2005. Human-toxicological effect and damage factors of carcinogenic and non-carcinogenic chemicals for life cycle impact assessment. *Integrated Environmental Assessment and Management*, 1(3): 181–244.

Ito, K., De Leon, S. F., and Lippmann, M. 2005. Associations between ozone and daily mortality. *Epidemiology*, 16(4): 446–457.

Jiang, R. T., Acevedo-Bolton, V., Cheng, K. C., Klepeis, N., Ott, W. R., and Hildemann, L. M. 2011. Determination of response of real-time SidePak AM510 monitor to secondhand smoke, other common indoor aerosols, and outdoor aerosol. *Journal of Environmental Monitoring*, 13(6): 1695–1702.

Kaur, S., Nieuwenhuijsen, M., and Colvile, R. 2005. Personal exposure of street canyon intersection users to $PM_{2.5}$, ultrafine particle counts and carbon monoxide in Central London, UK. *Atmospheric Environment*, 39(20): 3629–3641.

Kennedy S, Chroust C, Siegel A. 2012. Retail Sustainability Report Successes, Challenges, and a Vision for the Future.

Kim, Y. M., Harrad, S., and Harrison, R. M. 2001. Concentrations and sources of VOCs in urban domestic and public microenvironments. *Environmental Science and Technology*, 35(6): 997–1004.

Knibbs, L. D., Morawska, L., Bell, S. C., and Grzybowski, P. 2011. Room ventilation and the risk of airborne infection transmission in 3 health care settings within a large teaching hospital. *American Journal of Infection Control*, 39(10): 866–872.

Kumar, R., Ireson, A. D., and Orr, H. W. 1979. An automated air infiltration measuring system using SF6 tracer gas in constant concentration and decay methods. *ASHRAE Transactions* 85(2): 385–395.

Lee, C. W., and Hsu, D. J. 2007. Measurements of fine and ultrafine particles formation in photocopy centers in Taiwan. *Atmospheric Environment*, 41(31): 6598–6609.

Lee, S. C., Guo, H., Li, W. M., and Chan, L. Y. 2002. Inter-comparison of air pollutant concentrations in different indoor environments in Hong Kong. *Atmospheric Environment*, 36(12): 1929–1940.

Levy, J. I., Chemerynski, S. M., and Sarnat, J. A. 2005. Ozone Exposure and Mortality. *Epidemiology*, 16(4): 458–468.

Li, W. M., Lee, S. C., and Chan, L. Y. 2001. Indoor air quality at nine shopping malls in Hong Kong. *Science of the Total Environment*, 273: 27–40.

Liu, Y., Chen, R., Shen, X., and Mao, X. 2004. Wintertime indoor air levels of PM_{10}, $PM_{2.5}$ and PM_1 at public places and their contributions to TSP. *Environment International*, 30(2): 189–197.

Logue, J. M., McKone, T. E., Sherman, M. H., and Singer, B. C. 2011. Hazard assessment of chemical air contaminants measured in residences. *Indoor Air*, 21(2): 92–109.

Logue, J. M., Price, P. N., Sherman, M. H., and Singer, B. C. 2012. A method to estimate the chronic health impact of air pollutants in US residences. *Environmental Health Perspectives*, 120(2): 216.

Loh, M. M., Houseman, E. A., Gray, G. M., Levy, J. I., Spengler, J. D., and Bennett, D. H. 2006. Measured concentrations of VOCs in several non-residential microenvironments in the United States. *Environmental Science and Technology*, 40(22): 6903–6911.

Long C.M., Suh H.H., Koutrakis P. 2000. Characterization of indoor particle sources using continuous mass and size monitors. *Journal of the Air & Waste Management Association*;50:1236–50.

Marley, F. 2000. Utilization of an air-conditioning system to control the levels of radon and radon progeny in a workplace environment. *Radiation Protection Dosimetry*, 91(4): 403–407.

Maskey, S., Kang, T. H., Jung, H. J., and Ro, C. U. 2011. Single-particle characterization of indoor aerosol particles collected at an underground shopping area in Seoul, Korea. *Indoor air*, 21(1): 12–24.

McGowan, A., Jutras, R., Riopel, G., and Hanam, M. 2006. Heat transfer through roll-up doors, revolving doors and opaque nonresidential swinging, sliding and rolling doors. ASHRAE report No. RP-1236.

Molhave, L. 2003. Organic compounds as indicators of air pollution. *Indoor Air*, 13(s6): 12–19.

Monto, A. S. 2002. Epidemiology of viral respiratory infections. *The American Journal of Medicine*, 112(6(A)): 160–174.

Morawska, L., He, C., Johnson, G., Jayaratne, R., Salthammer, T., Wang, H., et al. 2009. An investigation into the characteristics and formation mechanisms of particles originating from the operation of laser printers. *Environmental Science and Technology*, 43(4): 1015–1022.

Mullen, N. A., Bhangar, S., Hering, S. V., Kreisberg, N. M., and Nazaroff, W. W. 2011. Ultrafine particle concentrations and exposures in six elementary school classrooms in northern California. *Indoor Air*, 21(1): 77–87.

Murray, D.M. and Burmaster, D.E. 1995. Residential air exchange rates in the United States: Empirical and estimated parametric distributions by season and climatic region. Risk Analysis, 15(4):459–465.

Murray, C.L. and Lopez., A.D. 1996. The global burden of disease: a comprehensive assessment of mortality and disability from diseases, injuries, and risk factors in 1990 and projected to 2020. Cambridge, MA: Harvard University Press.

National Retail Federation (NRF). 2010. Job Growth by Industry, 2008-2018. Available from: http://www.nrf.com/modules.php?name=Pages&sp_id=1243#1

Ochiai, N., Tsuji, A., Carlson, N., Daishima, S., and Cardin, D. B. 2002. Stabilities of 58 volatile organic compounds in fused-silica-lined and SUMMA polished canisters under various humidified conditions. *Journal of Environmental Monitoring*, 4(6): 879–889.

Offermann, F. J. 2009. Ventilation and indoor air quality in new homes. California Air Resources Board and California Energy Commission, PIER Energy-Related Environmental Research Program No. CEC-500-2009-085.

Ozkaynak H, Xue J, Weker R, Butler D, Koutrakis P, Spengler J. The particle team (PTEAM) study: analysis of the data. EPA; 1997.

Otake, T., Yoshinaga, J., and Yanagisawa, Y. 2004. Exposure to phthalate esters from indoor environment. J*ournal of Exposure Analysis and Environmental Epidemiology*, 14, 524–528.

Parthasarathy S., Fisk W.J., McKone T.E. 2013. Effect of ventilation on chronic health in offices and schools. Lawrence Berkeley National Laboratory.

Parodi, S., Vercelli, M., Garrone, E., Fontana, V., and Izzotti, A. 2005. Ozone air pollution and daily mortality in Genoa, Italy between 1993 and 1996. *Public Health*, 119(9): 844–850.

Persily AK, Gorfain J, Brunner G. Ventilation rates in US office buildings from the EPA BASE study. 2005. In: Proceedings of Indoor Air, The Tenth International Conference on Indoor Air Quality and Climate, Indoor Air 2005. page 4–9.

Pope, C. A., Burnett, R. T., Thurston, G. D., Thun, M. J., Calle, E. E., Krewski, D., et al. 2003. Cardiovascular mortality and long-term exposure to particulate air pollution: epidemiological evidence of general pathophysiological pathways of disease. *Circulation*, 109(1): 71–77. Pope, C. A., and Dockery, D. W. 2006. Health effects of fine particulate air pollution: lines that connect. *Journal of the Air and Waste Management Association*, 56(6): 709–742.

Pratt, G. C., Bock, D., Stock, T. H., Morandi, M., Adgate, J. L., Ramachandran, G., et al. 2005. A field comparison of volatile organic compound measurements using passive organic vapor monitors and stainless steel canisters. *Environmental Science and Technology*, 39(9): 3261–3268.

Qian, H., Li, Y., Seto, W. H., Ching, P., Ching, W. H., and Sun, H. Q. 2010. Natural ventilation for reducing airborne infection in hospitals. *Building and Environment*, 45(3): 559–565.

Ramachandran, G., Adgate, J. L., Hill, N., Sexton, K., Pratt, G. C., and Bock, D. 2000. Comparison of short-term variations (15-minute averages) in outdoor and indoor $PM_{2.5}$ concentrations. *Journal of the Air and Waste Management Association*, 50(7): 1157–1166.

Ramalho, O., Mandin, C., Ribéron, J., and Wyart, G. 2012. Air stuffiness and air exchange rate in French schools and day-care centers. *Presented at the 10th International conference on Industrial Ventilation, France*.

Rea, A. W., Zufall, M. J., Williams, R. W., Sheldon, L., and Howard-Reed, C. 2001. The influence of human activity patterns on personal pm exposure: A comparative analysis of filter-based and continuous particle measurements. *Journal of the Air and Waste Management Association*, 51(9): 1271–1279.

Rudel, R. ., Dodson, R. E., Perovich, L. J., Morello-Frosch, R., Camann, D. E., Zuniga, M. M., et al. 2010. Semi-volatile endocrine-disrupting compounds in paired indoor and outdoor air in two northern California communities. *Environmental Science and Technology*, 44 (17), 6583–6590.

Rudel, R. A., Camann, D. E., Spengler, J. D., Korn, L. R., and Brody, J. B. 2003. Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust. *Environmental Science and Technology*, 37 (20), 4543–4553.

Sakai, R., Siegmann, H. C., Hajime, S., and Voorhees, S. A. 2002. Particulate matter and particle-attached polycyclic aromatic hydrocarbons in the indoor and outdoor air of Tokyo measured with personal monitors. *Environmental Research*, 89(1): 66–71.

Sandberg, M. G. 1989. Predicting a time varying flow rate using the constant concentration and decay technique. *ASHRAE Transactions* 93 Part 1: 1381–1393.

Shaw, C. Y. 1981. Air tightness : supermarkets and shopping malls. *ASHRAE journal*, 23(3): 44–46.

Sherman, M. H. 1990. Tracer-gas techniques for measuring ventilation in a single zone. *Building and Environment*, 24(4): 365–374.

Siegel, J. A., Srebric, J., Crain, N., Nirlo, E., Zaatari, M., Hoisington, A., et al. 2013. ASHRAE Research Project 1596-RP: Ventilation and Indoor Air Quality in Retail Stores. No. RP-1596. ASHRAE.

Stock, T. H., Morandi, M. T., Pratt, G. C., Bock, D., and Cross, J. H. 1999. Comparison of the results of VOC monitoring with diffusive samplers and canisters. *Indoor Air*: 443–448. Presented at the Indoor Air.

Tang, J., Chan, C. Y., Wang, X., Chan, L. Y., Sheng, G., and Fu, J. 2005. Volatile organic compounds in a multi-storey shopping mall in guangzhou, South China. *Atmospheric Environment*, 39(38): 7374–7383.

Tringe, S. G., Zhang, T., Liu, X. G., Yu, Y. T., Lee, W. H., Yap, J., et al. 2008. The Airborne Metagenome in an Indoor Urban Environment. *PLoS One*, 3(4): 1–10.

Tsai FC, Smith KR, Vichit-Vadakan N, Ostro BD, Chestnut LG, Kungskulniti N. 2000. Indoor/outdoor PM_{10} and $PM_{2.5}$ in Bangkok, Thailand. *Journal of exposure analysis and environmental epidemiology*;10:15–26.

Turk B.H., Grimsrud D.T., Brown J.T., Geisling-Sobotka K.L., Harrison J., Prill R.J. 1989. Commercial building ventilation rates and particle concentrations. *ASHRAE Transactions*; 95: 422–33.

Vonderheide, A. P., Mueller, K. E., Meija, J., and Welsh, G. L. 2008. Polybrominated diphenyl ethers: Causes for concern and knowledge gaps regarding environmental distribution, fate and toxicity. *Science of the Total Environment*, 400(1): 425–436.

Wallace, L. A., Emmerich, S. J., and Howard-Reed, C. 2004. Source strengths of ultrafine and fine particles due to cooking with a gas stove. *Environmental Science and Technology*, 38(8): 2304–2311.

Wallace, L., and Ott, W. 2011. Personal exposure to ultrafine particles. *Journal of Exposure Science and Environmental Epidemiology*, 21(1).

Wang, Y., Zheng, B.S., Li, X.Y., and Wang, X. 2004. Radon in underground structure in Southeastern China. Presented at the 8th International Symposium on Metal Ions in Biology and Medicine, Budapest, Hungary.

Wargocki, P., Fanger, P. O., Krupicz, P., and Szczecinski, A. 2004. Sensory pollution loads in six office buildings and a department store. *REHVA Scientific*, 36(10): 995–1001.

Weichenthal, S., Dufresne, A., Infante-Rivard, C., and Joseph, L. 2008. Characterizing and predicting ultrafine particle counts in Canadian classrooms during the winter months: model development and evaluation. *Environmental Research*, 106(3): 349–360.

Weisel C.P., Zhang J.J., Turpin B.J., Morandi M.T., Colome S., Stock T.H., et al. 2005. Relationships of Indoor, Outdoor, and Personal Air (RIOPA) Part I. Collection Methods and Descriptive Analyses. Health Effects Institute.

Weschler, C. J., and Nazaroff, W. W. 2008. Semi-volatile organic compounds in indoor environments. *Atmospheric Environment*, 42(40): 9018–9040.

Wheeler A.J., Wallace L.A., Kearney J., Van Ryswyk K., You H., Kulka R,. et al. 2011. Personal, Indoor, and Outdoor Concentrations of Fine and Ultrafine Particles Using Continuous Monitors in Multiple Residences. *Aerosol Science and Technology;* 45:1078–89.

WHO. 2005. WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide, and sulfur dioxide. World Health Organization.

Wu, P. C., Li, Y. Y., Chiang, C. M., Huang, C. Y., Lee, C. C., Li, F. C., et al. 2005. Changing microbial concentrations are associated with ventilation performance in Taiwan's air-conditioned office buildings. *Indoor air*, 15(1): 19–26.

Wu, X., Apte, M. G., Maddalena, R., and Bennett, D. H. 2011. Volatile Organic Compounds in Small- and Medium-Sized Commercial Buildings in California. *Environmental Science and Technology*, 45(20): 9075–9083.

Yamamoto, N., Shendell, D. G., Winer, A. M., and Zhang, J. 2010. Residential air exchange rates in three major US metropolitan areas: results from the relationship among indoor, outdoor, and personal air study 1999-2001. *Indoor Air*, 20(1): 85–90.

Yu, K. N., Stokes, M. J., Lo, C. H., and Young, E. C. M. 1997. A survey of radon properties in underground shopping centers in Hong Kong. *Applied Radiation and Isotopes*, 48(6): 863–866.

Zhang, Y., Huang, W., London, S., Song, G., Chen, G., Jiang, L., et al. 2006. Ozone and daily mortality in Shanghai, China. *Environmental Health Perspectives*, 114(8): 1227–1232.

Zhang J, Moser D, Bengtson N, Effinger M. 2011. Advanced Energy Retrofit Guides: Retail Buildings. Pacific Northwest National Laboratory.Zhu, Y.,Hinds, W. C., Kim S., Sioutas, C. 2002. Concentration and size distribution of ultrafine particles near a major highway. *Journal of the Air & Waste Management Association52(*9): 1032-1042.

Zhu, Y., Fung, D. C., Kennedy, N., Hinds, W. C., and Eiguren-Fernandez, A. 2008. Measurements of ultrafine particles and other vehicular pollutants inside a mobile exposure system on Los Angeles freeways. *Journal of the Air and Waste Management Association*, 58(3): 424–434.

Zhu, Y., Hinds, W. C., Krudysz, M., Kuhn, T., Froines, J., and Sioutas, C. 2005. Penetration of freeway ultrafine particles into indoor environments. *Journal of Aerosol Science*, 36(3): 303–322.

APPENDIX E: OZONE IN FOURTEEN U.S. RETAIL STORES.

1. Typical sources and potential health effects

Ozone is an important indoor gas-phase compound. Even in the absence of typical indoor sources (e.g. photocopiers (Destaillats et al., 2008)), there is reason to believe that ozone may be a contaminant of concern in retail stores. Ozone is a contaminant generated though photochemical reactions between nitrogen oxides and VOCs in the troposphere, but most of our exposure to ozone occurs indoors (Weschler, 2006) because Americans spend approximately 87% of their time indoors (Klepeis et al., 2001). Indoor-to-outdoor ozone concentration ratios typically range 20-80% (Weschler et al., 1989), owing primarily to reactions between ozone and indoor surfaces.

Many large-scale epidemiological studies have evaluated the association between short-term exposure to ozone and daily mortality (Bell et al., 2004; Gryparis et al., 2004; Ito et al., 2005; Levy et al., 2005; Parodi et al., 2005; Zhang et al., 2006). Ozone engages in homogeneous reactions predominantly with compounds containing unsaturated carbon-carbon double bonds. The products of these reactions are generally unstable, which leads to the formation of significant by-products that are potentially damaging to humans (Weschler, 2006) and materials (Weschler, 2000).

Only two published studies have involved ozone concentrations in retail spaces (Chan et al., 2012; Lee and Hsu, 2007). Parameters related to the fate and transport of indoor ozone are well known in residences (Weschler, 2000; 2003), but have not been studied in the retail environment yet.

2. Methods

We collected real-time ozone concentrations at a fixed location on the sales floor of the retail site during the whole visit. We simultaneously monitored ambient ozone concentrations from the rooftop of the retail site wherever possible.

Indoor and outdoor ozone concentrations for all tests were monitored using Model 202 Ozone Monitor manufactured by 2B Technologies, with an uncertainty defined as the greater of ±2% or ±1.5 ppb, or obtained from either the Texas Commission on Environmental Quality (TCEQ) or the Pennsylvania Department of Environmental Protection (PA DEP) databases.

3. Results

3.1. Comparison between sites

Tables 37 and 38 list the measures of central tendency of ozone concentration during the 4-hour mobile sampling event for indoors and outdoors, respectively. The uncertainty for all ozone concentrations measured by a 2B Technologies monitor is the uncertainty reported by the manufacturer of ±1.5 ppb.

Table 37: Summary statistics of indoor ozone concentrations during mobile sampling.

Site	**Minimum[a] [ppb]**	**Maximum[a] [ppb]**	**Mean[a] [ppb]**	**Median[a] [ppb]**	**Number of data points**
HaP1	5.4	7.4	6.3	6.3	29
HaP2	0.9	3.4	2.4	2.5	50
MbP1	2.6	6.4	4.5	4.2	48
MbP2	1.5	3.4	2.2	2.2	47
MbP3	2.3	6.1	4.5	4.6	47
MbP4	12.9	16.7	14.8	14.7	47
MbT1	8.0	11.8	10.8	10.9	40
MbT2	3.3	7.1	5.8	5.9	48
MbT3	2.4	5.2	3.7	3.6	48
MbT4	0.8	6.2	3.5	3.4	47
MiP	0.1	2.9	1.7	1.9	45
MiT	1.1	7.3	3.6	3.3	47
EgP1	0.9	7.0	4.1	4.2	48
OhT	2.3	10.5	7.0	7.2	48
FfP	5.9	8.5	7.3	7.3	16
FfT1	1.4	4.0	2.3	2.1	48
FfT2	0.7	2.6	1.8	1.8	30
GeP	3.7	8.3	5.4	5.2	45
GeT1	13.0	21.0	17.5	18.0	31
GeT2	4.4	7.3	5.8	5.9	47
ScP	5.7	10.0	8.2	8.2	32
SdT	8.0	18.0	12.9	12	45

[a] All indoor concentrations are ±1.5 ppb. Site HaT excluded because of instrument failure.

Across all sites, indoor ozone concentrations averaged 5.8±4 ppb during the 4-hour mobile sampling event, which is similar to the average over the whole visit of 6.2±4.3 ppb. The stores sampled in this study did not utilize any of the typical indoor sources of ozone, such as electrostatic air filters, or photocopiers and laser printers. It should be noted that we monitored indoor ozone from a fixed location in the site, because of electrical power requirements, which might not be representative of the air sampled by mobile instruments during the mobile sampling event.

When we could not measure the ambient ozone concentration with a 2B Technologies monitor, we retrieved hourly data collected at a nearby (< 5 km radius for

Texas sites) sampling location operated by the TCEQ or the PA DEP. The uncertainty for these concentrations was determined using the spatial difference between the nearest state-operated monitoring sites. The uncertainty for ozone data supplied by TCEQ or the PA DEP was determined to be ±5 ppb.

Table 38: Summary statistics of outdoor ozone concentrations during mobile sampling.

Site	Minimum [ppb]	Maximum [ppb]	Mean [ppb]	Median [ppb]	Number of data points
HaP1	42	53	47	48	5[a]
HaP2	17	47	29	25	4[a]
HaT	32	51	42	42	49
MbP1	15	25	21	22	4[a]
MbP2	37	40	38	38	4[a]
MbP3	31	33	33	33	4[a]
MbP4	45	53	50	50	4[a]
MbT1	31	61	48	50	4[a]
MbT2	30	35	32	31	37
MbT3	28	37	34	35	4[a]
MbT4	27	56	41	39	45
MiP	44	58	53	54	4[a]
MiT	32	46	41	41	47
EgP1	29	34	31	31	4[a]
EgP2	31	34	33	34	4[a]
OhT	29	65	51	55	42
FfP	31	49	40	39	4[a]
FfT1	9	35	23	24	30
FfT2	16	21	19	19	3[a]
GeP	41	58	49	49	4[a]
GeT1	32	51	42	42	34
GeT2	18	24	21	21	4[a]
ScP	48	52	50	50	3[a]
SdT	38	47	43	45	3[a]

[a] Sites where the TCEQ or the PA DEP provided ambient ozone concentrations. The concentrations are 1-hour averages instead of 5-minute averages. The uncertainty associated this data is ±5 ppb instead of ±1.5 ppb.

As ozone is mainly the product of photochemical reactions in the atmosphere, outdoor concentrations are typically much higher than indoor concentrations. The outdoor ozone concentrations for this study averaged 38±10 ppb. There was no statistical difference between the average outdoor ozone concentrations in Texas and Pennsylvania.

Ozone is a known health concern, and is heavily regulated by various organizations. For instance the US National Ambient Air Quality Standard is set at 80 ppb (8-hour average), and the National Institute for Occupational Safety and Health recommends that ozone levels never exceed 100 ppb. The highest ozone concentrations measured for this study was 55 ppb outdoors at site OhT.

Figure 31 shows typical temporal profiles of indoor and outdoor ozone, in Texas (SdT) and Pennsylvania (MbP1). The uncertainty displayed is the instrument uncertainty reported by the manufacturer for indoor concentrations, and the relative spatial variation for outdoor concentrations.

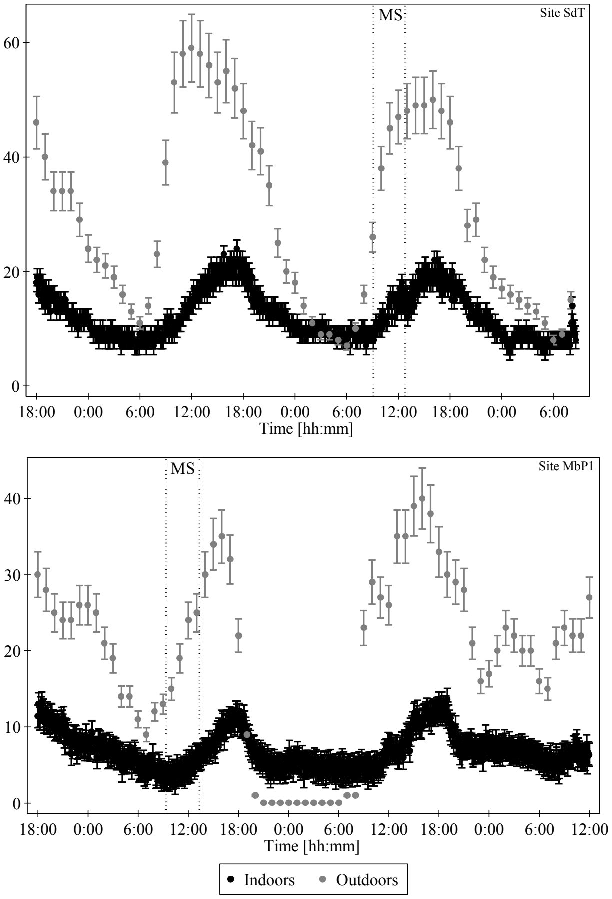

Figure 31: Indoor and outdoor ozone concentrations over time at Sites SdT and MbP1, respectively. MS indicates the mobile sampling event. Both samples were collected during summer.

As the formation of ozone requires sunlight, ozone concentrations are cyclical: minimum levels are reached at night (0 ppb at MbP1), while maxima are attained in the afternoon. Outdoor concentrations can vary by an order of magnitude over a 24-hour period. Indoor concentrations closely follow the variations of outdoor concentrations.

Figure 32 is a bar graph of indoor/outdoor ratios (I/O ratios) for the 4-hour mobile sampling event by site. The uncertainty displayed is the sum in quadrature of the standard deviation of both indoor and outdoor concentrations over the 4-hour period considered.

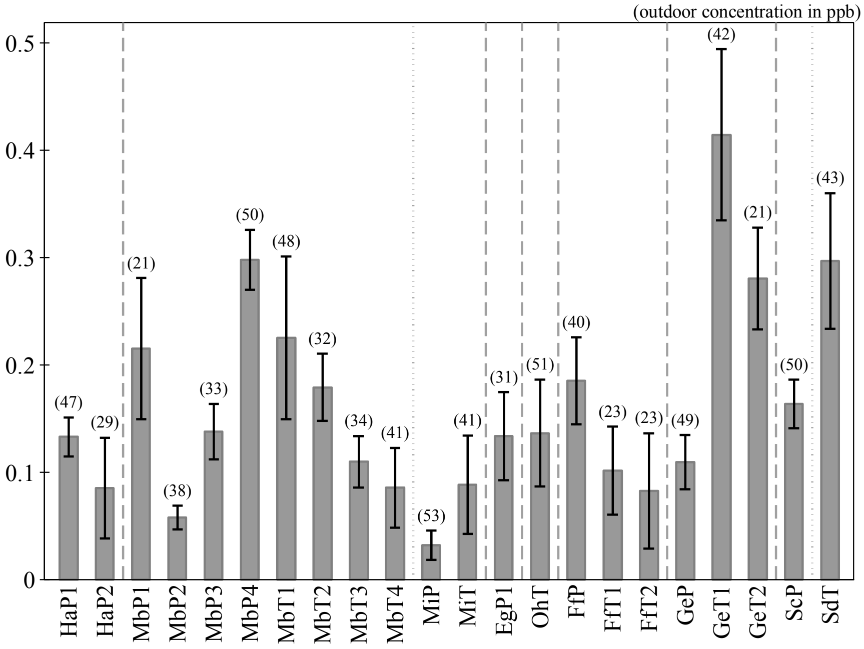

Figure 32: Indoor-to-outdoor ratios of ozone concentrations, by site.

I/O ratios are well below unity at all sites, confirming ozone originates outdoors. I/O ratios range from 0.03 to 0.41, with an average of 0.16±0.09. The results are in good agreement with I/O ratios reported in the literature. Weschler (2000) reviewed 25 studies reporting ozone I/O ratios in a variety of building with negligible indoor sources. Results ranged from 0.07 to 0.7, averaging 0.36±0.19 in residences. In schools, reported I/O ratios ranged from 0.3 to 0.8, averaging 0.53±0.19; similarly to offices where I/O ratios ranged from 0.22 to 0.9, averaging 0.52±0.21.

3.2. Associations with air exchange rate

Figure 33 is a graph of ozone indoor-to-outdoor ratios as a function of air exchange rates. Note that the uncertainty displayed on the ratios is the standard deviation of the 4-hour measurement. Ozone I/O ratios and air exchange rates are significantly but poorly correlated ($p=0.003$, $R^2=0.29$). Although the positive influence of air exchange rate is to be expected on the indoor concentrations of an outdoor contaminant, confounding factors should be taken into account. For instance indoor ozone is deeply influenced by removal to surfaces, and surface-to-volume ratios can vary between sites. Another possible confounding factor is the presence of indoor VOCs, as ozone is also depleted by homogenous reactions with VOCs such as terpenoids.

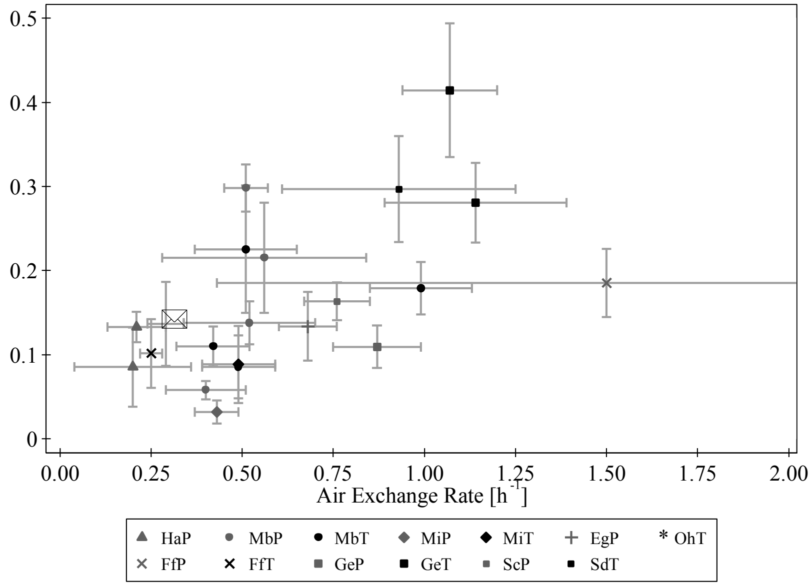

Figure 33: Indoor-to-outdoor ratios of ozone concentrations, by air exchange rate.

To account for some of these differences, we conducted ozone measurements using both normal and elevated air exchange rates at sites MiP and MiT. For the first set of tests, the RTUs were operated at elevated ventilation rates. For the second set of tests the ventilation rate was returned to normal operational conditions. Two sets of samples were collected at each ventilation rate. We will only report the second measurement in each ventilation mode to allow time for the sites to reach steady state conditions after changes in the air exchange rate. It should be noted that the uncertainties in ventilation rates for site MiT "touch" but do not overlap. The results of these tests are presented below.

Figure 34 shows the indoor-to-outdoor ozone ratio estimated using the average ozone concentrations monitored over the 4-hour mobile sampling period. The uncertainty displayed adds in quadrature the standard deviation of the indoor and outdoor ozone concentrations.

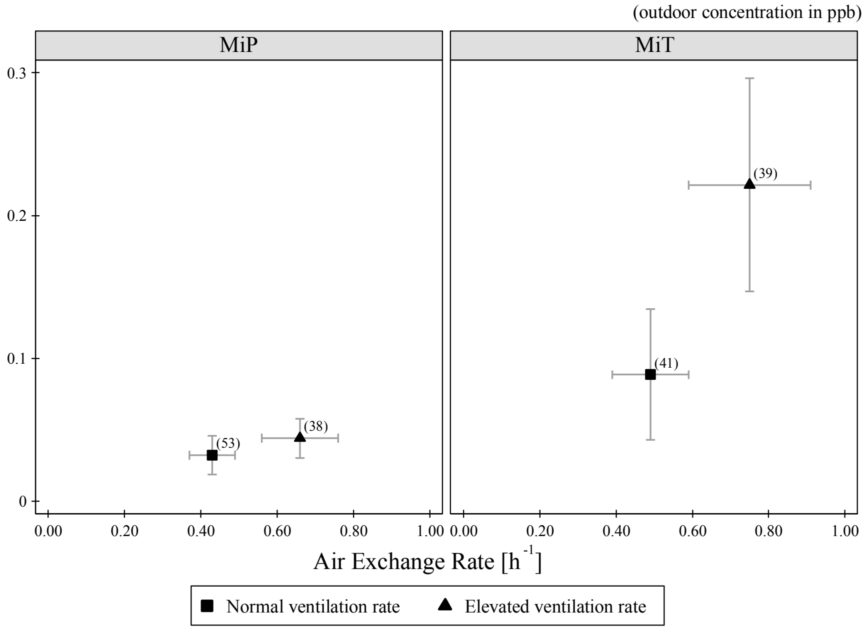

Figure 34: Ozone indoor-to-outdoor ratio as a function of air exchange rate, at both intervention Sites MiP and MiT. Note that average outdoor ozone concentrations [ppb] are provided for context.

Ozone and other outdoor contaminants are introduced to indoor spaces through ventilation. Increases in ventilation rates elevated the indoor concentration of these pollutants. The I/O ratios for ozone shown in Figure 34 suggest an increase in ventilation rate would have a negative impact on indoor ozone concentrations. Additionally, the outdoor ozone concentration decreased between the two samples by 28±4% at Site MiP, and to a lesser extent by 5±1% at Site MiT, contributing to the increase in the I/O ratios.

3.3. Whole building emission rates

The whole building emission rate (WBER) is the net amount of pollutant emitted per unit floor area for a given unit of time.

Figure 35 is a plot of the ozone WBERs for each site. The average ozone WBER was -270±122 μg/m^2.h. The WBERs for ozone are negative because ozone is an outdoor contaminant and the indoor space acts as a sink, as ozone is consumed by surface deposition and gas-phase reactions.

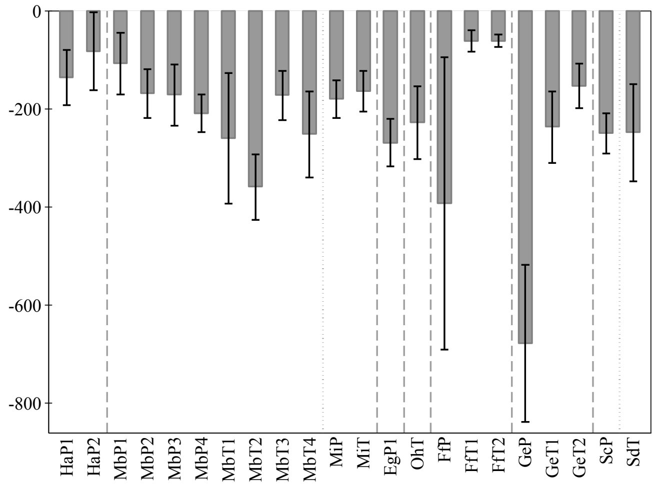

Figure 35: Ozone whole building emission rate (μg/m^2·h) at all sites.

Similarly, Figure 36 shows the whole building emission rates of ozone respectively at Sites MiP and MiT, estimated from the concentrations measured at the different air exchange rates. Sites MiP and MiT are both net sinks of ozone. The WBER for both sites also appear to be independent of ventilation rate for the range tested.

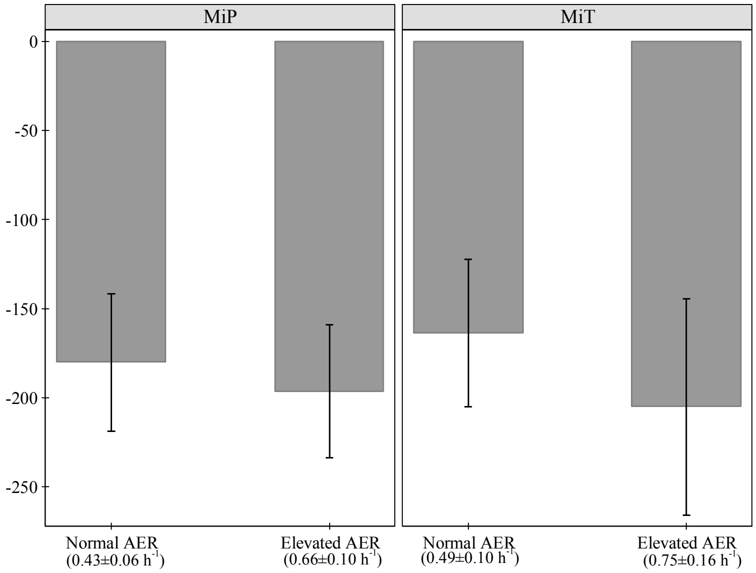

Figure 36: Ozone whole building emission rate ($\mu g/m^2 \cdot h$) at Sites MiP and MiT.

Given these negative ozone WBERs, we can further investigate the loss of ozone to surfaces. The parameter assessing ozone surface removal rate, $k_{dep}(A/V)$, is the product of the deposition velocity and the surface-to-volume ratio. It is related to the indoor-to-outdoor ratio by the expression shown in Equation 1. It is derived from a steady-state mass balance, with the following assumptions: (1) the space is well mixed, and (2) the penetration factor of the contaminant considered is unity (Weschler et al., 1989). There are reasons to question these assumptions, but generally this provides a useful way of examining differences in ozone loss between sites.

$$I/O = \frac{C_{in}}{C_{out}} = \frac{AER}{AER + k_{dep}\frac{A}{V}}$$ (Equation 1)

Where:
I/O = indoor to outdoor ratio [/],
C_{in}, C_{out} = indoor and outdoor concentrations [ppb],
AER = air exchange rate [h^{-1}],
k_{dep} = deposition velocity [m/h],
A = surface area available for deposition [m^2], and
V = volume of the space [m^3].

Figure 37 is a bar graph of the estimated surface removal rate k_{dep}(A/V) for all sites where indoor and outdoor ozone data was available. The range displayed takes into account the standard deviation on the I/O ratio and the uncertainty in the air exchange rate.

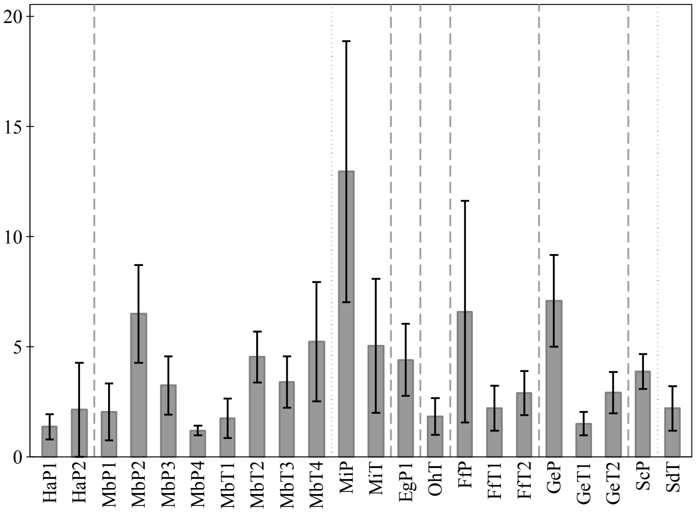

Figure 37: Ozone surface removal rate (h^{-1}) at all sites.

The average ozone surface removal rate across all sites was 3.9±2.7 h^{-1}. Modifying the mass balance to account for losses through the building envelope, and assuming a penetration factor of 0.7 instead of 1 (Stephens et al., 2012), the average $k_{dep}(A/V)$ is reduced to 2.5±1.9 h^{-1} . These results are in the lower range of literature of values for residences, which is expected as retail stores can have large unoccupied overhead volumes, hence lower surface area-to-volume ratios than residences. Weschler (2000) reviewed ten papers that reported removal rates for offices ranging from 2.5 to 4.3 h^{-1}, and for residences ranging from 2.8 to 5.4 h^{-1}. The ozone surface removal rates are, on average across all sites, eight times higher than air exchange rates, suggesting ozone is mainly consumed by deposition to surfaces.

4. Summary and conclusions

In general, the indoor and outdoor ozone concentrations monitored in the present investigation were one to two orders of magnitude below the US EPA regulatory limit. The stores sampled in this study did not seem to contain any indoor source of ozone, which was reflected by indoor-to-outdoor ratios estimated well below unity. Ventilation was shown to have a positive impact on indoor ozone concentrations, as ozone I/O ratios and air exchange rates were significantly, although poorly, correlated. It should be noted that confounding factors might have influenced this result, such as the presence of indoor VOCs with which ozone might react. Additionally, the sites studied were net sinks of ozone, and ozone was predominantly depleted by losses to surfaces.

References

Bell, M.L., McDermott, A., Zeger, S.L., Samet, J.M. and Dominici, F. (2004) Ozone and short-term mortality in 95 US urban communities, 1987-2000, Am Med Assoc, **292**, 2372–2378, Chan, W.R., Sidheswaran, M., Sullivan, D.P., Cohn, S. and Fisk, W.J. (2012) *Contaminant levels and source strengths in U.S. retail stores - A pilot study*, Lawrence Berkeley National Laboratory, 1–9.

Destaillats, H., Maddalena, R.L., Singer, B.C., Hodgson, A.T. and McKone, T.E. (2008) Indoor pollutants emitted by office equipment: A review of reported data and information needs, **42**, 1371–1388.

Gryparis, A., Forsberg, B., Katsouyanni, K., Analytis, A., Touloumi, G., Schwartz, J., Samoli, E., Medina, S., Anderson, H.R., Niciu, E.M., Wichmann, H.E., Kriz, B., Kosnik, M., Skorkovsky, J., Vonk, J.M. and Dortbudak, Z. (2004) Acute Effects of Ozone on Mortality from the 'Air Pollution and Health: A European Approach' Project, **170**, 1080–1087.

Ito, K., De Leon, S.F. and Lippmann, M. (2005) Associations Between Ozone and Daily Mortality, **16**, 446–457.

Klepeis, N.E., Nelson, W.C., Ott, W.R., Robinson, J.P., Tsang, A.M., Switzer, P., Behar, J.V., Hern, S.C. and Engelmann, W.H. (2001) The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants, Princeton, NJ: Princeton Scientific Pub. Co., c1991-c2005., **11**, 231–252.

Lee, C.-W. and Hsu, D.-J. (2007) Measurements of fine and ultrafine particles formation in photocopy centers in Taiwan, *Atmospheric Environment*, **41**, 6598–6609.

Levy, J.I., Chemerynski, S.M. and Sarnat, J.A. (2005) Ozone Exposure and Mortality, **16**, 458–468.

Parodi, S., Vercelli, M., Garrone, E., Fontana, V. and Izzotti, A. (2005) Ozone air pollution and daily mortality in Genoa, Italy between 1993 and 1996, **119**, 844–850.

Stephens, B., Gall, E.T. and Siegel, J.A. (2012) Measuring the Penetration of Ambient Ozone into Residential Buildings, *Environ. Sci. Technol.*, **46**, 929–936.

Weschler, C.J. (2000) Ozone in indoor environments: concentration and chemistry, *Indoor Air*, Wiley Online Library, **10**, 269–288.

Weschler, C.J. (2003) Indoor/outdoor connections exemplified by processes that depend on an organic compound's saturation vapor pressure, **37**, 5455–5465.

Weschler, C.J. (2006) Ozone's Impact on Public Health: Contributions from Indoor Exposures to Ozone and Products of Ozone-Initiated Chemistry, **114**, 1489–1496.

Weschler, C.J., Shields, H.C. and Naik, D.V. (1989) Indoor Ozone Exposures, **39**, 1562–1568.

Zhang, Y., Huang, W., London, S.J., Song, G., Chen, G., Jiang, L., Zhao, N., Chen, B. and Kan, H. (2006) Ozone and Daily Mortality in Shanghai, China, **114**, 1227–1232.

Appendix F: Association of human perception with concentrations of Volatile Organic Compounds in fourteen U.S. retail stores.

Identifying odorous compounds can be of interest to retailers since olfactory cues are believed to affect customers' shopping behaviors (Spangenberg et al., 1996; Douce and Janssens, 2013). This study quickly explores if the perception of store employees is associated with VOC concentrations exceeding their odor threshold.

1. Employee surveys

Surveys were handed to the store employees at all sites but Sites MiP and MiT. The overall response rate (# surveys returned/# surveys handed out) was 83%. Out of the five questions on the survey forms, the following three related to the perception of indoor air quality: "Q3b. Do you smell anything, and how strong is the smell? – Chemical smell" ("None/Weak/Heavy"), "Q3c. Do you smell anything, and how strong is the smell? – Other unpleasant smell (food, tobacco, perfume, etc…" ("None/Weak/Heavy"), and "Q4. How would you rate the overall indoor environmental quality of this store, based on the smells, cleanness and environmental factors?" ("Very good/Good/Neutral/Poor/Very poor"). Generally employees were satisfied with the quality of the air.

2. Comparison with odor thresholds and association with human perception

Standardized odor thresholds (OT) were obtained for 94 of 288 compounds identified in this study (Devos et al., 1990). Of these compounds, very few had indoor concentrations measured using Summa canisters that exceeded their respective odor thresholds, with the exceptions of ethylbenzene and hexanal (OT = 2.9 and 13.8 ppb, respectively) at home improvement store HaP, nonanal (OT = 2.3 ppb) at the furniture store FfP, and pentanal (OT = 6.0 ppb) at HaP2. When considering indoor concentrations measured using sorbent tubes, 3-methylbutanal, decanal and octanal were also found to exceed their respective odor thresholds of 2.3 ppb, 0.9 ppb and 1.4 ppb. Overall, up to six compounds were measured at concentrations above their odor thresholds at three to 12 test visits. However, surveys of employees did not find any strong associations between exceedances of odor thresholds and employee ratings of chemical smells, or other unpleasant smells (food, tobacco, perfume, etc…), and of the overall indoor environmental quality of the store. This finding should be taken with caution since odor thresholds are somewhat subjective, and vary by orders of magnitude for a select compound, depending on the reference chosen. Moreover, not all compounds found in the present investigation were the subjects of a published odor evaluation. Therefore, compounds other than the 94 selected might also exceed their odor threshold and modify the results of this analysis. In addition, little is known about odors thresholds for mixtures of compounds. Furthermore, the findings of this analysis are limited by the negative bias introduced by the survey questions that did not include a rating of smells commonly considered pleasant, such as terpenoids or the smell of baking bread.

References

Devos, M., Patte, F., Rouault, J., Laffort, P., and Van Gemert, L. J. (1990), Standardized Human Olfactory Thresholds. Oxford University Press, IRL Press.

Douce, L., and Janssens, W. (2013) The Presence of a Pleasant Ambient Scent in a Fashion Store: The Moderating Role of Shopping Motivation and Affect Intensity, Environment and Behavior, 45, 215–238.

Spangenberg, E. R., Crowley, A. E., and Henderson, P. W. (1996) Improving the store environment: do olfactory cues affect evaluations and behaviors?, The Journal of Marketing, 67–80.

References

[1] *Monthly Energy Review*. DOE/EIA-0035(2014/01). US Energy Information Administration, 2014.

[2] Teichman, K.Y. et al.: Wealth of intent, dearth of data. *High Performing Buildings*, 2013, pp. 34–43.

[3] Spengler, J.D., Chen, Q.: Indoor air quality factors in designing a healthy building. *Annual Review of Energy and the Environment*, **25** (1), 2000, pp. 567–600.

[4] U.S. Environmental Protection Agency: *Volatile Organic Compounds: Definition*.

[5] WHO European Centre for Environment and Health, WHO Regional Office for Europe: *WHO Guidelines for Indoor Air Quality: Selected Pollutants*. Copenhagen, Denmark: World Health Organization, 2010.

[6] Norbäck, D. et al.: Asthmatic symptoms and volatile organic compounds, formaldehyde, and carbon dioxide in dwellings. *Occupational and environmental medicine*, **52** (6), 1995, pp. 388–395.

[7] Nielsen, G.D. et al.: Recent trend in risk assessment of formaldehyde exposures from indoor air. *Arch Toxicol*, **87** (1), 2013, pp. 73–98.

[8] ASHRAE. *ASHRAE Standard 62.1-2013 Ventilation for Acceptable Indoor Air Quality*. Atlanta: American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc, 2013.

[9] Godish, T., Spengler, J.: Relationships between ventilation and indoor air quality: a review. **6** (2), 1996, pp. 135–145.

[10] Sundell, J. et al.: Ventilation rates and health: multidisciplinary review of the scientific literature. *Indoor Air*, **21** (3), 2011, pp. 191–204.

[11] U.S. Energy Information Administration: *Table B11. Selected Principal Building Activity: Part 1, Number of Buildings for Non-Mall Buildings, 2003*. 2008.

[12] U.S. Energy Information Administration: *Table B7. Building Size, Floorspace for Non-Mall Buildings, 2003*. 2008.

[13] U.S. Energy Information Administration: *Table E1. Major Fuel Consumption (Btu) by End Use for Non-Mall Buildings, 2003*. 2008.

[14] Won, D. et al.: A material emission database for 90 target VOCs. *Indoor Air*, 2005, pp. 4–9.

[15] Uhde, E., Salthammer, T.: Impact of reaction products from building materials and furnishings on indoor air quality—A review of recent advances in indoor chemistry. *Atmospheric Environment*, **41** (15), 2007, pp. 3111–3128.

[16] Nazaroff, W.W., Weschler, C.J.: Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmospheric Environment*, **38** (18), 2004, pp. 2841–2865.

[17] U.S. Department of Labor: *Industries at a Glance - Retail Trade: NAICS 44-45*. 2014.

[18] U.S. Department of Labor: *ATUS Latest Numbers: Purchasing Goods and Services*. 2013.

[19] U.S. Census Bureau: *Historical Adjusted Monthly Sales - Retail Total (excl. food services)*. 2014.

[20] Spangenberg, E.A. et al.: Improving the store environment: do olfactory cues affect evaluations and behaviors? *Journal of Marketing*, **60** (2), 1996, pp. 67–80.

[21] Douce, L., Janssens, W.: The Presence of a Pleasant Ambient Scent in a Fashion Store: The Moderating Role of Shopping Motivation and Affect Intensity. *Environment and Behavior*, **45** (2), 2013, pp. 215–238.

[22] Mølhave, L.: Organic compounds as indicators of air pollution. *Indoor Air*, **13** (s6), 2003, pp. 12–19.

[23] Salmon, A.G. et al.: *Technical support document for the derivation of noncancer reference exposure levels*. California Environmental Protection Agency, 2008.

[24] Krzyzanowski, M. et al.: Chronic respiratory effects of indoor formaldehyde exposure. *Environmental Research*, **52** (2), 1990, pp. 117–125.

[25] U.S. Environmental Protection Agency: *Formaldehyde (CASRN 50-00-0) - IRIS*. 2012.

[26] World Health Organization. International Agency for Research on Cancer *Monographs on the Evaluation of Carcinogenic Risks to Human, Volume 88: Formaldehyde, 2-Butoxyethanol and 1-tert-Butoxy-2-propanol*, 2006, World Health Organization, Lyon.

[27] Chao, C.Y., Chan, G.Y.: Quantification of indoor VOCs in twenty mechanically ventilated buildings in Hong Kong. *Atmospheric Environment*, **35** (34), 2001, pp. 5895–5913.

[28] Kim, Y.M. et al.: Concentrations and Sources of VOCs in Urban Domestic and Public Microenvironments. *Multiple values selected*, **35** (6), 2001, pp. 997–1004.

[29] Lee, C.-W., Hsu, D.-J.: Measurements of fine and ultrafine particles formation in photocopy centers in Taiwan. *Atmospheric Environment*, **41** (31), 2007, pp. 6598–6609.

[30] Caselli, M. et al.: Indoor contaminants from newspapers: VOCs emissions in newspaper stands. *Environmental Research*, **109** (2), 2009, pp. 149–157.

[31] Tang, J. et al.: Volatile organic compounds in a multi-storey shopping mall in guangzhou, South China. *Atmospheric Environment*, **39** (38), 2005, pp. 7374–7383.

[32] Bruno, P. et al.: Monitoring of volatile organic compounds in non-residential indoor environments. *Indoor Air*, **18** (3), 2008, pp. 250–256.

[33] Hotchi, T. et al.: Indoor air quality impacts of a peak load shedding strategy for a large retail building. *LBNL Report*, **59293**, 2006.

[34] Loh, M.M. et al.: Measured Concentrations of VOCs in Several Non-Residential Microenvironments in the United States. *Environ. Sci. Technol.*, **40** (22), 2006, pp. 6903–6911.

[35] Wu, X.M. et al.: Volatile Organic Compounds in Small- and Medium-Sized Commercial Buildings in California. *Environ. Sci. Technol.*, **45** (20), 2011, pp. 9075–9083.

[36] Eklund, B.M. et al.: Spatial and temporal variability in VOC levels within a commercial retail building. *Indoor Air*, **18** (5), 2008, pp. 365–374.

[37] Chan, W.R. et al.: *Contaminant levels and source strengths in U.S. retail stores - A pilot study*. LBNL-5547E. Lawrence Berkeley National Laborator, 2012.

[38] Grimsrud, D.T. et al.: *Investigation of appropriate ventilation rates for retail stores*. Indoor Air. 2011, pp. 1–6.

[39] U.S. Environmental Protection Agency: *A standardized EPA protocol for characterizing indoor air quality in large office buildings*. U.S. Environmental Protection Agency, 2003, pp. 1–311.

[40] ASTM International: *Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air*. D6196 – 03. West Conshohocken, PA: ASTM International, 2009.

[41] ASTM International: *Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)*. D5197 – 09. West Conshohocken, PA: ASTM International, 2010.

[42] ASTM International: *Standard Test Method for Determination of Volatile Organic Chemicals in Atmospheres (Canister Sampling Methodology)*. D5466 - 01. West Conshohocken, PA: ASTM International, 2007.

[43] ASHRAE et al.: *Performance Measurement Protocols for Commercial Buildings*. Atlanta, GA: American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., 2010, pp. 1–300.

[44] U.S. Environmental Protection Agency: *Appendix A: Common IAQ Measurements - A General Guide*. In: Building Air Quality: A Guide for Building Owners and Facility Managers. U.S. Environmental Protection Agency, 1991, pp. 1–11.

[45] U.S. Environmental Protection Agency: *Compendium Method TO-15: Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)*. EPA/625/R-96/010b. Cincinnati, OH 45268: U.S. Environmental Protection Agency, 1999.

[46] Batterman, S.A. et al.: Analysis and stability of aldehydes and terpenes in electropolished canisters. *Atmospheric Environment*, **32** (10), 1998, pp. 1647–1655.

[47] Wai-mei Sin, D. et al.: Development of an analytical technique and stability evaluation of 143 C3–C12 volatile organic compounds in Summa® canisters by gas chromatography–mass spectrometry. *Analyst*, **126** (3), 2001, pp. 310–321.

[48] Wang, D.K.W., Austin, C.C.: Determination of complex mixtures of volatile organic compounds in ambient air: canister methodology. *Anal Bioanal Chem*, **386** (4), 2006, pp. 1099–1120.

[49] U.S. Environmental Protection Agency: *Compendium Method TO-17: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes*. EPA/625/R-96/010b. Cincinnati, OH 45268: U.S. Environmental Protection Agency, 1999.

[50] U.S. Environmental Protection Agency: *Compendium Method TO-11A: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]*. EPA/625/R-96/010b. Cincinnati, OH 45268: U.S. Environmental Protection Agency, 1999.

[51] Haag, W.R.: *Rapid, continuous TVOC measurements using ppb-level PIDs*. Indoor Air. 2005, pp. 938–941.

[52] Coy, J.D. et al.: Field evaluation of a portable photoionization detector for assessing exposure to solvent mixtures. *AIHAJ-American Industrial Hygiene Association*, **61** (2), 2000, pp. 268–274.

[53] Carter, E.M. et al.: A coupled sensor-spectrophotometric device for continuous measurement of formaldehyde in indoor environments. *Journal of Exposure Science and Environmental Epidemiology*, 2013, pp. 1–6.

[54] Kumar, A., Viden, I.: *Simultaneous use of tube and canister system for sampling of volatile organic compounds (VOCs) in the atmosphere*. Indoor Air. 2005, pp. 2076–2080.

[55] Stock, T.H. et al.: Comparison of the results of VOC monitoring with diffusive samplers and canisters. *Indoor Air*, **99**, 1999, pp. 443–448.

[56] Dobos, R.T.: Field investigation comparing diffusion badge and charcoal tube monitoring for styrene. *Applied occupational and environmental hygiene*, **15** (9), 2000, pp. 673–676.

[57] Pfeffer, H.-U., Breuer, L.: BTX measurements with diffusive samplers in the vicinity of a cokery: Comparison between ORSA-type samplers and pumped sampling. *J. Environ. Monitor.*, **2** (5), 2000, pp. 483–486.

[58] Kim, K.H. et al.: *Evaluation of a PID-based portable detection system for TVOC as an indoor pollution analyzer*. Indoor Air. 2005, pp. 2674–2677.

[59] Pratt, G.C. et al.: A Field Comparison of Volatile Organic Compound Measurements Using Passive Organic Vapor Monitors and Stainless Steel Canisters. *Environ. Sci. Technol.*, **39** (9), 2005, pp. 3261–3268.

[60] Noguchi, T. et al.: Photocatalytic Degradation of Gaseous Formaldehyde Using TiO 2Film. *Environ. Sci. Technol.*, **32** (23), 1998, pp. 3831–3833.

[61] Zhang, Y. et al.: A model for analyzing the performance of photocatalytic air cleaner in removing volatile organic compounds. *Atmospheric Environment*, **37** (24), 2003, pp. 3395–3399.

[62] Wang, S. et al.: Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art. *Environment International*, **33** (5), 2007, pp. 694–705.

[63] Yu, K.-P. et al.: Effectiveness of Photocatalytic Filter for Removing Volatile Organic Compounds in the Heating, Ventilation, and Air Conditioning System. *Journal of the Air & Waste Management Association*, **56** (5), 2006, pp. 666–674.

[64] Obee, T.N.: Photooxidation of sub-parts-per-million toluene and formaldehyde levels on titania using a glass-plate reactor. *Environ. Sci. Technol.*, **30** (12), 1996, pp. 3578–3584.

[65] Ching, W.H. et al.: Solar photocatalytic degradation of gaseous formaldehyde by sol–gel TiO2 thin film for enhancement of indoor air quality. *Solar Energy*, **77** (2), 2004, pp. 129–135.

[66] Bourgeois, P.-A. et al.: Characterization of a new photocatalytic textile for formaldehyde removal from indoor air. *Applied Catalysis B: Environmental*, **128**, 2012, pp. 171–178.

[67] Saadoun, L. et al.: Synthesis and photocatalytic activity of mesoporous anatase prepared from tetrabutylammonium-titania composites. *Materials research bulletin*, **35** (2), 2000, pp. 193–202.

[68] Kibanova, D. et al.: Adsorption and photocatalytic oxidation of formaldehyde on a clay-TiO2 composite. *Journal of Hazardous Materials*, **211-212**, 2012, pp. 233–239.

[69] Ao, C.H. et al.: Photodegradation of formaldehyde by photocatalyst TiO2: effects on the presences of NO, SO2 and VOCs. *Applied Catalysis B: Environmental*, **54** (1), 2004, pp. 41–50.

[70] Obee, T.N., Brown, R.T.: TiO2 photocatalysis for indoor air applications: effects of humidity and trace contaminant levels on the oxidation rates of formaldehyde, toluene, and 1, 3-butadiene. *Environ. Sci. Technol.*, **29** (5), 1995, pp. 1223–1231.

[71] Destaillats, H. et al.: Key parameters influencing the performance of photocatalytic oxidation (PCO) air purification under realistic indoor conditions. *Applied Catalysis B: Environmental*, **128**, 2012, pp. 159–170.

[72] Huang, Y.-C. et al.: Improved Removal of Indoor Volatile Organic Compounds by Activated Carbon Fiber Filters Calcined with Copper Oxide Catalyst. *Clean Soil Air Water*, **38** (11), 2010, pp. 993–997.

[73] Sekine, Y., Nishimura, A.: Removal of formaldehyde from indoor air by passive type air-cleaning materials. *Atmospheric Environment*, **35** (11), 2001.

[74] Sekine, Y.: Oxidative decomposition of formaldehyde by metal oxides at room temperature. *Atmospheric Environment*, **36** (35), 2002, pp. 5543–5547.

[75] Ewlad-Ahmed, A.M. et al.: Removal of Formaldehyde from Air Using Functionalized Silica Supports. *Environ. Sci. Technol.*, **46** (24), 2012, pp. 13354–13360.

[76] Yamanaka, S. et al.: Production of scallop shell nanoparticles by mechanical grinding as a formaldehyde adsorbent. *J Nanopart Res*, **15** (4), 2013, p. 1573.

[77] Kim, H.-J. et al.: Efficient test method for evaluating gas removal performance of room air cleaners using FTIR measurement and CADR calculation. *Building and Environment*, **47** (C), 2012, pp. 385–393.

[78] Strommen, M., Gesser, H.D.: The trapping of indoor air contaminants. *Central European Journal of Chemistry*, **9** (3), 2011, pp. 404–409.

[79] Chin, P. et al.: Formaldehyde removal from air via a rotating adsorbent combined with a photocatalyst reactor: Kinetic modeling. *Journal of Catalysis*, **237** (1), 2006, pp. 29–37.

[80] Ao, C.H., Lee, S.C.: Indoor air purification by photocatalyst TiO 2 immobilized on an activated carbon filter installed in an air cleaner. *Chemical Engineering Science*, **60** (1), 2005, pp. 103–109.

[81] Shiraishi, F. et al.: A rapid treatment of formaldehyde in a highly tight room using a photocatalytic reactor combined with a continuous adsorption and desorption apparatus. *Chemical Engineering Science*, **58** (3), 2003, pp. 929–934.

[82] Sekine, Y. et al.: Simultaneous removal of formaldehyde and benzene in indoor air with a combination of sorption-and decomposition-type air filters. *Environmental technology*, **32** (16), 2011, pp. 1983–1989.

[83] Andersen, I.B. et al.: Indoor air pollution due to chipboard used as a construction material. *Atmospheric Environment*, **9** (12), 1975, pp. 1121–1127.

[84] Pickrell, J.A. et al.: Formaldehyde release from selected consumer products: influence of chamber loading, multiple products, relative humidity, and temperature. *Environ. Sci. Technol.*, **18** (9), 1984, pp. 682–686.

[85] Myers, G.E.: The effects of temperature and humidity on formaldehyde emission from UF-bonded boards: a literature critique. *Forest Products Journal*, **35** (9), 1985, pp. 20–31.

[86] Frihart, C.R. et al.: Formaldehyde Emissions from Urea-Formaldehyde-and No-Added-Formaldehyde-Bonded Particleboard as Influenced by Temperature and Relative Humidity. *Forest Products Journal*, **62**, 2012.

[87] Xu, J. et al.: Determination of partition and diffusion coefficients of formaldehyde in selected building materials and impact of relative humidity. *Journal of the Air & Waste Management Association*, **62** (6), 2012, pp. 671–679.

[88] van Netten, C. et al.: Temperature and humidity dependence of formaldehyde release from selected building materials. *Bulletin of Environmental Contamination and Toxicology*, **42** (4), 1989, pp. 558–565.

[89] Hawthorne, A.R., Matthews, T.G.: Models for estimating organic emissions from building materials: Formaldehyde example. *Atmospheric Environment (1967)*, **21** (2), 1987, pp. 419–424.

[90] Parthasarathy, S. et al.: Effect of Temperature and Humidity on Formaldehyde Emissions in Temporary Housing Units. *Journal of the Air & Waste Management Association*, **61** (6), 2011, pp. 689–695.

[91] Turner, W.J.N. et al.: A combined energy and IAQ assessment of the potential value of commissioning residential mechanical ventilation systems. *Building and Environment*, **60** (C), 2013, pp. 194–201.

[92] U.S. Environmental Protection Agency: *Energy Cost and IAQ Performance of Ventilation Systems and Controls*. EPA-4-2-S-01-001. U.S. Environmental Protection Agency, 2000.

[93] Apte, M.G. et al.: *Balancing energy conservation and occupant needs in ventilation rate standards for Big Box stores in California: predicted indoor air*

quality and energy consumption using a matrix of ventilation scenarios. LBNL-5551E. Lawrence Berkeley National Laboratory, 2013.

[94] Ng, L.C. et al.: *The IAQ and Energy Impacts of Reducing Formaldehyde Emissions in Commercial Buildings*. ASHRAE IAQ 2013 Proceedings: Environmental Health in Low Energy Buildings. 2013, pp. 1–8.

[95] Siegel, J.A. et al.: *Ventilation and indoor air quality in retail stores*. 1596. ASHRAE, 2013.

[96] Riley, W.J. et al.: Indoor Particulate Matter of Outdoor Origin: Importance of Size-Dependent Removal Mechanisms. *Environ. Sci. Technol.*, **36** (2), 2002, pp. 200–207.

[97] Won, D. et al.: Sorptive interactions between VOCs and indoor materials. *Indoor Air*, **11** (4), 2001, pp. 246–256.

[98] Plaisance, H. et al.: Field investigation on the removal of formaldehyde in indoor air. *Building and Environment*, **70** (C), 2013, pp. 277–283.

[99] Weschler, C.J.: Ozone in indoor environments: concentration and chemistry. *Indoor Air*, **10** (4), 2000, pp. 269–288.

[100] Weschler, C.J., Shields, H.C.: Production of the hydroxyl radical in indoor air. *Environ. Sci. Technol.*, **30** (11), 1996, pp. 3250–3258.

[101] Berge, A. et al.: Formaldehyde release from particleboard—evaluation of a mathematical model. *Holz als Roh-und Werkstoff*, **38** (7), 1980, pp. 251–255.

[102] U.S. Environmental Protection Agency: *Chapter 19—Building Characteristics*. In: *Exposure Factors Handbook*. U.S. Environmental Protection Agency, 2011, pp. 1–58.

[103] *Energy Standard for Buildings Except Low-Rise Residential Buildings*. 90.1. ASHRAE, 2013.

[104] Zaatari, M. et al.: The relationship between filter pressure drop, indoor air quality, and energy consumption in rooftop HVAC units. *Building and Environment*, **73** (C), 2014, pp. 151–161.

[105] Weisel, C.P. et al.: Relationships of Indoor, Outdoor, and Personal Air (RIOPA). Part I. Collection methods and descriptive analyses. *Research Report (Health Effects Institute)*, (130 Pt 1), 2005, pp. 1–107– discussion 109–27.

[106] Bennett, D.H. et al.: Ventilation, temperature, and HVAC characteristics in small and medium commercial buildings in California. *Indoor Air*, **22** (4), 2012, pp. 309–320.

[107] Godish, T., Rouch, J.: An Assessment of the Berge Equation Applied to Formaldehyde Measurements under Controlled Conditions of Temperature and

Humidity in a Mobile Home. *Journal of the Air Pollution Control Association*, **35** (11), 1985, pp. 1186–1187.

[108] NREL: National solar radiation database in 1991-2005, Typical meteorological year 3 - *Austin, TX; Phoenix, AZ; Seattle, WA.*, 2014.

[109] Hodgson, A.T. et al.: Sources of formaldehyde, other aldehydes and terpenes in a new manufactured house. *Indoor Air*, **12** (4), 2002, pp. 235–242.

[110] Steinemann, A.C.: Fragranced consumer products and undisclosed ingredients. *Environmental Impact Assessment Review*, **29** (1), 2009, pp. 32–38.

[111] Sack, T.M. et al.: A survey of household products for volatile organic compounds. *Atmospheric Environment. Part A. General Topics*, **26** (6), 1992, pp. 1063–1070.

[112] Missia, D.A. et al.: Indoor exposure from building materials: A field study. *Atmospheric Environment*, **44** (35), 2010, pp. 4388–4395.

[113] Hodgson, A.T. et al.: Emissions of Volatile Organic Compounds from New Carpets Measured in a Large-Scale Environmental Chamber. *Air & Waste*, **43** (3), 1993, pp. 316–324.

[114] Vitrac, O., Leblanc, J.-C.: Consumer exposure to substances in plastic packaging. I. Assessment of the contribution of styrene from yogurt pots. *Food Additives and Contaminants*, **24** (2), 2007, pp. 194–215.

[115] Singer, B.C. et al.: Cleaning products and air fresheners: emissions and resulting concentrations of glycol ethers and terpenoids. *Indoor Air*, **16** (3), 2006, pp. 179–191.

[116] Roffael, E.: Volatile organic compounds and formaldehyde in nature, wood and wood based panels. *Eur. J. Wood Prod.*, **64** (2), 2006, pp. 144–149.

[117] Miksch, R.R. et al.: Trace organic chemical contaminants in office spaces. *Environment International*, **8** (1-6), 1982, pp. 129–137.

[118] Tichenor, B.A.: Measurement of organic compound emission using small test chambers. *Environment International*, **15** (389-396), 1989.

[119] Wooley, J. et al.: Release of Ethanol to the Atmosphere During Use of Consumer Cleaning Products. *Journal of the Air & Waste Management Association*, **40** (8), 1990, pp. 1114–1120.

[120] Passant, N.R. et al.: Emissions of volatile organic compounds (VOCs) from the food and drink industries of the European community. *Atmospheric Environment. Part A. General Topics*, **27** (16), 1993, pp. 2555–2566.

[121] Pesis, E. et al.: Production of acetaldehyde and ethanol during maturation and modified atmosphere storage of litchi fruit. *Postharvest biology and technology*, **26** (2), 2002, pp. 157–165.

[122] Kwon, K.-D. et al.: Volatile pollutants emitted from selected liquid household products. *Environ Sci Pollut Res*, **15** (6), 2008, pp. 521–526.

[123] Apte, M.G., Erdmann, C.A.: *Associations of indoor carbon dioxide concentrations, VOCs, environmental susceptibilities with mucous membrane and lower respiratory sick building syndrome symptoms in the BASE study: Analyses of the 100 building dataset*. 51570. LBNL, 2002.

[124] Harper, M.: Sorbent trapping of volatile organic compounds from air. *Journal of Chromatography A*, **885** (1), 2000, pp. 129–151.

[125] Brymer, D.A. et al.: Viability of using SUMMA polished canisters for the collection and storage of parts per billion by volume level volatile organics. *Environ. Sci. Technol.*, **30** (1), 1996, pp. 188–195.

[126] Dutton, S.M. et al.: Evaluation of the Indoor Air Quality Procedure for Use in Retail Buildings. 2013.

[127] Hun, D.E. et al.: Formaldehyde in residences: long-term indoor concentrations and influencing factors. *Indoor Air*, **20** (3), 2010, pp. 196–203.

[128] Noris, F. et al.: Indoor environmental quality benefits of apartment energy retrofits. *Building and Environment*, **68** (c), 2013, pp. 170–178.

[129] Maruo, Y.Y. et al.: Formaldehyde measurements in residential indoor air using a developed sensor element in the Kanto area of Japan. *Indoor Air*, **20** (6), 2010, pp. 486–493.

[130] Chua, K.J. et al.: Achieving better energy-efficient air conditioning: A review of technologies and strategies. *Applied Energy*, **104** (C), 2013, pp. 87–104.

[131] Genest, F., Minea, V.: High-Performance Retail Store with Integrated HVAC Systems. *ASHRAE Transactions*, **112** (2), 2006.

[132] Witte, M.J., Henninger, R.H.: Evaluating the Ability of Unitary Equipment to Maintain Adequate Space Humidity Levels. *ASHRAE Transactions*, **116** (1), 2010.

[133] Gil-Lopez, T. et al.: Experimental analysis of energy savings and hygrothermal conditions improvement by means of air curtains in stores with intensive pedestrian traffic. *Energy & Buildings*, **67**, 2013, pp. 608–615.

[134] Rackes, A., Waring, M.S.: Using multiobjective optimizations to discover dynamic building ventilation strategies that can improve indoor air quality and reduce energy use. *Energy & Buildings*, **75**, 2014, pp. 272–280.

[135] Sherman, M.H., Hodgson, A.T.: Formaldehyde as a basis for residential ventilation rates. *Indoor Air*, **14** (1), 2004, pp. 2–8.

[136] *Airborne Toxic Control Measure To Reduce Formaldehyde Emissions From Composite Wood Products*. California Code of Regulations, 2008, pp. 1–59.

[137] Rackes, A., Waring, M.S.: Modeling impacts of dynamic ventilation strategies on indoor air quality of offices in six US cities. *Building and Environment*, **60** (C), 2013, pp. 243–253.

[138] Allouch, A. et al.: Transportable, fast and high sensitive near real-time analyzers: Formaldehyde detection. *Sensors & Actuators: B. Chemical*, **181**, 2013, pp. 551–558.

[139] Maruo, Y.Y., Nakamura, J.: Portable formaldehyde monitoring device using porous glass sensor and its applications in indoor air quality studies. *Analytica Chimica Acta*, **702** (2), 2011, pp. 247–253.

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