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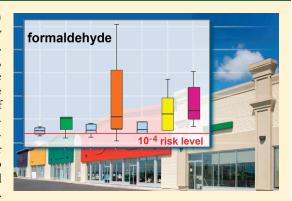
# Volatile Organic Compounds in Small- and Medium-Sized Commercial Buildings in California

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Supporting Information

ABSTRACT: While small- and medium-sized commercial buildings (SMCBs) make up 96% of the commercial buildings in the U.S., serving a large variety of uses, little information is available on indoor air quality (IAQ) in SMCBs. This study investigated 37 SMCBs distributed across different sizes, ages, uses, and regions of California. We report indoor concentrations and whole building emission rates of a suite of 30 VOCs and aldehydes in these buildings. There was a considerable range in the concentrations for each of the contaminants, especially for formaldehyde, acetaldehyde, decamethyl-cyclopentasiloxane, *d*-limonene, 2-butoxyethanol, toluene, 2,2,4-trimethyl-pentanediol diisobutyrate, and diethylphthalate. The cause of higher concentrations in some building categories generally corresponded to expected sources, for example, chloroform was higher in restaurants and grocery stores, and formaldehyde was higher in retail stores and offices.



Factor analysis suggests sources in SMCBs include automobile/traffic, cleaning products, occupant sources, wood products/coating, and plasticizers. The comparison to health guidelines showed that formaldehyde concentrations were above the chronic RELs required by the OEHHA ( $9 \mu g/m^3$ ) in 86% of the buildings. Data collected in this study begins to fill the knowledge gap for IAQ in SMCBs and helps us understand the indoor sources of VOCs to further improve indoor air quality in SMCBs.

#### ■ INTRODUCTION

Indoor air quality (IAQ) in commercial buildings is a public health concern and has been associated with Sick Building Syndrome symptoms and mucous membrane and lower respiratory irritation. Volatile organic compounds (VOCs) are a common group of indoor air pollutants, with some being classified as known or probable human carcinogens and some having neurologic, developmental, or reproductive effects at high levels. They are commonly found in building materials and furnishings, such as cabinetry and carpeting, and numerous consumer products, e.g., paints, adhesives, and air refreshers. <sup>2,3</sup>

The U.S. population spends approximately 87% of their time indoors, and of that, 21% is in nonresidential environments, primarily in commercial buildings. Small- and medium-sized commercial buildings (SMCBs), as defined here, are any low-rise building (less than four stories) with roof-top heating, ventilation, and air-conditioning (HVAC) units. These buildings are commonly found in small office complexes, schools, and strip malls, serving as places of work and for commercial, educational, and recreational activities. SMCBs make up 96% of the commercial buildings in the U.S. While there have been a number of studies on indoor VOCs in large commercial buildings, rery little information is available on SMCBs which have more diverse uses.

VOC levels in SMCBs are subject to the impact of chemical emissions from building materials and activities that take place in the buildings, building ventilation rates, and outdoor air pollution. SMCBs, such as dry cleaners, restaurants, and printing establishments, have substantial, often unique, indoor VOC sources. Office spaces can have localized sources, including copiers, intake and recirculation of polluted outside air, and introduction of pollutants brought into the building by occupants. Retail stores contain a wide range of new products that outgas a variety of VOCs, leading to higher levels indoors of these compounds. Thus, to the extent that the quality of the commercial indoor environment affects people's health and well-being, the time spent in SMCBs has a potential to significantly impact public

However, due to the largely disaggregated, heterogeneous nature of commercial buildings, information on indoor pollutant levels in SMCBs is very limited. To fill this knowledge gap, we collected information on the operation and maintenance of HVAC and air filtration systems, indoor pollutant levels in SMCBs, and the relation between the two. This paper focuses

Received: June 22, 2011
Accepted: September 2, 2011
Revised: August 30, 2011
Published: September 02, 2011

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on indoor levels of VOCs. Potential sources, differences in concentrations between types of SMCBs, and comparison with relevant health guidelines and existing literature are also explored.

#### ■ METHODS

Buildings Sampled. Thirty-seven unique buildings were included in the study, with three buildings sampled on two occasions, resulting in 40 sampling days. The selection of buildings was semi-randomized, providing a minimum coverage of the vast variety of SMCBs across space, age, size, and building use category. Buildings were almost evenly distributed across each of five regions of California: north-coastal, north-inland, southcoastal, south-inland, and central-inland. A total of 25 buildings built before 2000 and 12 buildings built after 2000 were included. We classified buildings into three size categories: small (1000-12 000 ft<sup>2</sup>), medium (12 000-25 000 ft<sup>2</sup>), and medium/large  $(25\,000-50\,000\,\text{ft}^2)$ . Thirty buildings were one-story, and seven were two stories. Twenty-four small buildings (two sampled twice), seven medium buildings (one sampled twice), and six medium/large buildings were included. The buildings varied in use, including seven retail establishments, five restaurants, eight offices, two each of gas station convenience stores, hair salons, healthcare facilities, grocery stores, dental offices, and fitness gyms, along with three miscellaneous buildings. Details on the building distribution can be found in the Supporting Information (SI).

Sample Collection and Analysis. For each building in the study, the air exchange rate and the concentrations of a suite of air pollutants including hydrocarbons, aldehydes, and chlorinated compounds were determined. These compounds, listed with their abbreviations in Table 1, were selected either because they are of health concern or were anticipated to have higher concentrations in commercial buildings. Compounds were measured at one or two indoor locations, depending on building size, and at one outdoor location for 4 h during normal working hours while the buildings were occupied. Samplers were placed at about 1 m above the ground, located as centrally as possible given logistic constraints. A total of 66 indoor VOC samples and 62 aldehyde samples were collected from 40 sampling days.

The majority of the compounds were collected onto multibed sorbent tubes with a primary bed of Tenax-TA sorbent backed with a section of Carbosieve III and analyzed by EPA method TO-17, using thermodesorption-GC/MS (Series 6890Plus/ 5973; Agilent Technologies). 14 Formaldehyde, acetaldehyde, and acetone were collected using a commercially available cartridge packed with acidified 2,4-dinitrophenylhydrazine (DNPH) coated silica gel and analyzed by EPA method TO-11A, using highperformance liquid chromatography (HPLC) (1200 Series; Agilent Technologies). 15 All samples were analyzed at Lawrence Berkeley National Laboratory. Ozone scrubbers were used on all DNPH cartridges to prevent aldehyde loss due to reaction with ozone on the absorbent. The VOC sample flow rate was  $1.25\,L/h$ for the initial five buildings, and for the remainder of the project, a flow rate of 1 L/h indoors and 2.5 L/h outdoors was used. Sampling flow rate for carbonyl was 0.5 L/min. More details on chemical analysis can be found in the SI. The building ventilation rate during operating hours was measured using a tracer (sulfur hexafluoride) decay method and was used in calculating whole building emission rate. The measurement method for ventilation rates can be found in the SI.

The quality assurance measures are also detailed in the SI. A total of 30% of samples were processed as travel blanks that were

carried to the field and returned unopened, and 24% were processed as field blanks that were carried to the field, installed on the sample pump, and then removed without pulling air through the sample and returned to the lab. Only the low molecular weight carbonyls had background concentrations near or slightly above the MDL. Duplicate samples were collected in parallel to the primary samples for 93.5% of the sample locations, resulting in a total of 1972 individual compound duplicate measurements where the compound concentrations were greater than the MDL. The difference between sample pairs was less than 10% for 65% of the measurements, with 92% of the measurements having a difference of less than 50%. Collection efficiency was determined for VOCs under field conditions using sampling tubes mounted in series, and the results ranged from 85% to 100%.

Concentrations below MDL were replaced with 1/2 MDL, while for samples between the MDL and the analytical limit of quantification (LOQ), determined as 10 times the standard deviation of low-level spikes, were reported as the value determined in the laboratory. Concentrations that were above the calibration range of the analytical method were replaced with a value slightly higher than the maximum calibration point, an underestimate of the actual value.

Data Analysis. Summary statistics were calculated for all the VOCs, with the average indoor concentration calculated and used in analyses for buildings where multiple sites were sampled collected. On the basis of potential expected sources, we classified the buildings into a specified building use category from the following list: nonmedical offices, grocery/restaurant, retail, dentist/health care, gas/auto services, hair salon/gym (both had significant use of personal care products), and miscellaneous. Three buildings fell into the miscellaneous category, including a public assembly building, a building used for religious purposes, and a daycare center. As VOC concentrations were log-normally distributed, the analysis of variance (ANOVA) was conducted on log-transformed concentrations to determine which compounds had significant concentration differences between building use categories.

Factor analysis was conducted on log-transformed indoor VOC concentrations to identify sources. Pearson correlation coefficients were first calculated to identify correlated compounds. Concentrations of m/p-xylene were highly correlated with ethylbenzene (R = 0.97) and o-xylene (R = 0.96) concentrations; thus, m/p-xylene was excluded from the analysis. Methylene chloride was also excluded due to a number of missing samples. Then, a trial analysis was conducted with 62 observations and 28 compounds, with multiple indoor samples considered as different observations. Though not statistically valid, seven factors with eigenvalues greater than 1 were extracted. To confirm the findings in the first trial, a second attempt only including the compounds with loadings >0.5 on the first five factors extracted was conducted. Since the initial factor pattern matrix was not unique, an oblique rotation after an orthogonal VARIMAX rotation was performed to achieve more interpretable factor loadings. Factor loadings greater than 0.50 are considered to be significant. Note that, with the limited number of observations from the sample of 37 buildings, the factor analysis does not quite reach statistical validity, but is helpful in identifying major source

Whole building emission rates,  $S(\mu g/h/m^2)$ , the apparent source strength for the combined mix of individual indoor

Table 1. Distribution of Indoor VOC Concentrations and Whole Building Emission Rates in SMCBs (N = 40, including three repeat measurements)<sup>a</sup>

|                                 | percent > MDL <sup>c</sup> (%) | indoor conce   | ntration (µg | $(m^3)$           |       | whole building emission rate $(\mu g/h/m^2)$ |       |      |  |  |
|---------------------------------|--------------------------------|----------------|--------------|-------------------|-------|--|-------|------|--|--|
| $compound^b$                    |                                | geometric mean | range        |                   | $N^d$ | geometric mean                               | range |      |  |  |
| benzene                         | 100                            | 0.69           | 0.29         | 2.11              | 29    | 1.00   | 0.01  | 4.49 |  |  |
| toluene                         | 100                            | 4.47           | 0.44         | 200 <sup>f</sup>  | 35    | 7.90   | 0.10  | 301  |  |  |
| ethylbenzene                    | 100                            | 0.62           | 0.08         | 34.7              | 32    | 1.06   | 0.09  | 45.2 |  |  |
| m/p-xylene                      | 100                            | 1.63           | 0.22         | 87.7 <sup>f</sup> | 30    | 2.71   | 0.22  | 114  |  |  |
| o-xylene                        | 100                            | 0.69           | 0.13         | 10.7              | 32    | 1.28   | 0.03  | 13.7 |  |  |
| styrene                         | 100                            | 0.37           | 0.03         | 3.6               | 40    | 0.71   | 0.05  | 13.9 |  |  |
| formaldehyde                    | 100                            | 16.4           | 1.41         | 102               | 39    | 25.4   | 2.23  | 393  |  |  |
| acetaldehyde                    | 100                            | 8.94           | 0.74         | 72.5              | 37    | 14.5   | 1.00  | 443  |  |  |
| acetone                         | 100                            | 28.3           | 1.10         | 1380              | 38    | 64.8   | 7.82  | 3405 |  |  |
| hexanal                         | 100                            | 3.45           | 0.53         | 27.5              | 40    | 6.18   | 1.56  | 277  |  |  |
| benzaldehyde                    | 98                             | 2.54           | 1.11         | 5.28              | 24    | 3.14   | 0.35  | 19.8 |  |  |
| octanal                         | 95                             | 1.46           | nd           | 16.1              | 39    | 2.65   | 0.61  | 219  |  |  |
| nonanal                         | 97                             | 4.25           | nd           | 20.9              | 38    | 7.80   | 1.44  | 557  |  |  |
| decanal                         | 92                             | 3.33           | nd           | 104               | 35    | 12.3   | 1.92  | 271  |  |  |
| methylene chloride <sup>e</sup> | 100                            | 0.83           | 0.25         | 17.1              | 30    | 1.39   | 0.08  | 44.1 |  |  |
| carbon tetrachloride            | 98                             | 0.46           | 0.05         | 2.87              | 23    | 0.72   | 0.03  | 8.72 |  |  |
| chloroform                      | 100                            | 0.3            | 0.05         | 2.62              | 40    | 0.73   | 0.02  | 36.2 |  |  |
| trichloroethylene               | 70                             | 0.02           | nd           | 1.93              | 26    | 0.07   | 0.01  | 11.0 |  |  |
| tetrachloroethylene             | 94                             | 0.18           | nd           | 118               | 32    | 0.30   | 0.03  | 178  |  |  |
| 1,4-dichlorobenzene             | 88                             | 0.05           | nd           | 2.16              | 35    | 0.14   | 0.02  | 4.39 |  |  |
| $\alpha$ -pinene                | 100                            | 1.67           | 0.26         | 33.8              | 40    | 2.85   | 0.47  | 122  |  |  |
| d-limonene                      | 100                            | 8.18           | 0.28         | $1100^{f}$        | 40    | 21.7   | 0.68  | 2313 |  |  |
| $\alpha$ -terpineol             | 86                             | 0.11           | nd           | 15.6              | 36    | 0.52   | 0.02  | 172  |  |  |
| n-hexane                        | 100                            | 1.04           | 0.17         | 180 <sup>f</sup>  | 34    | 1.51   | 0.15  | 534  |  |  |
| naphthalene                     | 100                            | 0.17           | 0.04         | 1.45              | 40    | 0.35   | 0.02  | 4.8  |  |  |
| 2-butoxyethanol                 | 100                            | 4.21           | 0.02         | 356 <sup>f</sup>  | 39    | 8.91   | 0.69  | 1329 |  |  |
| d5-siloxane                     | 100                            | 24.9           | 1.30         | 120 <sup>f</sup>  | 40    | 76.1   | 4.84  | 1636 |  |  |
| phenol                          | 100                            | 1.97           | 0.63         | 17.0              | 32    | 3.23   | 0.02  | 16.5 |  |  |
| TXIB                            | 100                            | 1.09           | 0.16         | 58.6              | 40    | 1.77   | 0.29  | 48   |  |  |
| diethylphthalate                | 100                            | 0.39           | 0.09         | 2.42              | 40    | 0.66   | 0.10  | 11.6 |  |  |

<sup>&</sup>lt;sup>a</sup> Note that one sample collected in a retail store in a room that conducted screen printing work had many extremely high concentrations and was excluded from this distribution, as this could be classified as a light industrial source rather than a retail source. The distribution by building use category, including geometric/arithmetic means and standard deviation, median, and max, are presented in Tables S5 and S6 (SI). <sup>b</sup> d5-siloxane = decamethylcyclopentasiloxane; TXIB = 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. <sup>c</sup> Detection percents were calculated based on the original samples, not the average for each building. A building could have detectable concentration at one sampling site but not at the other one. <sup>d</sup> The distribution of whole building emission rates were only calculated for the buildings with indoor/outdoor differences greater than zero, namely those having potential source(s). <sup>c</sup> Measurements of methylene chloride for six buildings were excluded due to suspected blank contamination. <sup>f</sup> Maximum values were actually above quantitative range and replaced by a value slightly higher than the maximum value we observed. nd, not detectable.

sources, were calculated for each building assuming a steadystate, well-mixed box model, incorporating outdoor concentrations, building ventilation rates, and building volumes with the following steady-state mass balance equation:

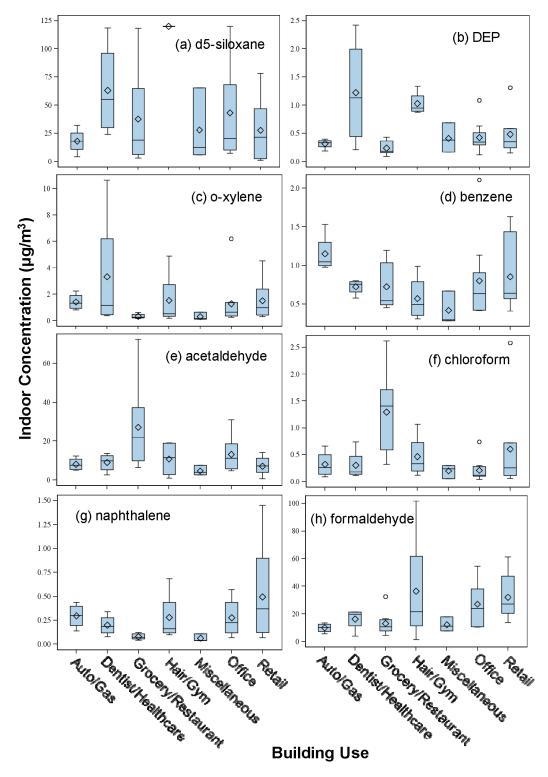
$$S = \frac{Q(C_{\rm i} - C_{\rm o})}{A}$$

where Q is the total ventilation rate of the building as measured by the tracer decay method (m³ h<sup>-1</sup>),  $C_i$  is the measured concentration in the building for the specified compound ( $\mu g/m^3$ ),  $C_o$  is the measured concentration outside of the building for the specified compound ( $\mu g/m^3$ ), and A is the floor area of the building space (m²). This model assumes that penetration of VOCs from the outdoors is unity 16 and that losses by reaction are less

than losses by air exchange, since the time scale of decay is at most  $1\times 10^{-3}/h$  for VOCs indoors compared with an air exchange rate of 0.1/h-1/h. All statistical analyses were conducted using SAS 9.2 for Windows (SAS Institute Inc., Cary, NC).

#### **■** RESULTS

Indoor Concentrations and the Variability by Building Use Category. The geometric means and ranges of measured indoor VOC concentrations across all buildings are presented in Table 1 (see Table S5 of the SI for the distributions by building use). The majority of the compounds were detected in all of the buildings, with the highest geometric mean levels observed for acetone, decamethylcyclopentasiloxane (d5-siloxane), acetaldehyde, *d*-limonene, and toluene.



**Figure 1.** Comparison of indoor concentrations for selected VOCs by building use category: (a) d5-siloxane, (b) DEP, (c) o-xylene, (d) benzene, (e) acetaldehyde, (f) chloroform, (g) naphthalene, and (h) formaldehyde. Note that the scale for each individual VOC is different.

We compared indoor VOC concentrations by building use, and statistically significant differences (p < 0.05) were observed for ethylbenzene, o-xylene, chloroform, tetrachloroethylene (PCE), naphthalene, phenol, 2,2,4-trimethylpentanediol diisobutyrate (TXIB), and diethyl phthalate (DEP). Concentrations of acetaldehyde, m/p-xylene, d5-siloxane, octanal, and benzene were

marginally different (p = 0.05-0.09) by building use category. Indoor concentration distributions of selected compounds by building use are presented in Figure 1.

Phenol, DEP, and d5-siloxane are used in personal care products, and higher concentrations of these compounds were found in buildings where occupants use personal care products or with higher occupant density. The concentrations of d5-siloxane were significantly higher in hair salons/gyms and dentist/health-care facilities, which might use more products containing d5-siloxane than other buildings. The level of d5-siloxane was also sometimes above the quantitative range in offices and groceries/restaurants, possibly due to high occupant density in the buildings (Figure 1a). Phenol is used in the manufacture of resins and nylon but also used in cosmetics, e.g., sunscreen and hair dyes and as a disinfectant and antiseptic. The concentrations of phenol were significantly higher in offices than other types of buildings. DEP was higher in hair salons/gyms and dentist/healthcare facilities (Figure 1b).

High concentrations of ethylbenzene, m/p-xylene and o-xylene were observed in a medium-sized healthcare building, and it is possible that these chemicals were used as solvents in the laboratory located in this building. Except for the case of the healthcare building, these three compounds had relatively higher concentrations in gas stations/fleet services and retailers (see o-xylene as an example in Figure 1c). Groceries/restaurants and miscellaneous buildings had low levels of these compounds. Concentrations of benzene were also high in gas stations/fleet services (Figure 1d), probably from gasoline evaporation. Concentrations of benzene above 2  $\mu$ g/m³ were observed in a retail store that included a room where screen-printing was conducted and an office where we suspect smoking occurred due to a spike in ultrafine particle concentrations at lunch time while field staff were not present.

Acetaldehyde occurs naturally in some foods such as ripe fruits and is also a byproduct of yeast used in baking. It was significantly higher in groceries/restaurants than other types of buildings, with concentrations up to 72.5  $\mu$ g/m³ (Figure 1e). Acetaldehyde is also a byproduct of combustion, and is emitted from many building materials and consumer products such as adhesives, coatings, lubricants, inks, and nail polish remover. Concentrations of chloroform were also significantly higher in groceries/restaurants (Figure 1f), potentially due to volatilization from tap water used for cleaning and cooking (both grocery stores included on-site cooking facilities).

While PCE was statistically significantly higher in retail stores, the authors do not consider this result generalizable, as two retail stores had extremely high concentrations of PCE, one being in the retail space that conducted on-site screen printing, which may have used PCE, and the second being in a bookstore with a high outdoor concentration measured at the site.

Naphthalene concentrations were high in some retail stores and low in groceries/restaurants and miscellaneous buildings (Figure 1g). Octanal concentrations were also found to be higher in retail stores.

An extremely high concentration of TXIB ( $\sim$ 60  $\mu$ g/m<sup>3</sup>), used as a plasticizer in vinyl flooring, was observed in a fitness gym that had recently replaced the flooring. Retail stores also had higher TXIB concentrations relative to buildings of other uses.

There were other compounds with sources of note that did not reach statistical significance between building use categories. Acetone is used in a variety of medical and cosmetic applications, which corresponds to the high concentrations observed in hair salons/gyms and dentist offices/healthcare buildings. Formaldehyde is emitted from carpet, pressed wood products, and many building materials and consumer products or results from indoor secondary chemical reactions, and higher concentrations were found in offices and retail stores, as well as one high concentration (101.7  $\mu$ g/m³) observed in a hair salon, likely from use of a

particular, unknown product (Figure 1h). High concentrations of *d*-limonene, 2-butoxyethanol, and toluene were also observed, corresponding to sources from cleaning/polishing/waxing agents, paints/adhesives, and solvent-containing materials, respectively.<sup>18</sup>

Whole building emission rates were also estimated, as shown in Table 1 (see Table S6 of the SI for the distributions by building use). Similar to the indoor concentrations, acetone, d5-siloxane, acetaldehyde, d-limonene, toluene, as well as 2-butoxyethanol had high whole building emission rates in SMCBs. The variations of whole building emission rates were similar to the pattern of the variations of indoor concentrations, that is, compounds with significant variation on indoor concentrations also had varied whole building emission rates by building use category. Significant differences (p < 0.05) by building use category were observed for chloroform, PCE, octanal, naphthalene, phenol, and TXIB, and marginal significant differences (p = 0.05 - 0.09) were observed for o-xylene, hexanal, DEP, and benzene.

In addition, a gas station convenience store, an office, and a restaurant were measured in both the summer and winter. Higher summer concentrations were observed for a number of VOCs, including many aldehydes, chlorinated compounds, and esters, for example, formaldehyde, acetone, nonanal, trichloroethylene, and phenol. This was probably due to the higher emission rate of these chemicals as temperature goes up. In addition, photochemical reactions with ozone, which generate aldehydes, are expected to be more intense in the summer. <sup>19</sup> In contrast, *d*-limonene and d5-siloxane had lower concentrations in the summer than in the winter. The reason was unclear, since the measured ventilation rates were higher in winter in these buildings due to comfortable winter temperatures in California, which was supposed to reduce indoor VOC concentrations.

Comparison to Health Guidelines. The indoor concentrations were compared to the reference concentrations (RfC) for chronic inhalation exposure defined in the U.S. EPA Integrated Risk Information System (IRIS; U.S. EPA 2010), the Permissible Exposure Limits (PELs) defined by the Occupational Safety and Health Administration (OSHA; U.S. Department of Labor, 1993), and the reference exposure levels (RELs) suggested by the California Office of Environmental Health Hazard Assessment (OEHHA; California Environmental Protection Agency, 2008), with the values of all guidelines listed in the SI. We note that the measured concentrations are for a 4-h period; however, as the concentrations were measured during a typical business day, they are likely to be somewhat representative of typical concentrations. The majority of the compounds met all three guidelines in all buildings. However, three compounds, formaldehyde, acetaldehyde, and PCE, had concentrations above the guidelines in some buildings. Elevated air concentrations of formaldehyde and acetaldehyde could lead to respiratory irritation and trigger asthma attacks or damage the reparatory tract.<sup>20</sup> PCE is a central nervous system depressant and can cause dermal irritation.<sup>21</sup> Concentrations were above the chronic RELs required by the OEHHA for formaldehyde (9  $\mu$ g/m<sup>3</sup>) in 86% of the buildings. Concentrations of formaldehyde in three buildings, including a retail store, an office, and a hair salon, were above the acute inhalation REL of 55  $\mu$ g/m<sup>3</sup>. In addition, an extremely high concentration of PCE was observed in the retail store with screen printing, with a level that was 3 times higher than the chronic inhalation REL (35  $\mu$ g/m<sup>3</sup>). Additionally, the concentration in a bookstore was 34.8  $\mu$ g/m<sup>3</sup>, which was very near the REL; however, the high indoor concentration was likely due to high outdoor concentrations. More than 50% of the

Table 2. Results of Factor Analysis<sup>a</sup>

| compounds        | 1    | 2    | 3    | 4    | 5    | communality |
|------------------|------|------|------|------|------|-------------|
| benzene          | 0.87 |      |      |      |      | 0.71        |
| toluene          | 0.70 |      |      |      |      | 0.66        |
| ethylbenzene     | 0.65 |      |      |      |      | 0.53        |
| formaldehyde     |      |      |      |      | 0.77 | 0.76        |
| acetaldehyde     |      |      |      |      | 0.73 | 0.56        |
| octanal          |      |      | 0.75 |      |      | 0.58        |
| nonanal          |      |      | 0.81 |      |      | 0.65        |
| decanal          |      |      | 0.61 |      |      | 0.47        |
| d-limonene       | 0.35 | 0.55 |      |      |      | 0.64        |
| lpha-terpineol   |      | 0.69 |      |      |      | 0.70        |
| n-hexane         | 0.78 |      |      |      |      | 0.70        |
| d5-siloxane      |      | 0.78 |      |      |      | 0.63        |
| TXIB             |      |      |      | 0.74 |      | 0.60        |
| diethylphthalate |      |      |      | 0.69 |      | 0.66        |

<sup>&</sup>lt;sup>a</sup> The analysis includes 62 observations and 14 compounds. Factor loadings shown are after an oblique rotation and an orthogonal VARIMAX rotation. Factor loadings greater than 0.30 in absolute value are shown and loadings greater than 0.50 are considered to be significant.

buildings had acetaldehyde concentrations above the US EPA RfC for chronic inhalation exposure (9  $\mu$ g/m<sup>3</sup>).

A number of the compounds measured are classified as carcinogens. Levels of benzene, carbon tetrachloride, and chloroform in the majority of buildings had levels between the EPA inhalation risk level concentrations of  $10^{-6}$  and  $10^{-5}$ , while acetaldehyde levels were primarily between the  $10^{-5}$  and  $10^{-4}$  levels, and 88% of the buildings had formaldehyde concentrations above the  $10^{-4}$  level (specifics listed in Table S10 of the SI).

**Source Apportionment.** The final factor analysis was conducted with 62 observations and 14 compounds (as shown in Table 2), and five factors were obtained, explaining 63% of the variance in the indoor concentrations of the VOCs in the analysis. Factor 1 represents outdoor sources, with high loadings of benzene, toluene, ethylbenzene and n-hexane, primarily emitted from automobile sources. Factor 2, with high loadings of d-limonene,  $\alpha$ -terpineol, and d5-siloxane, are possibly related to cleaning products. Factor 3 represents higher molecular weight aldehydes, while factor 5 represents lower molecular weight aldehydes. Factor 4 had high loadings of TXIB and DEP, probably related to plasticizer sources. Since it was suspected that the plasticizer factor was driven by a gym with recent floor renovation, we repeated the analysis without the gym, and obtained the same factor pattern.

We acknowledge the limitations of this analysis due to the small number of observations and multiple observations from the same buildings, which may not allow us to build an unbiased correlation matrix. The analysis may not be statistically valid, though interpretable results were obtained.

Formaldehyde and Potential Sources. One hypothesis for the high formaldehyde concentrations is that the building ventilation rates might not be sufficient based on required standards. To test the hypothesis, we calculated the hypothetical indoor formaldehyde concentrations based on the actual outdoor concentrations and actual whole building emission rate, combined with the air exchange rate based on the required California Title 24 ventilation value based on building area. The actual

whole building emission rate was calculated from the measured indoor and outdoor concentrations combined with the actual air exchange rate. However, increasing the ventilation to the required rate in all buildings was not sufficient to reduce formaldehyde concentration to below the OEHHA standard in 76% of the buildings, indicating the need for source reduction of formaldehyde from building materials and consumer products (details on Title 24, the analysis, and results are in the SI).

Two common indoor sources of formaldehyde in commercial buildings are composite/compressed wood furniture and carpet, either by direct emissions or through secondary reactions from compounds emitted directly from the carpet or other compounds absorbed onto carpets. Comparisons suggest that indoor formaldehyde concentrations were significantly higher with the presence of carpet (Table 3). An association with new carpet or new wood furniture was not found, potentially due to the small sample size. An association with wood furniture was not found, potentially because wood furniture was present in all buildings and we were unable to obtain specific information on composite/compressed versus solid wood furniture, as this is difficult to identify. The comparison excluded an extremely high concentration observed in a hair salon, which was likely from products used in the salon.

Since the presence of carpet shows a significant impact on indoor formaldehyde concentration, we further examined the interaction between carpeting and building use category using a regression model with log-transformed formaldehyde concentrations as the dependent variable. Indoor formaldehyde concentrations were significantly different (p = 0.04) between different types of buildings (we note that for these analyses, one hair salon with a high concentration, likely related to product use, was excluded). By including "presence of any carpet" in the regression model, the carpet variable is significant (p = 0.04), while the difference by building use category becomes marginally significant (p = 0.08), indicating that the presence of carpet more than building use category plays the major role in determining indoor formaldehyde concentration. Evaluating "primary flooring being carpet" resulted in both building use category (p = 0.02) and carpet (p = 0.01) as significant factors in influencing indoor formaldehyde concentrations.

## **■** DISCUSSION

This study reports VOC levels in a variety of SMCBs, distributed across different sizes, ages, uses, and regions of California. Data collected in this study address the knowledge gap for air quality in SMCBs and thus help us understand the indoor sources of VOCs to facilitate further improvements to indoor air quality.

The comparison to health guidelines highlights concern on the indoor level of formaldehyde. Elevated air concentrations can lead to eye, throat, and respiratory irritation, as well as cancer. At high concentrations, formaldehyde may trigger asthma attacks. Our analysis indicated that increasing ventilation rates could not fully resolve indoor formaldehyde pollution. To address this, it is recommended to reduce formaldehyde emission rates from building materials, furniture, and other products.

There are only a limited number of studies on commercial buildings available in the U.S. The Building Assessment Survey and Evaluation (BASE) study measured concentrations of a number of VOCs in 100 office buildings nationwide in the 1990s, including primarily large buildings.<sup>23</sup> The geometric

Table 3. Impact of Presence of Carpet and Wood Furniture on Indoor Formaldehyde Concentration ( $\mu g/m^3$ )

| category  |   | N  | mean | STD  | 25th % | median | 75th % | 95th % | comparison <sup>a</sup> |
|---|---|----|------|------|--------|--------|--------|--------|-------------------------|
| any carpet present  | Y | 26 | 23.3 | 13.0 | 13.9   | 21.4   | 27.2   | 51.2   | p = 0.007               |
|   | N | 10 | 14.2 | 17.3 | 5.73   | 9.79   | 11.6   | 61.2   |                         |
| primary flooring is carpet  | Y | 22 | 24.5 | 13.7 | 16.5   | 22     | 32.5   | 51.2   | p = 0.01                |
|   | N | 15 | 14.8 | 14.2 | 5.99   | 11.4   | 20.5   | 61.2   |                         |
| new carpet is primary floor covering  | Y | 5  | 16.3 | 9.69 | 8.91   | 17.9   | 25.2   | 25.5   | p = 0.60                |
|   | N | 33 | 20.9 | 15.0 | 10.5   | 18.6   | 22.8   | 54.4   |                         |
| new wood furniture present  | Y | 6  | 20.0 | 11.8 | 11.4   | 20.6   | 25.2   | 38.1   | p = 0.96                |
|   | N | 30 | 20.9 | 15.4 | 10.1   | 18.3   | 25.5   | 54.4   |                         |
| <sup>a</sup> Comparison is based on log transformed indoor concentration of formaldehyde, using analysis of variance. |   |    |      |      |        |        |        |        |                         |

Table 4. Comparison of Indoor VOC Concentrations ( $\mu g/m^3$ ) with Other Studies

|                   | 10 small/medium offices |             | 12 California office blo | 100 BASE bld | gs (EHE <sup>23</sup> ) | A call center office bldg (Hodgson et al. <sup>10</sup> ) |                |             |
|-------------------|-------------------------|-------------|--------------------------|--------------|-------------------------|---|----------------|-------------|
| compound          | geometric mean          | range       | geometric mean           | range        | geometric mean          | range   | geometric mean | range       |
| benzene           | 0.70                    | 0.42-2.11   | 0.98                     | <0.1-2.7     | 3.45                    | nd-17.3   |                |             |
| toluene           | 4.84                    | 1.72-113    | 2.60                     | 0.58 - 17    | 9.37                    | nd-365  | 4.63           | 2.83-10.9   |
| ethylbenzene      | 0.69                    | 0.23-3.97   | 0.50                     | 0.27 - 0.98  | 1.66                    | nd-29.6   |                |             |
| m/p-xylene        | 1.67                    | 0.49-14.0   | 2.12                     | 0.93 - 4.6   | 5.66                    | nd-96.4   | 2.17           | 1.35-4.86   |
| o-xylene          | 0.77                    | 0.27-6.20   | 0.66                     | 0.30 - 1.4   | 2.18                    | nd-38.4   |                |             |
| styrene           | 0.51                    | 0.12 - 3.60 | 0.40                     | < 0.1 - 0.95 | 0.93                    | nd-8.51   |                |             |
| formaldehyde      | 23.0                    | 10.5-54.4   |                          |              | 15.0                    | N/A   | 14.6           | 6.63 - 30.7 |
| acetaldehyde      | 11.0                    | 4.73-30.9   |                          |              | 7.00                    | N/A   | 5.40           | 2.52 - 12.8 |
| acetone           | 27.3                    | 8.68-85.1   |                          |              | 32.5                    | 4.03 - 223  | 33.3           | 9.50-97.4   |
| hexanal           | 3.19                    | 0.95-11.6   | 0.46                     | < 0.2 - 1.9  | 4.20                    | nd-19.5   | 4.71           | 2.50-9.01   |
| benzaldehyde      | 3.08                    | 1.46 - 5.28 | 0.47                     | < 0.1 - 1.5  |                         |   |                |             |
| nonanal           | 4.20                    | 1.59 - 7.05 |                          |              | 3.71                    | 1.16 - 23.6   |                |             |
| methylene chlorid | e 0.89                  | 0.25-4.02   |                          |              | 1.58                    | nd-360  |                |             |
| carbon tet.       | 0.58                    | 0.31 - 1.17 |                          |              | 1.00                    | nd-3.86   |                |             |
| chloroform        | 0.15                    | 0.05 - 0.74 |                          |              | 0.41                    | nd-9.63   |                |             |
| TCE               | 0.03                    | nd-0.28     | 1.80                     | 0.23 - 6.9   | 0.40                    | nd-17.5   |                |             |
| PCE               | 0.18                    | 0.03 - 1.57 |                          |              | 1.78                    | nd-33.0   |                |             |
| 1,4-DCB           | 0.10                    | 0.03-0.95   |                          |              | 0.74                    | nd-60.9   |                |             |
| lpha-pinene       | 2.07                    | 0.29 - 15.8 |                          |              | 0.61                    | nd-12.2   | 2.12           | 0.50 - 4.85 |
| d-limonene        | 5.72                    | 0.28 - 167  | 1.20                     | <0.2-5.6     | 6.57                    | nd-137  | 4.62           | 1.23 - 27.3 |
| n-hexane          | 0.82                    | 0.30 - 6.08 | 0.55                     | <0.1-1.6     | 2.50                    | nd-20.6   |                |             |
| naphthalene       | 0.22                    | 0.07 - 0.57 |                          |              | 0.65                    | nd-8.80   |                |             |
| 2-butoxyethanol   | 4.59                    | 0.90 - 176  | 1.60                     | <0.4-27      | 4.98                    | nd-102  | 18.8           | 6.33-92.3   |
| d5-siloxane       | 25.5                    | 7.40 - 120  |                          |              |                         |   | 37.9           | 16.7 - 112  |
| phenol            | 4.38                    | 1.94 - 17.0 |                          |              | 1.72                    | nd-10.4   |                |             |
| TXIB              | 0.89                    | 0.42-1.86   |                          |              | 0.77                    | nd-8.37   |                |             |

means of the concentrations of formaldehyde, acetaldehyde,  $\alpha$ -pinene, and phenol in small/medium office buildings that we observed were 40%—300% higher than those in the large office buildings in the BASE study (Table 4). In contrast, aromatic compounds, n-hexane, naphthalene, and several chlorinated compounds showed from 2 to >10 times lower concentrations in SMCB offices. Daisey et al. measured VOCs in 12 California office buildings during the same time period, finding lower concentrations of the aromatic compounds and n-hexane than those measured in BASE, with levels generally comparable to levels measured in the SMCB offices. Note that BASE and Daisey et al.'s studies were conducted in the 1990s and might not represent current levels in large office buildings, such that temporal changes in product

composition and use may be responsible for part of the differences. Formaldehyde is emitted from composite/pressed wood furniture, and as the popularity of composite/compressed wood furniture continues to increase, so may have formaldehyde concentrations. Hodgson and Levin have observed decreases of concentrations of benzene, PCE, and other aromatics hydrocarbons in U.S. from the 1980s through the 2000s, which was attributed to the reduction of the production and use of these chemicals. A recent study conducted in a large call center office building in Northern California reported similar concentrations for many VOCs to the levels we observed in the small/medium office buildings. However, again, the formaldehyde and acetaldehyde concentrations in SMCB were 1.6—2.0 times of those in the call center.

There are also a few existing studies on VOC levels in retail stores or restaurants. Loh et al. reported VOC concentrations in a number of primarily large retail stores and restaurants in Boston, MA, and found that the geometric mean concentrations for formaldehyde and several aromatic hydrocarbons were higher in stores than in other microenvironments, particularly in certain store types. 12 For example, formaldehyde was highest in houseware and furniture stores, and toluene was particularly high in multipurpose stores. We also found high levels of formaldehyde and toluene in retail stores, with geometric means of 28.5 and 9.9  $\mu$ g/m<sup>3</sup>, respectively. Except for formaldehyde and PCE, the concentrations of aromatic hydrocarbons and other chlorinated compounds were relatively lower in the small/medium retail stores we measured than those reported by Loh et al. In addition, Loh et al. reported high chloroform levels in restaurants  $(1.1 \,\mu\text{g/m}^3)$ , which is similar to the levels we observed in groceries/restaurants, with a geometric mean of 1.04  $\mu$ g/m<sup>3</sup>. Hotchi et al. observed concentrations >10  $\mu$ g/m<sup>3</sup> for formaldehyde, 2-butoxyethanol, toluene, and d5-siloxane in the sales area of a large mulitipurpose store in the San Francisco Bay Area. 11 However, except for 2-butoxyethanol which is likely related to floor cleaning and waxing, the concentrations of the other three compounds observed in small/medium retail stores were 1.5-1.8 times higher than the concentrations in the mulitpurpose store, and the concentrations of acetone, d-limonene, and PCE were 13-55 times higher in small/medium retail stores. We were unable to draw conclusions based on the limited existing data on IAQ in retail stores, since the type of products sold in stores varies. SMCBs serve more varied uses than large commercial buildings, which primarily function as offices, and the type of products and the activities in the building influence the IAQ. Thus, it is challenging to obtain representative samples covering the large variety of retail stores to provide any comparable data.

Data on whole building emission rates in SMCBs are extremely scarce. Whole building emission rates can be used in environmental modeling, in order to evaluate the risks and impacts of the changing ventilation rate and to compare against emission rates from products. However, whole building emission rates for commercial buildings were rarely reported in previous studies and such factors were only available for limited chemicals. The whole building emission rates per unit area obtained from small/medium offices in our study were 1-10-fold lower than those reported by Hodgson et al. for a large call center office building, 10 though the indoor VOC concentrations were similar, indicating a greater dilution rate due to the high ventilation rate of a large, densely occupied building. Jia et al. measured VOC concentrations in office and work zone, respectively, in 10 small/medium mixed-use buildings in southeast Michigan. 24 The source emission rates for the building they reported for office space are basically the same as what we observed in offices for benzene, toluene, m/p-xylene,  $\alpha$ -pinene, phenol, and naphthalene. Among the compounds measured in both studies, the only exception is that the mean source emission rate for *d*-limonene we observed was 16.5 mg/h, much higher than the mean of 6.9 mg/h reported by Jia et al., though with similar medians and maxima, indicating more intense use of fragrant cleaning products in the office buildings we studied. A rough comparison was also made to a residential study conducted in inner-city homes in Los Angeles, CA, where emission rates were reported in units of  $\mu$ g/h for an average floor area of 900 ft<sup>2</sup> (range 500-2500 ft<sup>2</sup>). The median whole building emission rate of VOCs in SMCBs were from 2.5 times higher for

benzene to 28 times higher for trichlorobenzene than residential environments. However, conclusions cannot be made until more careful comparison on a per unit area basis is conducted.

Though limited by the sample size, the factor analysis helps us understand the sources in SMCBs. The sources highlighted in our analysis include automobile/traffic sources, cleaning products, occupant sources, wood products/coating, and plasticizers. SMCBs are mostly located next to major roads and have parking lots close to the buildings, which affects low-rise buildings more than large buildings. Moreover, the building envelope of SMCBs are usually not as tight as large commercial buildings. As a result, automobile sources appear to have a larger impact on the IAQ in SMCBs. A factor related to automobiles was also observed in the analysis of BASE data. Factor analysis also suggests air fresheners and cleaning sources, which are represented by d-limonene and  $\alpha$ -terpineol, and occupant sources, such as personal care products, presented by high loading of d5siloxane. Aldehydes usually appear in a single factor in previous studies,  $^{1,10}$  which is associated with compressed wood products and furniture coating sources. However, in our analysis, the lower molecular weight and higher molecular weight aldehydes were extracted into two separate factors. TXIB and DEP appear in the same factor, indicating plasticized material sources.

The indoor air quality in SMCBs is more variable than that in large commercial buildings, with more variability in indoor sources, ventilation rates, and maintenance conditions. A full understanding of indoor air quality in SMCBs requires larger studies to cover the great variability of SMCBs.

#### ■ ASSOCIATED CONTENT

Supporting Information. Details on building selection, chemical analysis and QA/QC, ventilation rates, whole building emission rates, VOC concentrations by building use category, and relevant VOC guidelines. This material is available free of charge via the Internet at http://pubs.acs.org.

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## **■** ACKNOWLEDGMENT

This research was funded by the California Energy Commission (CEC), Public Interest Energy Research (PIER) Program through contract 500-02-023 with the California Air Resources Board (ARB). The authors would like to thank all of the building operators and owners and our field staff, Amber Trout and Michael Powers. Additionally, all work conducted at LBNL is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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