Per-Person and Whole-Building VOC Emission Factors in an Occupied School with Gas-Phase Air Cleaning.

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Citation Details  
Per-person and whole-building VOC emission factors in an occupied school with gas-phase air cleaning

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1. Abstract

Using real-time measurements of CO₂ and volatile organic compounds (VOCs) in the air handler of an occupied middle school, we quantified source strengths for 249 VOCs and apportioned the source to the building, occupants and their activities, outdoor air, or recirculation air. For VOCs quantified in this study, there is a source to the outdoors of 8.6±1.8 g/h in building exhaust air, of which 5.9±1.7 g/h can be attributed to indoor sources (the building and occupants and their activities). The corresponding whole-building area emission factor from indoor sources is 1020±300 µg m⁻² h⁻¹, including reactive VOCs like isoprene and monoterpenes (33±5.1 and 29±5.7 µg m⁻² h⁻¹, respectively). Per-person emission factors are calculated for compounds associated with occupants and their activities, e.g., monoterpenes are emitted at a rate 280±80 µg person⁻¹ h⁻¹. The air handler included carbon scrubbing, reducing supply air concentrations of 125 compounds by 38±19% (mean ± std. dev.) with net removal of 2.4±0.4 g/h of organic compounds from the building. This carbon scrubber reduces steady-state indoor concentrations of organics by 65 µg/m³ and the contribution of indoor sources of VOCs to the outdoor environment by ~40%. These data inform the design and operation of buildings to reduce human exposure to VOCs inside buildings. These data indicate potential for gas-phase air cleaning to improve both indoor air quality and reduce VOC emissions from buildings to the outdoor environment.

Synopsis: VOCs are emitted indoors and are exhausted outdoors; gas-phase air cleaning in buildings may ameliorate indoor and outdoor air quality impacts of VOC emissions

Keywords: PTR-MS, activated carbon, indoor source strength, indoor VOCs, urban air quality
2. Introduction

Humans spend nearly 90% of their time indoors,\textsuperscript{1} where levels of volatile organic compounds (VOCs) can accumulate to concentrations higher than outdoors.\textsuperscript{2,3} While indoor VOC concentrations are routinely quantified, the strength (i.e., emission rate) of the myriad sources that contribute to their accumulation is largely unquantified.\textsuperscript{4} VOCs and their chemical reaction products degrade perceptions of indoor environmental quality,\textsuperscript{5–7} alter indoor chemistry,\textsuperscript{8–10} and adversely impact respiratory health\textsuperscript{11–15} and cognition.\textsuperscript{16} Furthermore, emissions of VOCs indoors are increasingly recognized for their impact on outdoor air quality. Human occupants and their activities\textsuperscript{4,17–20} and the use of volatile chemical products (VCPs)\textsuperscript{21–23} (e.g. personal care products, solvents, adhesives, inks, etc.) emit VOCs indoors. Once exhausted outdoors, these compounds participate in the production of outdoor air pollutants, like ozone and secondary organic aerosol (SOA),\textsuperscript{24} and other species that may influence air quality at regional scales. For example, emissions of fragranced personal care and cleaning products contribute meaningfully to urban ozone production in New York City\textsuperscript{23} and VCPs can contribute to more SOA potential in cities than that contributed by vehicles\textsuperscript{25}.

The recent application of real-time chemical ionization mass spectrometers to indoor environments has enabled the identification and quantification of VOC emission rates on a per-person basis. Tang et al.\textsuperscript{17} quantified VOCs in a university classroom setting with between 26 to 67 college-aged students present. This study found that occupants and their activities were responsible for 57% of emissions, and that compounds associated with personal care products and human metabolism were the dominant sources. Stönner et al.\textsuperscript{18} quantified per-person VOC emission rates in a German cinema occupied by 50-230 people; the study was arranged to distinguish between compounds emitted by adults and children. Pagonis et al.\textsuperscript{19} measured VOCs
inside of a university art museum that nearly 300 people cycled through in the course of an evening. Across studies, emission rates of some compounds associated with human metabolism and activity (e.g., isoprene and monoterpenes) were in reasonable agreement; emission rates of other compounds were more variable, e.g., ethanol and acetaldehyde. These results imply the need for more studies of diverse populations and buildings to better characterize indoor VOC source strengths.

Indoor environments contain diverse sources of VOCs. With temporally and spatially resolved VOC measurements, source strengths can be separated into contributions from outdoor air, supply air, building materials, etc. using mass balance principles. For instance, Tang et al. found that 57% of VOC emissions originated from occupants, 35% from supply air and 8% from indoor, non-occupant sources. In contrast, Lunderberg et al. quantified and apportioned more than 200 VOCs in two California homes over multiple seasons, finding that continuous indoor sources from buildings and building materials were the largest contributor to exposure, though occupant-related activities proved to also be a significant source. At the university art museum where Pagonis et al. took place, surface deposition and ventilation were the dominant VOC sinks in the building.

In all buildings, indoor air is exchanged for outdoor air via ventilation and/or infiltration. These processes exhaust indoor VOCs and products of indoor VOC chemistry to the outdoors while simultaneously introducing VOCs of outdoor origin to the indoor space. Outdoor air ventilation is of concern if a building is in proximity to sources of air pollution, like roadways. Many buildings are located near major roadways: 40% of urban populations and 15% of schools are located near a major highway or road. Concentrations of traffic-related air pollution (TRAP) VOCs are elevated within a zone of 500-2000 meters downwind of a major roadway.
Exposure to TRAP has been proven to be a source of health-related issues for humans—particularly for vulnerable populations, such as children.32

Air cleaning systems are an option to improve ventilation air quality. Air handlers typically include particle filters but systems targeting gas-phase compounds are rarely present. Prior studies investigating gas-phase air cleaning in schools have focused on portable systems. Estimates of activated carbon air cleaning effectiveness show mixed results for reducing concentrations of VOCs in school indoor air,33–35 often noted to result from variability in the indoor source strength across periods of air cleaner state (i.e., on and off). To our knowledge, there exist no comprehensive in-situ assessments of whole-building activated carbon air cleaning performance.

The present study took place at Harriet Tubman Middle School (HTMS), an institution built in close proximity to Interstate-5, a heavily trafficked highway in Portland, Oregon, USA.36 The building was renovated in 2018, including the addition of high-efficiency particle filters and an activated carbon gas-phase air scrubber to the building air handling system. An air monitoring campaign evaluated outdoor and indoor air quality at the school site over three deployment phases, each lasting for six weeks.37 This study focuses on the final field campaign, which included high-time resolution measurements of organic compounds via proton transfer reaction – time of flight mass spectrometry (PTR-ToF-MS) and other air pollutants at multiple locations in the HTMS air handling system. With these data, we quantify airflows, VOC source strengths, and single-pass removal efficiencies of VOCs through the carbon scrubber for the occupied middle school. This study fills a gap in quantifying sources and sinks of VOCs in K-12 institutions, environments important to children’s health.38,39

3. Materials and Methods

3.1 Site description
Harriet Tubman Middle School (2231 N Flint Ave, Portland, OR 97227) is located in Portland, Oregon, USA and in 2019 had an enrollment of 472 students with 33 faculty members.\(^{40}\) The renovated air handling system that serves the entire school is shown in Fig. 1, along with a schematic showing sampling locations in the air handler. The renovated air handling system includes MERV8 particle filters (Camfil Farr 30 x 30, 2") followed by MERV16 high-efficiency particle filters (Camfil, Durafil ES\(^2\), V-bank). A functionalized activated carbon scrubber (Camfil, LGX048) is present downstream the MERV16 filter bank. The air handler is active each Monday through Friday, 06:00 to 18:00 local time, during which the system circulates, conditions, and cleans a mixture of return and outdoor air that is sent to the building as supply air. The building air temperature was stable across the study period (May 27\(^{th}\), 2019 the unoccupied day, and three subsequent days when the building was occupied) averaging 23 °C±0.7 °C during the timeframe of 09:00–18:00.

**Figure 1.** Schematic of Harriet Tubman Middle School and the renovated air handler installed in Summer 2018. The volume of the building is 36,800 m\(^3\) and the reported occupancy for 2019 was 505. The air-cleaning system was outfitted with MERV 8, MERV 16, and activated carbon filters. Volatile organic compound concentrations were monitored at return air, outdoor air, and supply air monitoring points. RA = return air, OA = outdoor air, SA = supply air. MERV = minimum efficiency reporting value, a standard metric for reporting particle removal efficiency of mechanical filters. AHU = air handling unit.

### 3.2 Instrumentation and Calibration

VOC sampling was conducted using a proton transfer reaction – time of flight – mass
spectrometer (PTR-ToF-MS, Ionicon, PTR-1000) measuring across 17–280 amu for compounds with a proton affinity higher than that of H2O (i.e. most VOCs).31 The operating conditions were: T_{drift} = 60°C, P_{drift} = 2.2 mbar, U_{drift} = 600V, which resulted in electric field strength to number density ratio E/N = 135 Td (Townsend, 1 Td = 10^{-17} V cm^2). VOC concentrations were sampled in three locations in the AHU by use of a switching valve, which alternated between return aeq.ir, outdoor air, and supply air in regular, ten-minute intervals (see Fig. 1). For identification and quantification details and a list of select compounds that were putatively identified, see further description and Table S1 in the Supporting Information. Additionally, two sensors (Onset MX1102) were used to measure temperature, relative humidity, and CO2 concentrations in return and supply air. CO2 sensors were calibrated prior to deployment, however, we observed sensor drift over the course of the campaign. We developed a correction for the CO2 monitors from a regression of the supply air vs. return air measured CO2 concentrations for the period from 02:00–04:00, when the air handler was idle and the building was post-occupancy for greater than six hours. Further details concerning the instrumentation, sampling method, and analysis of data collected during the field campaign can be found in Laguerre et al. 2020.37

3.3 Data analysis

3.3.1 Source strength analysis

The mass balance shown in eq. 1, similar to Tang et al.,17 enables calculation of the mass of a VOC emitted into the building:

\[
M = \lambda_{SA}V \int_{t_0}^{t_1} (C_{L,RA} - C_{L,SA}) \, dt + V \int_{t_0}^{t_1} dC_{RA}
\]

where \(M\) is the total mass of a compound emitted into the school (µg), \(\lambda_{SA}\) is the supply air change rate (h^{-1}), \(V\) is the school’s volume (m^{3}), \(t_0\) and \(t_1\) are the beginning and end, respectively,
of a period of analysis on a given day (h), and $C_{i,RA}$ and $C_{i,SA}$ are the concentration of a VOC ($\mu g/m^3$) measured at the return and supply air monitoring points, respectively.

While time-varying VOC concentrations were measured with PTR-ToF-MS, lack of access to the ducting prohibited direct measurement of time-varying airflow. Additionally, while annual enrollment data is available, occupancy ($N$) is variable day-to-day. In the Supporting Information (including the schematic shown in Fig. S1), we describe our method to determine the outdoor air change rate ($\lambda_{OA}$), supply air change rate ($\lambda_{SA}$), and the number of occupants present in the building ($N$) across each day.

VOC source strengths were calculated similar to a prior study$^{17}$ and were apportioned into four categories. The school was unoccupied on Monday, May 27th due to the Memorial Day holiday while the air handler operated on its normal weekday schedule (operational from 06:00 – 18:00, local time). We first calculated the mass emitted (eq. 1) of each VOC in the absence of occupants on May 27th over an analysis period of ~10:00 – 12:00. This timeframe was selected as it encompassed the same timeframe of analysis of subsequent occupied days. Source strengths calculated during the unoccupied day are categorized as emissions from the building ($S_{Building}$, $\mu g/h$), shown in eq. 2:

$$S_{Building} = \left( \frac{M}{t_1 - t_0} \right)_{vacant\ day}$$

where all terms are as described previously.

The source strength attributable to occupants and their activities, $S_{Occupants}$ ($\mu g/h$) is calculated as shown in eq. 3:

$$S_{Occupants} = \left( \frac{M}{t_1 - t_0} \right)_{occupied\ day} - \left( \frac{M}{t_1 - t_0} \right)_{vacant\ day}$$
where all terms are as described previously, $t_1$ and $t_0$ on occupied days are the end and beginning
of a period of stable occupancy, respectively, which occurred within the 10:00– 12:00 timeframe
and is determined as described in the Supporting Information.

Whole-building emission factors are determined by normalizing the sum of $S_{Building}$ and
$S_{Occupants}$ by the building footprint (m$^2$) and per-person emission factors are determined by
normalizing $S_{Occupants}$ by the occupancy (persons). For these calculations the average of $S_{Occupants}$
over the three occupied days was used.

Supply air acts as a source of VOCs to the building, with contributions from outdoor air
and recirculation air. The indoor source strength from supply air recirculated from the building
after passing through the activated carbon scrubber ($S_{supply,recirc}$, µg/h) is shown in eq. 4:

$$S_{supply,recirc} = \left(\lambda_{SA} - \lambda_{OA}\right)C_{i,RA}V \times (1 - \eta_i)$$

(4)

where $S_{supply,recirc}$ is the source strength in recirculation air (µg/h), $\lambda_{OA}$ is the outdoor air change
rate (h$^{-1}$), $\eta_i$ is the removal efficiency across the air handler (-) and other terms are as defined
previously.

The indoor source strength of supply air from outdoor air after passing through the
activated carbon scrubber ($S_{supply,outdoor}$, µg/h) is shown in eq. 5:

$$S_{supply,outdoor} = \lambda_{OA} C_{i,OA}V \times (1 - \eta_i)$$

(5)

where $C_{i,OA}$ is the concentration of a VOC in outdoor air (µg/m$^3$), time-averaged over the period
of analysis, and other terms are as defined previously.

3.3.2 Air handler removal efficiency and sink strength

Removal efficiency across the air handling system that included activated carbon scrubbing
is calculated using a time-averaged mass balance on the air handler as shown in eq. 6:
\[ \eta_i = 1 - \frac{\lambda_{SA} C_{i-SA}}{\lambda_{SA} C_{i,RA} - \lambda_{OA} C_{i,RA} + \lambda_{OA} C_{i,OA}} \]  

where all terms are as defined previously.

The sink strength across the air handler, \( S_{\text{air handler}} \) (\( \mu g/h \)), is determined from eq. 7:

\[ S_{\text{air handler}} = [(\lambda_{SA} - \lambda_{OA}) C_{i,RA} V] \times (\eta_i) + [\lambda_{OA} C_{i,OA} V] \times (\eta_i) \]  

where all terms are as described previously.

Note that in eq. 7, a positive value of \( S_{\text{air handler}} \) indicates removal of the compound across the air handler. A full description of the assumptions used to calculate removal efficiency can be found in the Supporting Information, including a schematic of the air handler in Fig. S2.

3.3.3 Whole-building emissions to the outdoors

The VOC source strength from building exhaust to the outdoors, \( S_{\text{exhaust}} \) (\( \mu g/h \)), is shown in eq. 8:

\[ S_{\text{exhaust}} = \lambda_{EA} C_{i,EA} V \]  

where \( \lambda_{EA} \) is the exhaust air change rate (h\(^{-1}\)), assumed to equal the outdoor air change rate \( \lambda_{OA} \), since the building is designed for balanced ventilation, \( C_{i,EA} \) is the compound’s exhaust air concentration (\( \mu g/m^3 \)) which is assumed to equal \( C_{i,RA} \) since return air is immediately exhausted after entering the air handler (see Fig. 1), and other terms are as described previously.

The VOC source strength from building exhaust to the outdoors can also be determined by summing the relevant sources to the building, as shown in eq. 9:

\[ S_{\text{exhaust}} = \lambda_{OA} C_{i,OA} V + S_{\text{building}} + S_{\text{occupants}} - S_{\text{air handler}} \]  

where all terms are as described previously.

The contribution of indoor processes to VOC source strength in building exhaust to the outdoors \( S_{\text{exhaust, indoor}}, \mu g/h \) is defined in eq. 10:
\[ S_{\text{exhaust, indoor}} = S_{\text{exhaust}} - \lambda_{OA} C_{i, OA} V = S_{\text{building}} + S_{\text{occupants}} - S_{\text{air handler}} \] (10)

where all terms are as described previously.

The derivation leading to eqs. 9 and 10 is shown in the Supporting Information, including Fig. S3, which shows a schematic of building airflows. Note that we assess the role of removal across the air handler by comparing the result of eqs. 9 and 10 with and without the contribution of the carbon scrubber (i.e., the latter where \( S_{\text{air handler}} = 0 \)).

3.3.4 Uncertainty analysis

Uncertainties in reported parameters are either the greater of variability across parameter estimates made during each occupied day (evaluated as the standard deviation across three days) or the propagated error. Error propagation was conducted using the relevant equation for source strength or removal efficiency. Error in each parameter used in uncertainty analysis is summarized in Table S2 of the Supporting Information. Note that in the case of \( S_{\text{Building}} \), only propagated error is reported since there were not multiple estimates made for this parameter.

4. Results and Discussion

4.1 Occupant density and airflows

Results of calculations to determine the occupancy (\( N \)), outdoor air change rate (\( \lambda_{OA} \)), and supply air change rate (\( \lambda_{SA} \)) are shown in Table 1. The school district estimated the total number of students and faculty to be 505,\(^{40} \) which is in close alignment with the average calculated occupancy of 513. A validation of flowrate estimates made here is that the facilities engineer reported a design supply air flowrate of 68,000–100,000 m\(^3\)/h, in the lower range during spring due to mild outdoor temperatures. Our calculated average supply air flowrate (\( \lambda_{SA} \times V \)) is 66,000 m\(^3\)/h. This value is in general agreement with the facility engineer’s explanation of the system operation.
Table 1: Summary of occupancy and air change rates calculated for the studied middle school.

<table>
<thead>
<tr>
<th>Date</th>
<th>N</th>
<th>S^*</th>
<th>$\lambda_{OA}$ (h^{-1})</th>
<th>SE^0</th>
<th>$r^2$</th>
<th>$\lambda_{SA}$ (h^{-1})</th>
<th>S_{SA} (h^{-1})^e</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/28/19</td>
<td>448</td>
<td>87</td>
<td>0.85</td>
<td>0.023</td>
<td>0.94</td>
<td>2.0</td>
<td>0.21</td>
</tr>
<tr>
<td>5/29/19</td>
<td>540</td>
<td>98</td>
<td>0.87</td>
<td>0.032</td>
<td>0.93</td>
<td>1.7</td>
<td>0.23</td>
</tr>
<tr>
<td>5/31/19</td>
<td>552</td>
<td>120</td>
<td>1.15</td>
<td>0.035</td>
<td>0.94</td>
<td>1.7</td>
<td>0.24</td>
</tr>
<tr>
<td>Average</td>
<td>513</td>
<td>100</td>
<td>0.96</td>
<td>0.030</td>
<td>0.94</td>
<td>1.8</td>
<td>0.23</td>
</tr>
</tbody>
</table>

*estimated uncertainty from error propagated through equation S1 of the Supporting Information
#standard error (SE) of the slope of the linear regression to determine outdoor air change rate
&estimated error in supply air change rate from sensitivity analysis on equation S2 of Supporting Information; value reported is the estimated standard deviation.

The semi-validation of occupancy and airflow calculations through independent parameter estimates demonstrates that our approach is reasonable. However, this method may not be widely applicable to other building types, as it relies on occupancy trends that include discrete step-changes from no occupancy to full occupancy (and vice versa) and a period of stable occupancy. Uncertainties in determined outdoor and supply air change rates are likely higher than those that would result from direct measurements.

4.2 Source apportionment

Shown in Fig. 2 are the results of the source apportionment of indoor VOC source strengths across the 249 compounds quantified in this analysis; the twenty compounds with the highest total indoor source strength are detailed in the inset. Our estimates of source strength include the impact of indoor VOC transformation and partitioning that may alter indoor concentrations as air moves through the building to the return air monitoring point in the air handler. Thus, subsequent area and per-person emission factor calculations based on these source strengths also include these effects.

We observe total source strengths that range over more than three orders of magnitude, from -0.02 mg/h to 1800 mg/h. The distribution ($10^{th}$ percentile = 3.6 mg/h, median = 13 mg/h, $90^{th}$ percentile = 120 mg/h) of total indoor source strength shows high skew (skewness = 5.8);
many compounds have small source (or sink) strength relative to the compounds shown in the inset of Fig. 2. Source and sink strengths enable indoor exposure modeling and the apportionment enables identification of opportunities for intervention. For example, compounds with high contributions from outdoor air (e.g., m108_1, shown in the inset) would not be effectively addressed through increased outdoor air exchange. Conversely, m59 (putatively identified as acetone), with high relative contributions from indoor sources, will have substantial reductions in indoor concentration with increased outdoor air exchange. As will be discussed in Sections 4.3 and 4.4, these data also enable estimation of whole-building area emission factors and per-person emission factors.

Figure 2. Source apportionment for 249 VOCs, with the 20 compounds with the highest source strengths shown in the inset. Putatively identified compounds include acetone (m59), methanol (m33_2), acetaldehyde (m45_1), acetic acid (m61_1), ethanol (m47_2), formic acid (m47_1), isopropanol (m61_2), isoprene (m69_2), formamide (m46_1), and monoterpenes (m137 + m81). Of the twenty largest indoor source strengths, nine are putatively identified; the compound identification process is detailed in the Supporting Information and shown in Table
Acetone (m59)—a byproduct of human metabolism\(^43\) that is also found in building materials and vehicle exhaust\(^44\)—has the highest total source strength; the majority (51%) of its presence was due to occupants and recirculated air. Methanol (m33\_2) and ethanol (47\_2) have the second and eighth highest source strengths, respectively, both alcohols that include human exhaled breath as a source.\(^45\) The majority of ethanol’s presence is due to occupants and recirculation air, while the primary source of methanol is the building itself and recirculated air, likely due to methanol’s inclusion in industrial solvents and adhesives. Acetaldehyde (m45\_1), the compound with the third highest source strength, is formed in the body due to the breakdown of ethanol\(^46\) and is also present in building materials such as linoleum and laminate.\(^47\) Its source strength is distributed close to evenly between occupants and the building. Isoprene (m69\_2), a byproduct of human metabolism,\(^48\) and monoterpenes (m137 + m81), a family of compounds present in personal care and cleaning products,\(^49,50\) are apportioned primarily to occupants. Note that custodial cleaning activities occurred after the end of the school day and are not included in source strength estimates made here. Acetic acid (m61\_1) and formic acid (m47\_1) are present primarily due to building emissions,\(^51\) while isopropanol (m61\_2) is present most prominently in recirculation air, implying persistence across the carbon scrubber. In fact, we observe a highly variable net emission of isopropanol across the air handler (see Table S3), perhaps due to its presence in solvents used in the supply air fans or desorption/emission from the carbon scrubber. For a detailed tabulation of quantified source apportionment across all 249 compounds, see Table S3.

Indoor ozone mixing ratios during the campaign are consistently near-zero (<2 ppb, the uncertainty of the instrument) while outdoor ozone levels range <2–48 ppb.\(^37\) A major contributor to low indoor ozone mixing ratios is removal to the activated carbon scrubber in the
air handler; this is shown in a prior study. While we assume that reactions with ozone are not a major contributor to VOC loss in this study, even low levels of ozone may contribute to transformation of indoor organic compounds. If occurring, transformation and sorptive processes are accounted for in our estimates of emission rates since our measurements of VOCs and ozone are made in the return air of the building.

For example, several compounds (including m47_2, putatively identified as ethanol) show a negative $S_{Building}$; a recent study shows ethanol partitions readily into a variety of indoor surfaces. In the case of ozone chemistry, a recent study shows low levels of ozone result in measurable emissions of 6-MHO, ranging 0.05–0.4 ppb/h. There exist two possible peaks where 6-MHO may be observed in our mass spectra: the parent compound, with protonated mass 127.1123 and a dehydrated form at protonated mass 109.101177. As shown in Table S3, we have closer agreement in our mass identification with the dehydrated form (m/z 109_3), though we note this analysis is speculative as we did not calibrate for 6-MHO. At this signal, $S_{occupants}$ and $S_{building}$ total 12±1.8 mg/h, or 0.06 ppb/h. When considering the high occupancy of the school, the low potential emission of 6-MHO is in general alignment with the expected very low-ozone environment. Interestingly, on Monday of our study, the building was unoccupied for ~50 hours and we observe $S_{building}$ of 4±0.6 mg/h, or 0.02 ppb/h. This value is ~50% lower than that observed in Liu et al. after 50 h of no occupancy; we speculate that this is again indicative of low indoor ozone, but still indicates a potential modest contribution of indoor ozone chemistry to reported VOC source strengths in this study.

Fig. 3 presents a visualization of four compounds of particular interest at the near-roadway school. As expected, for VOCs typically associated with human activity such as monoterpenes and isoprene, occupant contributions account for the highest percentage of
apportionment. In contrast, for benzene—found in vehicle exhaust—supply air accounts for the highest percentage of apportionment. This suggests that benzene is entering the school after being pushed through the air-cleaning system, albeit at reduced concentrations than would be present absent the activated carbon scrubber. As for xylenes/ethylbenzene, the building itself accounts for the highest percentage of apportionment. We speculate that this result is due to the relatively low concentrations of outdoor xylenes/ethylbenzene during the study period (averaging 0.2 µg/m³ across daytime periods over the three occupied days) and that these compounds are present in solvents, a variety of consumer products, and building materials.

Figure 3. Apportionment of source strength (mg/h) for four select compounds of interest: monoterpenes and isoprene, which are associated with human activity, as well as benzene and xylenes/ethylbenzene, which are associated with vehicle exhaust.

4.3. Whole-building emissions and area emission factors
Using the data presented in Fig. 2 and an estimate of the building footprint (5800 m², determined via Google Earth, see Fig. S4), approximations of whole-building emission flux can be made. Note that VOC measurements made in the return air (AHU-1, see Fig. 1) of the air handler are representative of exhaust air, as a portion of return air is immediately exhausted through a louvered “penthouse” above AHU-1. While the building was intended to remain nearly balanced in return and supply airflow rate, infiltration and exfiltration are likely occurring through the building envelope. Spatially resolved VOC measurements and estimates of infiltration rates and mechanical ventilation rates would enable further exploration on the impact of infiltration on whole-building emission rates. Further, chemical reactions can occur on building envelope surfaces and envelope materials may directly emit VOCs. On the whole, we speculate these processes cause our estimates to be slightly lower than the true whole-building emission rate.

The total whole-building VOC source strength in building air exhausted to the outdoors via the air handler is calculated from eq. 8; summing over all quantified VOCs in this study, we calculate $S_{\text{exhaust}}$ of 8.5±0.4 g/h. Note that this source strength includes the contribution of outdoor air moving through the building to provide ventilation. The VOC source strength in building exhaust air determined here by summing the relevant building sources and sinks (i.e., eq. 9) yields a whole-building VOC source strength of 8.6±1.8 g/h. These two estimates of whole-building VOC source strength are within propagated uncertainty, indicating reasonable mass closure is achieved.

The unoccupied building ($S_{\text{Building}}$) and occupants and their activities ($S_{\text{Occupants}}$) are sources of VOCs to the outdoor environment that are generated indoors; these two sources sum to 5.9±1.7 g/h, a substantial contribution to the whole-building VOC emission rate in exhaust air.
On an area-normalized basis, the unoccupied building and the occupants and their activities emit a total of 1020±300 µg m\(^{-2}\) h\(^{-1}\). This area emission factor from indoor sources is consistent with recent estimates of urban oxygenated VOC fluxes of 1000–3000 µg m\(^{-2}\) h\(^{-1}\), and approximately 20–50% of the non-methane VOC emission flux estimated for an urban area in the same study.\(^{60}\) The building area emission factor of each VOC analyzed in this work is reported in Table S3 with putative identification available in Table S1. This study provides evidence that occupied buildings may represent a substantial fraction of the urban non-methane VOC emission inventory. Note that in this study, only one siloxane is quantified (hexamethyldisiloxane, D3). In Section 4.4 we use prior reported estimates of per-person emissions of D4-D6 siloxanes to estimate that these three compounds may contribute an additional ~1.4 g/h to the indoor source strength quantified here.

Two compounds of specific interest include isoprene and monoterpenes, reactive VOCs important in indoor and outdoor air chemistry. Normalizing the contributions from \(S_{\text{Building}}\) and \(S_{\text{Occupants}}\), whole-building area emission factors were 29±5.7 µg m\(^{-2}\) h\(^{-1}\) for monoterpenes and 33±5.1 µg m\(^{-2}\) h\(^{-1}\) for isoprene. For comparison, plants are important monoterpene sources, emitting in the range of ~10–500 µg m\(^{-2}\) h\(^{-1}\) across the United States, with the higher limit representative of dense forest in the southeast United States.\(^{61}\) The isoprene emission flux from this middle school is ~10% of the rate measured in a major metropolitan area\(^{62}\) and the isoprene and monoterpene area emission factors determined here are within the range reported for urban land-use in the United Kingdom.\(^{63}\) Notably, these prior estimates of monoterpene and isoprene area emission factors includes biogenic sources, like urban tree canopy. The isoprene and monoterpene area emission factors determined for HTMS are of non-plant origin. This implies occupied buildings are an important source of reactive organic compounds to the outdoor.
environment. Since buildings comprise >20% of the footprint of an urban environment, estimation of emission fluxes from buildings may be needed to improve accuracy of urban and regional VOC emission inventories.

### 4.4 Per-person emission factors

Four studies quantifying per-person VOC emission factors served as a reference for this work, including a study in a university classroom, a cinema, an art museum, and a residential test house. In contrast, our study of a middle school includes ~505 individuals, approximately 90% of them children between the ages of 11 and 16. A list of per-person emission factors for the 249 VOCs quantified here is shown in Table S3.

Per-person emission factors are, in general, consistent with prior studies, though we observe higher values for isoprene, monoterpenes, ethanol, methanol, and acetaldehyde. For example, isoprene emissions (270±60 µg person\(^{-1}\) h\(^{-1}\) here vs. 60–162 µg person\(^{-1}\) h\(^{-1}\) across three studies\(^{17–19,65}\)) may be higher due to eating and physical exercise activities that occur inside the school; there exists an indoor gymnasium and cafeteria in the building volume served by the air handling system. Monoterpene emissions (280±80 µg person\(^{-1}\) h\(^{-1}\) here vs. 25–300 µg person\(^{-1}\) h\(^{-1}\) across three studies\(^{17–19,65}\)) are in close agreement with the “high personal care product use” noted by Arata et al.,\(^{65}\) consistent with expectations of usage of scented personal care products in the studied middle-school population. Ethanol emissions vary substantially in this study (770±3200 µg person\(^{-1}\) h\(^{-1}\)), in-line with prior estimates.\(^{17–19,65}\) We suspect this high variability is due to ethanol in cleaning, sanitizing, and personal care products that are used throughout the building in unknown frequency and quantity. Cooking is also a known source of ethanol and other VOCs;\(^{65}\) cooking activity each day likely also contributes to the observed variability in ethanol emissions. Methanol emissions are less variable than ethanol (350±250 µg person\(^{-1}\) h\(^{-1}\))
and are in agreement with an estimate made in the afternoon by Arata et al.\textsuperscript{65} Acetaldehyde emissions measured here (590±250 µg person\(^{-1}\) h\(^{-1}\)) are higher than those measured previously, ranging 114–242 µg person\(^{-1}\) h\(^{-1}\) across three studies.\textsuperscript{17–19} 

Siloxanes are an important class of compounds with environmental concerns that are emitted in large quantities into indoor environments due to personal care product use.\textsuperscript{66,67} Our campaign was originally designed to study select traffic-related air pollutants, and so our analytical window extends from 17–280 amu. This means we can estimate only the source strength of hexamethyldisiloxane (D3), tentatively identified at mass \m_223 (see \textbf{Table S1} for exact mass). At this signal, we estimate a per person emission factor of 5.3±6.7 µg person\(^{-1}\) h\(^{-1}\), which is similar to the median D3 emission reported by Tang et al.\textsuperscript{17} (3.3 µg person\(^{-1}\) h\(^{-1}\)). The sum of D4–D6 siloxanes reported by Tang et al.\textsuperscript{17} gives a median per-person emission rate of 2800 µg person\(^{-1}\) h\(^{-1}\). At the average occupancy of ~500 in the school studied here, this equates to 1.4 g/h of potentially unquantified indoor VOC emissions. If added to the 5.9 g/h of quantified VOC emissions in this study, the estimated D4-D6 contribution to the source strength of the school is ~20%. This is in close agreement with Tang et al.\textsuperscript{17} showing D4-D6 contribute ~27% of total indoor VOC source strength.

\textbf{4.5 Removal efficiency of VOCs in an air handler with activated carbon scrubber}

Shown in \textbf{Fig. 4} and \textbf{Fig S5} of the supporting information are the calculated removal efficiency of the 249 studied compounds, categorized by net removal, net source, or no effect. The categorization is based on evaluation of propagated uncertainty relative to 0% removal. If the lower bound of uncertainty is >0%, we categorize net removal; if the upper bound of uncertainty is <0%, net source; if the uncertainty includes 0%, no effect.
Summing the result of eq. 7 for VOCs measured in this study, the carbon scrubber removes a net $2.4 \pm 0.4$ g/h of VOCs. This is a substantial reduction in indoor VOC source strength; for steady-state conditions with an outdoor air exchange rate of 1 h$^{-1}$ (see Table 1), the carbon scrubber results in a 65 µg/m$^3$ decrease in indoor organic compound concentration. In Fig. S6 of the supporting information, we evaluate whether the challenge concentration upstream the scrubber or compound protonated molecular weight can explain variance in observed removal efficiency; there is no easily discernible relationship between these two variables and the determined removal efficiency.

\[ \text{Xylene/Ethylbenzene (90\%±9\%) } \]
\[ \text{Monoterpenes (77\%±12\%) } \]
\[ \text{Isoprene (58\%±15\%)} \]
\[ \text{Ethanol (56\%±18\%)} \]
\[ \text{Acetaldehyde (48\%±13\%)} \]
\[ \text{Styrene (41\%±18\%)} \]
\[ \text{Acetone (32\%±11\%)} \]
\[ \text{Toluen (22\%±19\%)} \]
\[ \text{Benzene (21\%±12\%)} \]

**Figure 4.** Single-pass removal efficiencies across the carbon scrubber for the 125 compounds with significant net removal and 8 compounds with significant net source. Note that there were 116 compounds with no significant observed effect – see the supporting information in Figure S5 for a plot of removal efficiencies and uncertainty associated with these compounds. Note that for clarity in the above figure, the vertical axis extends to -60% and the lower-bound of uncertainty on the two right-most compounds are not shown; the uncertainty bounds are symmetric around the indicated estimate of removal. Reported removal efficiencies and uncertainties for all measured compounds can be found in Table S3 of the Supporting Information.
Monoterpenes and isoprene are removed relatively effectively across the scrubber, at 77±11% and 58±15%, respectively. Since monoterpenes and isoprene are important compounds in indoor chemistry, this result implies carbon scrubbing may “quench” chemistry that produces harmful secondary products, like secondary organic aerosol. Select alcohols, aldehydes, and ketones associated with human activity are removed with lower efficiency, such as ethanol (56±18%), acetaldehyde (48±13%), acetone (32±11%) and methanol (21±14%). For BTEX compounds, xylenes/ethylbenzene have high removal efficiency of 90±9%, while toluene and benzene are lower, at 22±19% and 21±12% respectively. We suspect that the lower measured removal efficiencies are indicative of a source of toluene and benzene in the air handler downstream the scrubber, rather than such a large range in removal across BTEX compounds.

Laguerre et al. found that during the same sampling campaign approximately one month prior to this study period, the removal efficiencies of xylenes/ethylbenzene, toluene, and benzene across the carbon scrubber were 89%, 91%, and 93%, respectively. In that campaign, BTEX compounds were measured directly upstream and downstream the carbon scrubber using sorbent cartridges analyzed off-line with GC/MS, possible due to the battery powered sampling pumps that could be placed directly in the air handler. Access for PTR-ToF-MS sampling lines were limited to locations identified in Fig. 1.

The fate of volatile organic compounds emitted indoors may include indoor chemical transformation, partitioning to indoor surfaces, or emission to the outdoors via exhaust in the air handler or exfiltration. As discussed in Section 4.3, we estimate a net whole-building area emission factor due to the building and occupants of 5.9±1.7 g/h. Since the carbon scrubber removes 2.4±0.4 g/h, the contribution of indoor processes to VOC emissions in building exhaust (\(S_{\text{exhaust, indoor}}\), eq. 10) is reduced from ~5.9 g/h to ~3.5 g/h, a 40% reduction. Note this calculation
credits the removal of a VOC of outdoor origin to the reduction of the whole-building emission factor since the air cleaning system is part of the building.

While it is generally known that carbon scrubbing can reduce indoor VOC levels, it is rarely employed in buildings. This is due, in part, to many important unknowns that remain concerning cost, carbon breakthrough time, and system-level impacts (e.g., pressure drop and resulting energy implications) that limit practical application. However, this study shows that carbon scrubbing may also yield a meaningful reduction in VOCs emitted outdoors from a building, a previously unrecognized benefit to gas-phase air cleaning in buildings. The potential for both indoor and outdoor air quality improvement may compel further research needed to resolve the challenges that limit widespread use of activated carbon air cleaning in buildings.

4.6 Study limitations

There existed a narrow window of opportunity to conduct this study; it was enabled by a weekday holiday where the building was unoccupied and the air handler operated on its normal weekday schedule. This single day for estimation of emissions from the unoccupied building is a source of uncertainty. For this reason, we limited the analysis of occupied days to those close in time (the same week) to the unoccupied day. Because we relied on injection of CO₂ by metabolic activity of occupants to determine air change rates, airflows could not be empirically determined for the unoccupied day—instead, we assumed the average values of airflows over the three occupied days applied to the unoccupied day. Estimates of air change are made in the afternoon and assumed to apply during the period of VOC analysis earlier in the day. While we include efforts to validate the reasonableness of our estimates, future studies should seek to directly monitor airflows through the building to complement the high time resolution monitoring enabled by on-line mass spectrometry. Finally, our analysis is predicated upon an assumption of
mixing in the school building as air enters the building from supply air, pollutants emit into the school, and air is then returned to the air handler. It is possible that the spatial distribution of emissions throughout the school introduced uncertainty into our estimate of source strengths. However, our sampling location within the air handler allowed for mixing among the various return branches prior to return via a single duct that served the air handler where our measurement occurred. Reasonable agreement between measured air change rates and occupancy with design values and enrollment, as well as per-person estimates of metabolic emissions generally consistent with what prior estimates are present in the literature, indicate accuracy for the whole-building approach used here.

Author Contributions

BS contributed data curation, formal analysis, visualization, writing – original draft, and writing – review & editing; AL contributed data curation, formal analysis, investigation, methodology, writing – original draft, and writing – review & editing; ETG contributed conceptualization, funding acquisition, investigation, methodology, project administration, resources, supervision, validation, visualization, writing – original draft, and writing – review & editing.

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Supporting Information
The Supporting Information is available free of charge on-line and includes additional description of PTR-MS compound identification and quantification; a table describing putatively assigned empirical formulas and exact masses; a description of the mass balance derivations that enabled parameter estimations; a table showing parameter uncertainty estimates; a detailed table of calculated source strengths, removal efficiencies, and associated uncertainties; regression of calculated removal efficiencies vs. potential explanatory variables; and relevant tables and figures in Tables S1-S3 and Figures S1-S6.
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