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Formaldehyde Emissions from Ventilation Filters Under Different Relative Humidity Conditions

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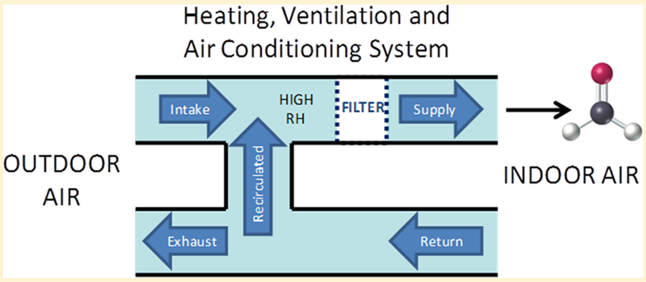
Supporting Information

ABSTRACT: Formaldehyde emissions from fiberglass and polyester filters used in building heating, ventilation, and air conditioning (HVAC) systems were measured in bench-scale tests using 10 and 17 cm^2 coupons over 24 to 720 h periods. Experiments were performed at room temperature and four different relative humidity settings (20, 50, 65, and 80% RH). Two different air flow velocities across the filters were explored: 0.013 and 0.5 m/s. Fiberglass filters emitted between 20 and 1000 times more formaldehyde than polyester filters under similar RH and airflow conditions. Emissions increased markedly with increasing humidity, up to 10 mg/h-m^2 at 80% RH. Formaldehyde emissions from fiberglass filters coated with tackifiers (impaction oils) were lower than those from uncoated fiberglass media, suggesting that hydrolysis of other polymeric constituents of the filter matrix, such as adhesives or binders was likely the main formaldehyde source. These laboratory results were further validated by performing a small field study in an unoccupied office. At 80% RH, indoor formaldehyde concentrations increased by 48−64%, from 9−12 $\mu g/m^3$ to 12−20 $\mu g/m^3$, when synthetic filters were replaced with fiberglass filtration media in the HVAC units. Better understanding of the reaction mechanisms and assessing their overall contributions to indoor formaldehyde levels will allow for efficient control of this pollution source.



INTRODUCTION

Heating, ventilation, and air conditioning (HVAC) systems are present in commercial buildings, hospitals, schools, industrial facilities, and in a large fraction of the residential building stock in the U.S. These systems are fitted with filters to remove airborne particles from incoming outdoor air and from recirculated indoor air. Air filtration considerably reduces the burden of airborne particulate matter, thus improving indoor air quality while protecting the fan, motor, heat exchangers, and other HVAC hardware. A significant portion of air supplied by an HVAC system is often recirculated indoor air to reduce energy costs associated with heating and air conditioning. Typical HVAC filters do not remove volatile organic compounds (VOCs) and other gas phase pollutants, and may become instead a source of airborne pollutants.[1]

A number of studies[1−5] have shown an association between HVAC filters and lowered perceived air quality, particularly when filters were loaded with particles and dust. Mysen et al. (2006)[6] have shown that air quality improved significantly when filters were removed from the supply duct. HVAC filters and fiberglass insulation may also become substrates for microbial colonies that emit VOCs associated with poor indoor air quality.[7,8] Chemical reactions can take place on filter media, releasing byproducts to the gas phase.[9−14] Dust, particulate matter, and sorbed chemicals collected on HVAC filter surfaces are susceptible to attack by ozone and other reactive atmospheric species such as hydroxide (OH) radicals and nitrogen oxides. HVAC filters are the first major surface on which these atmospheric species can react during their transit into the indoor environment. When only outdoor air is supplied, the ozone concentration at the filter surface is approximately equal to its outdoor air concentration (up to 50−100 ppbv in some U.S. cities), which is much higher than typical indoor air concentrations (5−30 ppbv). However, when a mixture of outdoor and recirculated indoor air circulates through HVAC filters, the ozone concentration at the filter surface can be significantly lower. Ozone was shown to react with filter materials and with particles and dust deposited on their surface, leading to partial ozone decomposition and to the emission of low to moderate levels of oxidation byproducts.

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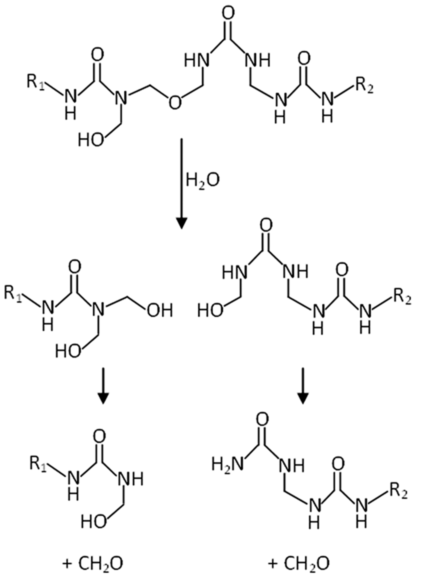
While heterogeneous oxidation on building surfaces has been the chemical process most commonly studied indoors, our recent study showed that some filter types may become sources of formaldehyde even in the absence of ozone.[14] These preliminary results suggested that the reaction involved the decomposition of additives present in the filter media in the presence of water vapor. Fibers used in filtration media and insulation are often coated with binders, adhesives, and tackifiers that preserve their integrity and, in the case of filters, improve their efficiency. Often, adhesives and binders for nonwoven filtration media include formaldehyde-based polymeric resins in their formulation.[15] The functional groups present in these filter additives may undergo reaction with water to give rise to a variety of decomposition products. For example, urea-formaldehyde resins are known for releasing free formaldehyde upon reversible hydrolytic degradation,[16] as illustrated in Scheme 1.

Scheme 1. Possible Mechanism of Reversible Hydrolytic Depolymerization of Urea-Formaldehyde Resin Leading to the Release of Free Formaldehyde



Formaldehyde is a ubiquitous pollutant present in indoor air. Numerous studies[17−19] have reported the presence of formaldehyde in office buildings and residences. Its reported mean concentrations in office buildings and homes were 14 $\mu g\ m^{-3}$ and 21 $\mu g\ m^{-3}$, respectively, with detected levels as high as to 60−70 $\mu g\ m^{-3}$.[19] Formaldehyde has been classified as a human carcinogen by the World Health Organization (WHO).[20,21] The State of California established relatively low reference exposure indoor levels for chronic (9 $\mu g\ m^{-3}$) and acute (55 $\mu g\ m^{-3}$) respiratory health effects.[22] A different guidance was recently established by the WHO.[23] Formaldehyde has prominent indoor sources that include building materials, wood-based furnishings, household products, and unvented combustion. It is also produced as a byproduct of other indoor chemical reactions.[24] Hence, the contribution of HVAC filter media as a formaldehyde source needs to be assessed in relative terms with respect to those known major indoor sources. In polluted atmospheres, incoming outdoor air may also be considered an additional source.[25]

In this study, we measured formaldehyde emission rates from clean HVAC filters exposed to various relative humidity (RH) levels. Laboratory experiments were performed at different air face velocities across the filter media. The emission rates were used to estimate impacts on indoor formaldehyde levels under typical scenarios. In addition, field tests were performed in an office space serviced by an HVAC system containing the same filters used in the bench-scale studies. These tests confirmed that fiberglass filters increased indoor air formaldehyde levels.

EXPERIMENTAL SECTION

Bench-Scale Experiments. The bench-scale experiments used two groups of commercially available HVAC filters corresponding to different brands and models. One group contained four types of fiberglass filters, all from the same filter manufacturer, with different levels of tackifier coatings (F1−F3) and uncoated (F4). The other group contained three types of polyester filters (P1−P3), all from distinct filter manufacturers, two of which had tackifier coatings. The filters employed in these tests were all nonpleated panel or pad filters of thickness between 2.5 and 5.0 cm. The particle removal efficiency ratings of these filters ranged from MERV 6 to MERV 9. Sample coupons were cut from unused filter and tested under a wide range of relative humidity conditions (from 20% to 80% RH) in order to assess the effect of humidity on formaldehyde emission rates. Bench-scale experiments were performed at a low air velocity of $\nu = 0.013$ m/s and at a higher setting of $\nu = 0.5$ m/s. The latter is similar to velocities through the media of pleated filters in real HVAC applications. Experiments explored short-term (24−96 h) and long-term (168−720 h) emissions. The summary of bench-scale experiments describing filter types and test conditions is presented in Table S-1 (Supporting Information, SI).

An experimental apparatus similar to that used for low velocity tests has previously been described.[14] Briefly, a clean air supply was split into two streams: one corresponding to dry air and the other saturated by passing through a water bubbler. The humidity was controlled by adjusting the ratio of saturated to dry air flow. The two streams were mixed in a 20-L environmental chamber. A temperature and relative humidity sensor (HMD-70, Vaisala, Finland) measured the conditions within the mixing chamber. The air then passed through a Teflon flow tube reactor containing a filter coupon of 47-mm diameter (surface area = $1.7 \times 10^{-3}\ m^2$) at a flow rate of 1.4 ± 0.1 L/min. With this flow rate, the velocity of the air entering the filter sample was $\nu = 0.013$ m/s, which is 3% of a typical velocity of air passing through the filter media in a deployed pleated air filter and even less than the typical air velocity through a nonpleated filter. The experiments took place under room temperature in the range from 22 °C to 27 °C. Four different RH settings of (20 ± 5)%, (50 ± 5)%, (65 ± 5)%, and (80 ± 5)% were employed. For all tests, the background formaldehyde concentration in the supply air was checked before installing the filter coupon. The filter coupon was then quickly installed and continuously exposed to the air flow. Air samples were collected through sample ports located downstream.

The experimental setup used for experiments at high velocity has previously been described.[26] Briefly, clean air was circulated through a humidifier and a dilution stream of dry air used to achieve the desired RH. The temperature and RH were monitored downstream of the filter using a calibrated APT logging system (Automated Performance Testing, TEC,

Table 1. Formaldehyde Concentration Changes $\Delta[CH_2O]$ across Filters in Low and High Face Velocity Experiments

filter	formaldehyde concentration change across filter, $\Delta[CH_2O]$ ($\mu g/m^3$)					
	low face velocity ($\nu = 0.013$ m/s)[a]			high face velocity ($\nu = 0.5$ m/s)[b]		
	50% RH	65% RH	80% RH	20% RH	50% RH	80% RH
F1	0.4	2.0 ± 0.1	5.9 (8.2 ± 0.5)	1.2 ± 0.2	4.9 ± 0.6	10.8 ± 0.4
F2	0.3		5.6			
F3	0.3		6.4 (7.7 ± 0.1)			
F4	5.2 ± 0. 1	9.3 ± 0.1	37.1 ± 0.5 (31.8 ± 0.6)		4.3 ± 0.4	12.9 ± 0.7
P1			1.3 ± 0.1			1.4 ± 0.3
P2			0.5 ± 0.1			0.8 ± 0.2
P3						0.8 ± 0.3

[a] Corresponding to samples collected between 24 and 48 h. [b] Measured at the end of 48 h.

Minneapolis). A 10-cm^2 sample was cut out from the filter and placed inside a holder in the flow system, operating at temperatures in the range from 24 °C to 27 °C. Air samples were collected through sample ports located upstream and downstream of the filter holder. The air flow rate was 30 L/min resulting in a face velocity of $\nu = 0.5$ m/s. Three different RH settings of (20 ± 5)%, (50 ± 5)%, and (80 ± 5)% were employed. Initial samples were collected at the end of 24 h, and long-term tests were conducted for a period of up to 240 h.

Field Experiments. One of the filters found to have the highest formaldehyde emissions in laboratory studies (F4) was installed in HVAC units servicing a small unoccupied commercial office space, to evaluate the indoor air formaldehyde concentration increase. A synthetic filter (P1), which in laboratory studies emitted formaldehyde at a low rate, was used as the reference. Experiments were carried out over a month-long period. The office space consisted of two separate zones, separated by a wall, of 42.7 m^3 and 52.8 m^3 respectively. Each zone was serviced by an independent HVAC unit provided with independent outdoor intake and recirculation duct work. The air flow rates through the supply air registers, return air grilles, and HVAC outdoor intakes were measured using a balometer. Before the experiments were conducted, visible cracks between zones were sealed with tape. Interzonal air leakage was measured by releasing carbon dioxide alternatively in each of the office spaces and monitoring the levels simultaneously in both spaces using CO_2 monitors (EGM 4, PP systems). Humidifiers (Honeywell Cool Moisture Humidifier) were operated in the spaces during test periods as needed to maintain the indoor RH at 50% or 80%. Indoor air humidity and temperature levels were monitored using temperature and RH loggers (HOBO U10−003, Onset Corporation) and an Automated Performance Testing (APT) system (The Energy Conservatory, Minneapolis). The experimental matrix is presented in Table S-2 (SI). Filters were changed weekly between F4 to P1 in each zone. For measurement of formaldehyde concentrations, samples were collected in both zones and outdoors. These samples were collected approximately four days after the start of an experimental condition. Sulfur hexafluoride (SF_6) decays were used to determine the air exchange rates at various times, with SF_6 concentrations measured using calibrated Miran SapphIRe portable ambient analyzers.

Sampling and Analysis of Volatile Aldehydes Emitted by Filters. 2,4-Dinitrophenylhydrazine (DNPH)-impregnated silica gel cartridges (XpoSure, #WAT047205, Waters Corp., U.S.) were used to collect volatile aldehyde samples. For outdoor air samples, the cartridges were preceded by an ozone scrubber (Sep-Pak WAT054420, Waters Corp., USA). The flow through the samplers, on the order of 500 mL/min in low-velocity bench-scale experiments and 1 L/min in high-velocity bench-scale experiments, was measured immediately before starting and at the end of each sampling period. The corresponding volume of air sampled was ~720 L in low-velocity bench-scale experiments, and between 60 and 180 L in high-velocity bench-scale experiments and field experiments, with an experimental uncertainty below ±3%. The samplers were extracted with 2-mL acetonitrile aliquots, and analyzed by HPLC with UV detection (Agilent 1200), following the EPA TO-11 method, which has been validated for the high humidity conditions (up to 80% RH) used in this study.[27] Formaldehyde was quantified with a calibration curve prepared with authentic standards of the DNPH hydrazone derivatives (Sigma-Aldrich, U.S.). The average formaldehyde concentration in reactants blanks was determined to be equivalent to <0.02 $\mu g/m^{-3}$. The limit of detection of the method was between 0.1 and 0.2 $\mu g/m^{-3}$.

RESULTS AND DISCUSSION

Bench-Scale Experiments. Table 1 summarizes formaldehyde concentration changes $\Delta[CH_2O]$ across the filter media, defined as follows:

$$\Delta[CH_2O] = [CH_2O]_d - [CH_2O]_u \qquad (1)$$

where $[CH_2O]_d$ and $[CH_2O]_u$ are the concentrations downstream and upstream of the filter, respectively. The reported concentrations are based on the integrated air samples collected between 24 and 48 h of the exposure. In bench-scale experiments, duplicate samples were taken for most of the experiments and, in these cases, the average of the measurements are reported ± the absolute difference between the determinations. When high levels of formaldehyde were recorded (e.g., fiberglass filters under 80% RH), experimental errors were 1−5%, but increased to ~20% for measurements carried out at low RH and with low-emitting polyester filters. Upstream (background) formaldehyde concentrations were below 0.9 $\mu g/m^3$. Results of experiments with an indoor RH of approximately 20% are not reported in Table 1 because the measured downstream concentrations were similar to upstream (background) and the formaldehyde emission could be regarded as negligible. In addition to replicate measurements for each filter coupon, tests were conducted for filters F1, F3, and F4 at 80% RH using a different new filter coupon, and results for the second determination are also reported in Table 1 in parentheses. It can be seen that the variations among different coupons of the same filter type were on the order of

15−25%, significantly higher than the experimental error of replicate measurements taken with the same filter coupon, which may be caused by the material inhomogeneity of the filter media. Therefore, we used 20% for the estimated measurement uncertainty related to the determination of $\Delta[CH_2O]$.

Figure 1(a) shows the formaldehyde concentration change downstream of the filter as a function of time for the long-term tests at low face velocity conducted for filters F1 and F4. Results indicate that the formaldehyde emission decreased moderately over time. For example, the formaldehyde emission at the end of one month was still over 70% of that measured between 24 and 48 h exposure for filter F1 under 80% RH.

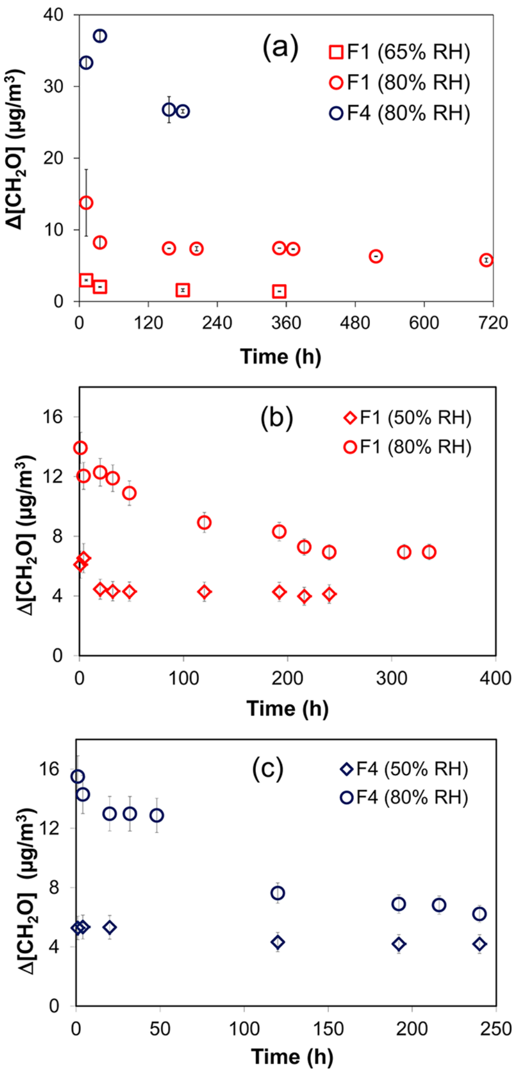


Figure 1. Formaldehyde concentration increase downstream of filters (a) F1 and F4 for different RH at a face velocity of $\nu = 0.013$ m/s, (b) F1, and (c) F4 for different RH levels in experiments performed with a face velocity of $\nu = 0.5$ m/s over a period of 10 days.

Fiberglass filters F1 (with a heavy tackifier coating) and F4 (not coated) and three polyester filters (P1−P3) were used to study formaldehyde emissions under high face velocity conditions ($\nu = 0.5$ m/s). Table 1 summarizes formaldehyde emission results for these filters. Similar to the findings for low-velocity experiments, formaldehyde concentrations increased at higher RH. We report in each case the average of two 1-h integrated samples taken at the end of a 48-h period, subtracting the upstream concentration. The average background formaldehyde concentrations upstream of the filter were <0.4 μg/m³, and were subtracted from downstream values to determine emission rates. The experimental error in each case corresponds to one standard deviation.

Figure 1(b),(c) shows the formaldehyde concentration measured downstream of filters F1 and F4 exposed to 50% and 80% RH, respectively, as a function of time. It can be observed that initial formaldehyde concentrations decrease with time and approximately stabilize after ∼100 h of continuous exposure to the air flow. Formaldehyde emissions from polyester filters were negligible after the first 24 h.

In separate tests, liquid samples of three different brands/models of tackifiers available commercially were applied to an inert substrate and exposed to a flow of air at 80% RH. No significant formaldehyde emissions were observed leading to the conclusion that tackifiers do not participate in the hydrolysis reaction.

Estimation and Comparison of Formaldehyde Emission Rates for Different Scenarios. The formaldehyde emission rate per unit filter face area E_F (in μg/h-m²) for each experiment was calculated as follows

$$E_F = (f\Delta[CH_2O])/A \quad (2)$$

where f is the air flow rate (m³/h), and A is the exposed filter face area (m²). Figure 2 plots formaldehyde emission rate E_F as a function of RH for the four fiberglass filters tested. For the filter media for which repeat tests were conducted, the average of replicates was used in Figure 2. The uncertainty of E_F was estimated at ±25%, arising mainly from the experimental error for $\Delta[CH_2O]$ determined above (eq S1 of the SI). Flow rates were measured in the lab with a precision of ±1% using a calibrated flow meter (Bios DryCal or mini-Buck Calibrator M-5). The uncertainty associated with the area measurement is negligible. Results indicate that the formaldehyde emission rate increased as RH increased for all four fiberglass filters, regardless of tackifier loading, and that the effect was not linear. The formaldehyde emission rate at 80% RH increased about 5−7 times compared to that at 50% RH. The limited data measured at 50%, 65%, and 80% RH for filter F1 and F4 indicated an approximate exponential increase in emission rate with RH as shown in Figure 2. The strong dependence of formaldehyde emission rate on relative humidity suggests that hydrolysis is possibly the main mechanism causing formaldehyde emission. In addition, the emission rates from

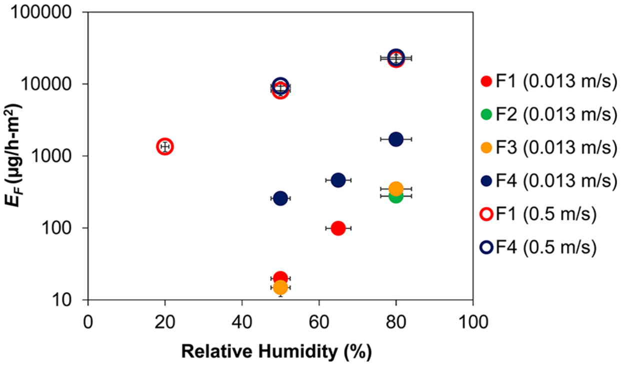


Figure 2. Formaldehyde emission rate (E_F) as a function of RH in low ($\nu = 0.013$ m/s) and high ($\nu = 0.5$ m/s) face velocity experiments.

fiberglass filters with tackifier coatings (F1, F2, and F3) were similar regardless of the amount of tackifier coating for all RH levels, but were significantly lower than that from the otherwise identical fiberglass filter without tackifier. This finding implies that other additives (such as fiberglass binders), rather than the tackifier, are likely to be the main source of formaldehyde emission. This is further indicated by the fact that formaldehyde emission was much lower for all tackfier-coated polyester media even at 80% RH. Although high emissions from fiberglass filter products have not been previously reported, formaldehyde emission from other fiberglass building products that use formaldehyde-based binders (such as fiberglass insulation) has been recognized and reported as a significant indoor source of formaldehyde.[17]

Figure 3 shows the variation of formaldehyde emission rates (E_F) with face velocity comparing fiberglass filters with (F1) and without (F4) a tackifier layer, at the end of 24 and 240 h of continuous operation at 80% RH. The emission rates at low face velocities for filter F4 were about three times higher than for filter F1, indicating that the tackifier does not seem to be the main source of formaldehyde, but rather a barrier separating water vapor from other additives that are likely more susceptible to undergo hydrolysis. While filter F1 presents lower formaldehyde emission rates compared to filter F4 at low face velocity, this difference becomes negligible at high velocity, both during short-term and long-term tests shown in Figure 3(a),(b), respectively. This phenomenon may be explained by mass transfer resistance associated to the presence of a tackifier coating on the surface of the fibers, or by the larger amount of water vapor delivered to the filters at high air velocity. An increase in velocity increases the mass transfer coefficient and decreases the resistance offered to the reaction on the filter surface. In the absence of tackifier coating in filter F4, the reaction may be limited exclusively by the rate of hydrolysis.

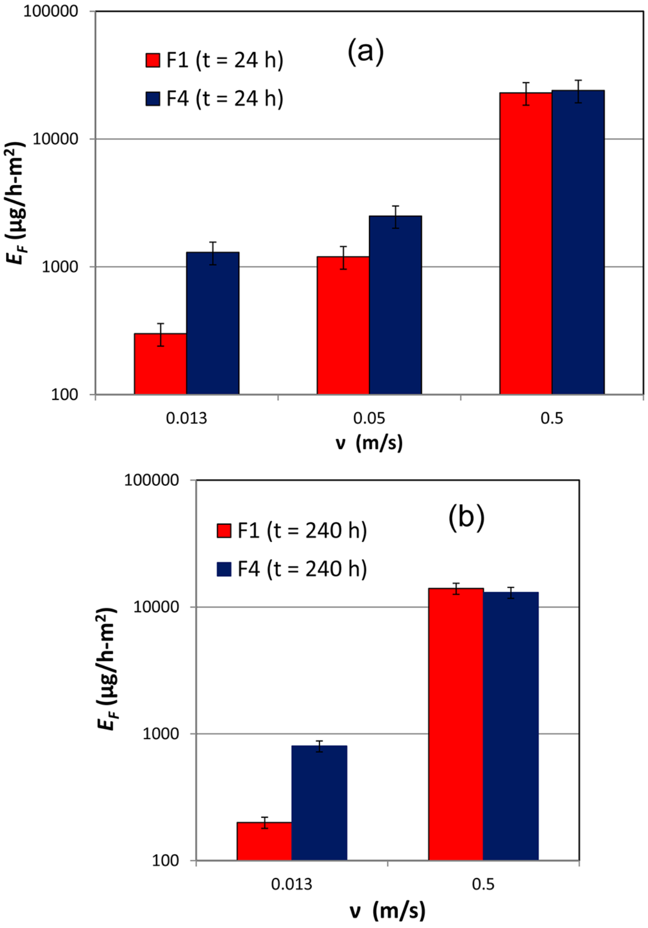


Figure 3. Formaldehyde emission rate E_F from filter types F1 and F4 at different face velocities and RH of 80%: (a) at the end of 24 h (b) at the end of 240 h.

Field Studies. *Air Flows and Air Exchange Rates.* The net air flow through supply registers in zone 1 and the return air flow were both 0.27 m^3/s, with the outdoor air intake rate estimated as 0.03 m^3/s. The corresponding values for zone 2 were 0.19 m^3/s, 0.18 m^3/s, and 0.02 m^3/s, respectively. Typical precisions of measurements performed with a balometer under these conditions are 20–30%.[28] These air flows correspond to an estimate (2.3 ± 0.6) m/s face velocity for the filter installed in HVAC unit serving zone 1, and to (1.5 ± 0.4) m/s for HVAC unit serving zone 2. The carbon dioxide decay tests showed that there was no measurable air transport between the two zones. Outdoor air exchange rates of 2.7 h^{-1} for zone 1 and 1.5 h^{-1} for zone 2 were determined from the SF_6 decay curves. A recirculation rate of 88% of total supply air flow was computed for each of these zones, based on the air flows through the HVAC system and the outside air exchange rate. Calculations using the measured rates of outdoor air flow into the HVAC units yielded very similar results. Outdoor temperatures measured over week-long periods were in the range from 14 °C to 26 °C, while the indoor temperatures were maintained in the range from 22 °C to 23 °C (Table S2 of the SI). From the humidity measured indoors and outdoors and the air flow rates, the RH at the filters ranged between 38% and 52%, with an average of 44%, when the humidity indoors was maintained at 50%. The RH at the filters ranged from 69% to 83%, with an average of 71%, when indoor RH was maintained at 80%.

Formaldehyde Emissions. In field measurements, the background indoor air formaldehyde levels with filter type P1 installed in the HVAC units were (10.3 ± 0.5) and (9.5 ± 0.5) $\mu g/m^3$ for zones 1 and 2, respectively. The outdoor levels were between 1.1 and 1.8 $\mu g/m^3$ during the experimental period. The indoor/outdoor (I/O) ratios of 6 to 20 in the absence of a highly emitting HVAC filter highlights the importance of other formaldehyde sources, in agreement with several previous studies.[17] Figure 4 compares formaldehyde concentrations in zones 1 and 2 when the indoor RH was maintained at 50% and 80% over different weeks. The experimental errors correspond to the difference between two simultaneous duplicate determinations. The experimental uncertainty of indoor formaldehyde measurements was between 4 and 9%. With 50% RH indoors and 44% RH near the filter surface, the average incremental formaldehyde concentration in the two zones caused by F4 was about 2 $\mu g/m^3$, which is an approximate 20% increase in formaldehyde concentration. Similarly, with an indoor RH of 80% and approximately 71% RH near the filter surface, the F4 filter increased formaldehyde levels by 48% in zone 1 and by 64% in zone 2, as shown in Figure 4. The incremental formaldehyde concentrations $[CH_2O]_{F4} - [CH_2O]_{P1}$ in each zone were proportional to the corresponding face velocity in each of the two HVAC units. The formaldehyde emission rates of filter F4 at 80% RH indoors (71% RH at the filter surface) were estimated to be equal to 28 mg/h-m^2 and 33 mg/h-m^2 for zones 1 and 2, respectively, each with an experimental uncertainty of ~30%

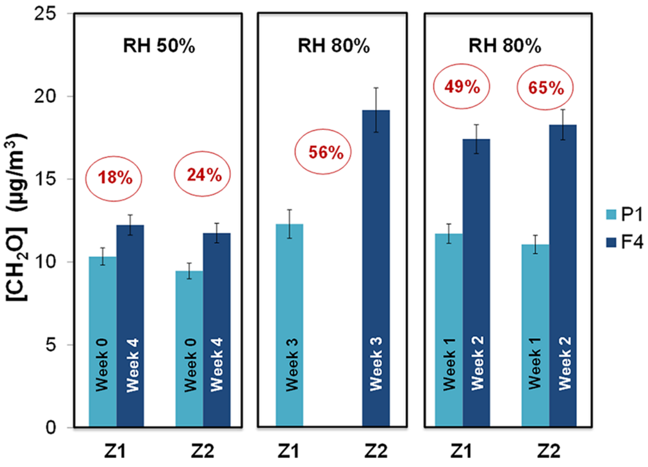


Figure 4. Indoor formaldehyde levels [CH_2O] in zone 1 (Z1) and zone 2 (Z2) at 50% RH and 80% RH indoors for filters P1 or F4 installed in the HVAC units during different weeks. Percent increases are reported in red circles.

(comprising both uncertainties in the determination of formaldehyde levels and air flows). These emission rates are consistent with an extrapolation of bench-scale results predicting emission rates at 80% RH of 29 mg/(h-m^2) and 33 mg/(h-m^2), respectively, for the face velocities measured in the two zones. With 50% RH indoors (44% RH at the filter), the estimated formaldehyde emission rates from F4 during the field studies were 12 mg/(h-m^2) and 11 mg/(h-m^2) for zones 1 and 2, respectively, also with an experimental uncertainty of ~30%. From the bench-scale studies at 50% RH and 0.5 m/s face velocity, the same filter type emitted 9 mg/h-m^2, and at 20% RH, the formaldehyde emissions were negligible. The field study data are consistent with the laboratory findings, and indicate that filter F4 can be a significant source of formaldehyde in indoor air when the humidity is high.

To provide another comparison, during week 3, filter P1 was installed in zone 1 and filter F4 was installed in zone 2, with indoor RH maintained at 80% in both zones. The formaldehyde concentration in zone 2 was significantly higher than the formaldehyde concentration measured simultaneously in zone 1, as shown in Figure 4. It should be noted that the background concentration in both spaces was very similar; thus, the higher formaldehyde concentration in zone 2 can be almost exclusively attributed to filter type F4 installed in the HVAC unit.

Implications for Indoor Formaldehyde Levels. The largest increases in indoor formaldehyde concentrations were estimated based on the highest steady-state emission rate measured for fiberglass filter media (F4) at high velocity (0.5 m/s) in bench studies. Assuming all outdoor air passes through the air filter, i.e., there is negligible outdoor air entry into the building via infiltration or other processes that bypass the filter, and that emission rates from other sources are unaffected by the formaldehyde released from filters, the incremental increase in steady-state indoor air concentration caused by the filter is equal to the concentration increase across the filter. Therefore, for a building using high-emitting HVAC filter(s), it is expected that the indoor formaldehyde concentration would increase by 4 and 6 μg/m^3 when the filter is exposed to 50% RH and 80% RH, respectively (Table S-3 of the SI). These levels are comparable to reference exposure levels for chronic exposures set by the California EPA.[22] In commercial buildings, the mixed air section of the HVAC system (combining outdoor and return air) is the most common location for particle filters. For nearly 100% recirculated indoor air, RH at the filter will be the same as indoors. HVAC systems often operate an air-side economizer during moderate weather conditions to enable “free” cooling. When the system is operating in the economizer regime, outdoor air increases beyond the minimum ventilation requirements up to 100% of the total supply airflow, and the filter may be exposed periodically to high RH in humid climates. However, under economizer-mode conditions, the air temperature at the filters may be substantially less than room temperature. Formaldehyde emission rates from indoor sources decrease with lower air temperature.[17] If the formaldehyde emission rates from filters decrease with air temperature, then its impact on indoor levels may be less than those indicated in Table S-3 of the SI.

In order to estimate the duration of formaldehyde emissions from filters after being installed, the mass of polymers, binders, and other extractable materials present on the filter F4 was determined by weighing samples before and after sonicating in 20 mL of methylene chloride for 20 min. The mass of extracted material was determined by drying the solvent from the extracts after sonication. An average concentration of (58 ± 5) g/m^2 was obtained for 5 samples. The mass of the extracts was estimated as 20% by weight of the filter material. Considering that average steady state formaldehyde emission rates of 9.3 and 12.5 mg/h-m^2 were estimated for 50% and 80% RH, respectively, we estimate the duration of steady-state formaldehyde emissions between 49 and 65 days, assuming that 25% of the extracted material can be hydrolyzed to formaldehyde. HVAC filters are usually changed every 120 to 190 days, and often HVAC systems operate only about half of the time. Hence, emissions from certain filters under high RH may be a persistent significant source of indoor formaldehyde in buildings over a significant part of their deployment period. It should be kept in mind that several assumptions are included in this simple analysis. The results presented here correspond to unused filters only, but emissions from soiled filters are likely to be higher due to the moisture retention capacity of dust and particles deposited on its surface, as previously shown.[14] However, given the suppression of formaldehyde emissions by tackifiers, coating of the fibers by certain indoor chemicals adsorbing during operation may have a similar attenuating effect. Our experiments, performed in unoccupied environments, do not explore fully these variables.

The increase in formaldehyde emission rates with RH in the absence of oxidative conditions (e.g., ozone) suggests that formaldehyde is formed as a byproduct of the hydrolysis of filter additives. In field experiments, contributions of outdoor formaldehyde or ozone-initiated heterogeneous chemistry were negligible. High emissions measured from filters that do not contain tackifiers, as well as the absence of emissions from pure impaction oils in contact with humidified air, indicate that tackifiers are not the source of the formaldehyde. Instead, our results suggest that formaldehyde is most likely emitted from hydrolysis of other additives, such as polymers and fiber binders. Water vapor may be the limiting reactant of hydrolysis under the operating regime of these filters. Formaldehyde emission rates increased roughly in proportion to the air velocity, indicating that the reactants participating in the hydrolysis process are not significantly depleted when the system operates at high face velocity.

While the findings of this study are robustly supported by the experimental data, there are limitations and questions that remain unanswered. Among the experimental variables not fully studied are the effects of temperature, a wider range of air velocities, the presence of dust and particles on the filter surface, the frequency and duration of periods of high humidity, and the role of condensed water impinging on the filter surface. Additional experiments that quantify these effects are needed in order to predict more precisely the impact of emissions from such filters on indoor formaldehyde concentrations. In addition, only a very limited number of fiberglass filters, all from a single manufacturer, were employed in this study. Evaluations of formaldehyde emissions from a larger variety of fiberglass filters are needed before drawing general conclusions about formaldehyde emission from fiberglass filters.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Summary of bench-scale experiments describing filter types and test conditions (Table S-1); experimental matrix for field studies (Table S-2); uncertainty of E_F, arising mainly from the experimental error for $\Delta[CH_2O]$ (eq S1); and formaldehyde concentration increase across filter and emission rates for samples of F4 media at high air velocity (Table S-3). This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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