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SUMMARY
We used Proton Transfer Reaction – Mass Spectrometry (PTR-MS) and conventional sampling methods to monitor and identify trace level organic pollutants formed in heterogeneous reactions between ozone and HVAC filters in real time. Experiments were carried out using a bench-scale flow tube reactor operating with dry air and humidified air (50% RH), at realistically high ozone concentrations (150 ppbv). We explored different filter media (i.e., fiberglass and cotton/polyester blends) and different particle loadings (i.e., clean filter and filters loaded with particles for 3 months at the Lawrence Berkeley National Laboratory and the Port of Oakland, CA). Detailed emission dynamics of very low levels of certain organic pollutants from filter media upon ozone exposure in the presence of moisture have been obtained and analyzed.

KEYWORDS
HVAC filter, ozone, building-related symptoms, secondary pollutants, PTR-MS.

INTRODUCTION
Used HVAC particle filters can be a strong sensory pollutant source, decrease perceived indoor air quality (IAQ) and increase sick building syndrome (SBS) (Beko et al., 2008; Hyttinen et al. 2006). Reactions of ozone with organic compounds present on the filter surfaces have been assumed to be a very important factor that contributes to the sensory pollutions from particle filters. Previous studies have reported that particle filters could remove a fraction of ozone from air stream. As for reaction products, although production of formaldehyde and other carbonyl compounds has been reported to correspond well to the ozone removal rate for dusty and sooty fiberglass filters (Hyttinen et al. 2006), systematic studies on how the production of secondary pollutants is influenced by environmental conditions such as relative humidity, filter media types as well as particle loading types are very limited. In addition, the intermediate reaction products and low-volatility compounds from ozone and HVAC filter interaction are largely unknown due to limitation in commonly used sampling and analysis methods (i.e., cartridge and sorbent tube). Real-time measurement of pollutants emitted from HVAC filters at trace levels is desired to better elucidate the nature and dynamics of O_3-HVAC filter interactions.

Recent findings from the EPA BASE study have shown a strong association of synthetic filters with increased reporting of building-related health symptoms (BRS) at work, particularly when outdoor ozone levels are elevated [Buchanan et al, 2008]. The goal of this study is to test for chemical mechanisms that would help explain these findings, and provide a much more solid scientific foundation for guidance on building filtration methods.

METHODS

Experiments were carried out using a bench-scale flow tube reactor operating with dry air and humidified air (50 %RH), at realistically high ozone concentrations (150 ppbv). A clean airflow was split into two similar streams, one of which was run through a 47mm circular specimen of filter media, while the other was used as a reference. The ozone level was controlled with an UV ozone generator upstream of the filters, and the humidity was adjusted by circulating part of the incoming airflow through a water bubbler (humidifier). Water-saturated air was diluted with a similar flow of dry air to avoid the entrainment of water droplets from the bubbler, obtaining RH ~ 50%. The ozone level was measured at 5-min intervals, alternatively at the filter and the reference flow, using a photometric monitor (API 400). Samples were collected through ports located downstream of the exposed filters. The experimental setup was operated under room temperature, in the range 21-24 ^{o}C, controlled by the laboratory thermostat. Stainless steel, Teflon tubing, Teflon-lined Tygon tubing and Teflon filter holders were used to minimize ozone loss to the surfaces of the flow system. HVAC filters were exposed to air containg 150 ± 5 ppbv of ozone at the inlet for periods of 100 to 1000 min, using dry and humidified air (at 50 ± 5 %RH). The airflow through the filter was in most cases 1.3 L/min, corresponding to a face velocity of 0.013 m/s.

We explored different filter media, which included fiberglass, polyester, cotton/polyester blends and synthetic polymers (polyolefin). These were among those listed most frequently in the BASE study. A set containing each of the filters was installed in the ventilation system of a building at the Lawrence Berkeley National Laboratory (LBNL), and another set was deployed in the HVAC system of a building at the Port of Oakland, CA. In both cases, filters were used for a period of 3 months. The choice of these two locations was due to their very different surroundings (i.e., proximity to diesel emissions by trucks and freeway traffic in the Port, and predominantly biogenic emissions at LBNL). Samples from clean and used filters deployed at the Port of Oakland and LBNL were tested with and without ozone. Tests were conducted at LBNL first using DNPH-coated silica gel cartridges to determine volatile aldehyde average concentrations. In these tests, we also recorded ozone breakthrough curves by measuring [O_3] levels downstream of the filter and in the reference line (equivalent to upstream ozone levels), at 5-minute intervals. The difference in ozone concentration between each period corresponding to downstream of the filter and the average of the reference periods immediately before and after was recorded as $\Delta[O_3]$. Selected media samples were then tested at Syracuse University (SU) with a primary focus of minitoring and identifying trace level organic pollutants formed in heterogeneous reactions between ozone and HVAC filters in real-time by PTR-MS, and this effort is still ongoing. For PTR-MS measurements, full scans that monitored all signals between m/z 20 and m/z 200 were used, and results were reported as normalized counts per second (ncps) which is directly proportional to the species concentration.

RESULTS AND DISCUSSION

Ozone Uptake Rates

Figure 1 illustrates typical ozone breakthrough under humidified air, recorded by exposing synthetic media used in the Port of Oakland to 150 ppb O_3. The curve in red corresponds to ozone concentration on the reference airflow, and the curve in blue to the ozone measured downstream of the sample. Each data point represents a 5-min average. The change in ozone concentration ($\Delta[O_3]$) can be calculated from the difference between those two curves. The green curve represents the percent change in ozone, $\%\Delta[O_3] = \frac{\Delta[O_3]}{[O_3]_{ref}} \times 100$ with respect to inlet (*i.e.*, reference) ozone concentration, $[O_3]_{ref}$. Our experimental approach allowed us to obtain very precise values of $\Delta[O_3]$ over long periods of time, even in the presence of fluctuations due to flow or lamp intensity instabilities. Fluctuations such as those showed in the blue and red curves were not present in $\Delta[O_3]$.

Byproduct Formation

Figure 2 shows example PTR-MS results of several compounds detected for cotton/polyester filter taken from Port of Oakland under various test conditions. Time t=0 was the time point at which the media sample began to be exposed to the supply air by switching the system from the bypass to the test loop. Results clearly indicate that the emission of formaldehyde, acetaldehyde and acetic acid from the sample media were all highest and persisted longest for the case of ozone exposure in the presence of moisture. Presence of ozone under dry air condition led to a high peak value for all these three compounds initially, but they all decreased to background levels in a very short period of time (i.e., < 5 minutes). These observations were qualitatively correspondent well to the average aldehyde concentrations determined by DNPH and provided more detailed dynamic information.

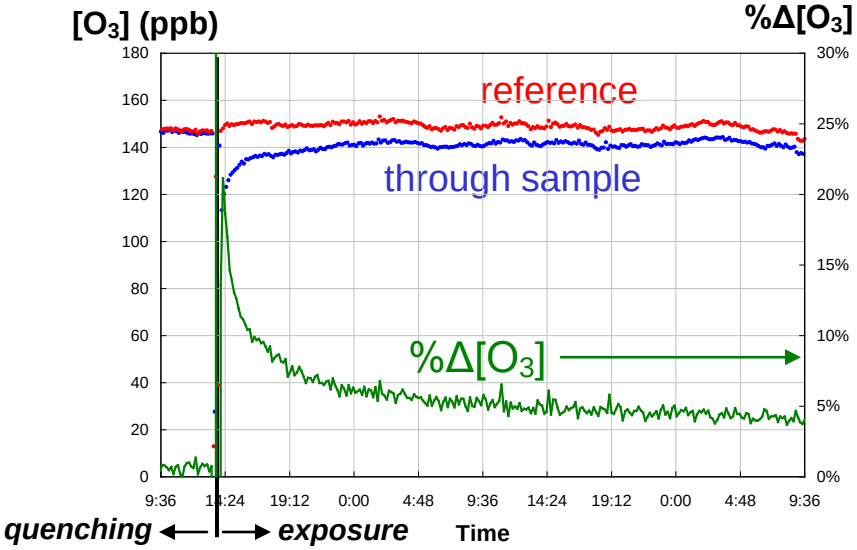

Figure 1. Ozone breakthrough curve under humidified air for synthetic media used in the Port of Oakland.

CONCLUSIONS

The results illustrate that very low levels of certain organic pollutants are being emitted upon ozone exposure in the presence of moisture and detailed emission dynamics can be captured well by PTR-MS method. Flow conditions in these experimens were more than one order of magnitude lower than typical HVAC conditions, but results can be extrapolated to higher airflows assuming that the reaction is not limited by mass transport.

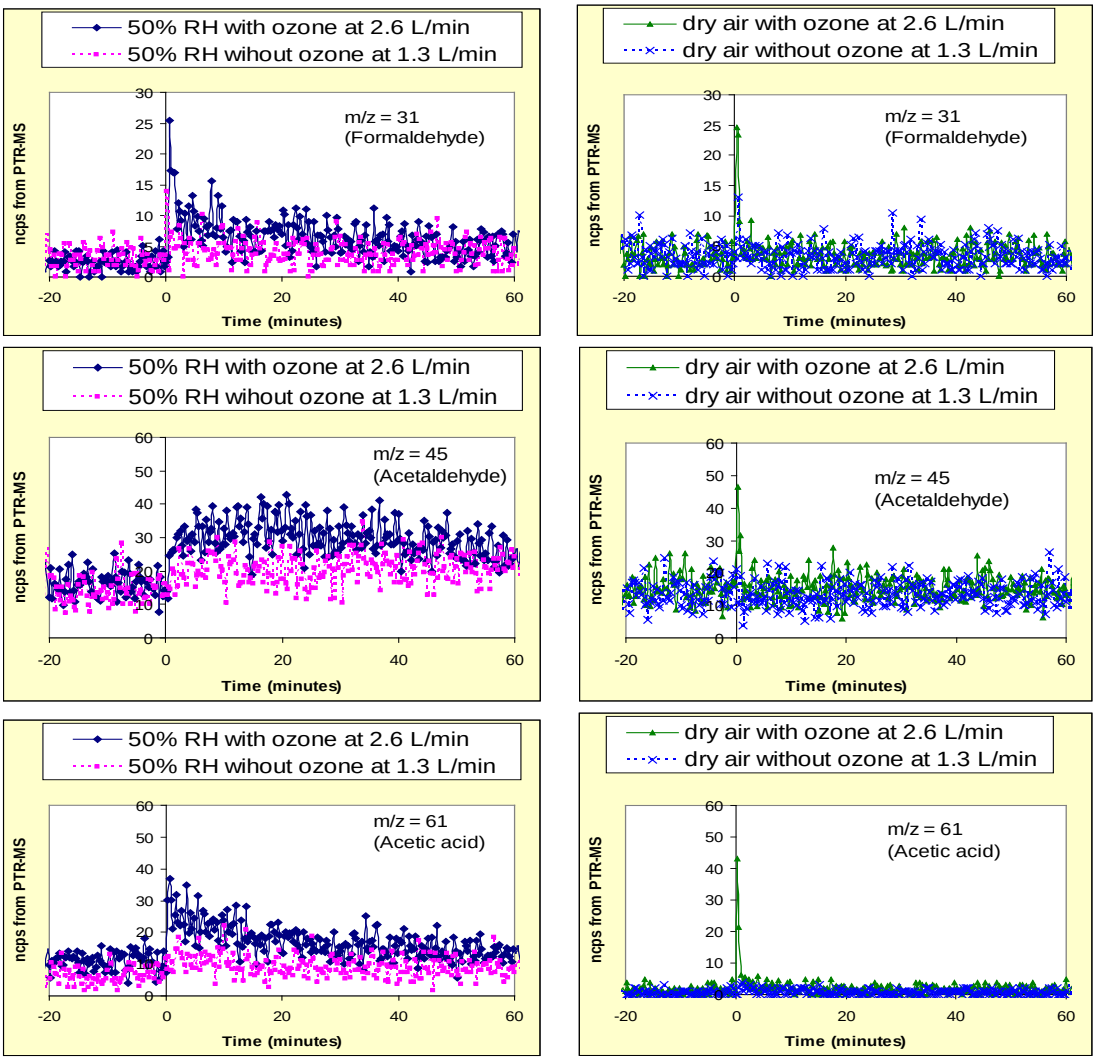

Figure 2. PTR-MS results for cotton/polyester media deployed at the Port of Oakland.

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