

Initial studies of oxidation processes on filter surfaces and their impact on perceived air quality

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ABSTRACT

Ozone concentrations were monitored up- and downstream of used filter samples at airflows of 1.0 and 0.2 l s⁻¹. The ozone concentration in the air upstream of the filters was ~75 ppb, while the concentration downstream of the filter was initially ~35% lower at 1 l s⁻¹ and ~55% lower at 0.2 l s⁻¹. Within an hour the removal efficiency had decreased to roughly 5% at 1 l s⁻¹ and 10% at 0.2 l s⁻¹. These filter samples were then placed in either nitrogen or ambient air for 48 h. Afterwards it was found that there was partial regeneration of the filter's ozone removal capabilities. In companion studies, human subjects assessed air passing through various filter samples. This occurred when samples were first placed in the test rig (each of three filters equivalent); immediately after the samples had sat for 48 h in ozone, nitrogen or air (ozone-treated worse than air-treated worse than nitrogen-treated); and after ambient air had passed through the 'treated' filters for 2 h. In the last case all filters were more acceptable than they had been right after the 48-h treatments. However, the ozonized filter was still the most polluting of the three.

INDEX TERMS

Organic compounds; Ozone; Perceived air quality; Ventilation filters

INTRODUCTION

Ventilation filters can be a significant source of indoor air pollution (Pejtersen *et al.*, 1989; Pasanen *et al.*, 1994; Clausen *et al.*, 2002) with consequent impact on SBS symptoms and performance (Wargocki *et al.*, 2003). In considering filters as a pollution source, it is helpful to be mindful of the fact that organic compounds are present in the air partition between the gas phase and the surface of airborne particles. The resulting distribution is a function of a compound's vapour pressure and is most significant for compounds with vapour pressures in the range of ~10⁻⁸ to 10⁻¹² atm. When a filter captures particles, this partitioning continues between the surface of the collected particles and organic compounds in the air stream (Weschler, 2003). Some of the organic compounds associated with the captured particles are in equilibrium with their counterparts in the air flowing through the filter. However, this equilibrium can be perturbed by changes in temperature, relative humidity and airborne organic concentrations. Each of these parameters changes fairly frequently in actual building HVAC systems, often on a time scale of hours. In some cases these changes will result in air stream concentrations that are too small to support the existing concentrations on the filters. Other organic compounds associated with captured particles may, at the time of their retention, already have higher surface concentrations than can be supported by that in the air stream (e.g., particles from combustion processes). Still other organic compounds are generated on the surface of filters through chemical transformations, and many of these newly formed products are absent in the air upstream of the filter. When the concentration of an organic compound on the surface of the filter is larger than its equilibrium concentration in the

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air stream (for any of the reasons outlined above), desorption will occur. Desorption can be a slow process; it may take hours or days to establish equilibrium (see Won *et al.*, 2000, 2001). Additionally, desorption is influenced by the rate at which air passes through the filter; Alm *et al.* (2000) and Strøm-Tejsen *et al.* (2003) have found that emissions of sensory pollutants from a filter are proportional to the flow rate.

Oxidation processes, especially those driven by ozone, are the dominant chemical transformations occurring on filter surfaces. A recent study carried out by Hyttinen *et al.* (2003) indicated that used air filters remove a fraction of ozone from the air stream (an average of 4–10% during a 6–9 h interval). Presumably, this removal is accompanied by the production of chemicals, some of which will subsequently desorb from the filter. The purpose of the present study is to further improve our understanding of oxidation processes occurring on filter surface and their impact on perceived air quality.

METHODS

Oxidation Processes on the Filter Surface

Ozone concentrations were monitored up- and downstream of used filter samples at two different airflows in a small-scale test rig (Figure 1). The test rig was situated in a 40 m³ low polluting office ventilated with outside air at 500 m³ h⁻¹. Filter samples (100 mm diameter) had been cut from a used 0.6 × 0.6 m² EU7 fibreglass filter. Four samples were examined, two at a nominal airflow (1.0 l s⁻¹) and two at a low airflow (0.2 l s⁻¹). After monitoring the ozone concentrations for approximately 1 h, the samples were placed in static atmospheres of either nitrogen or ambient air (ozone concentration <5 ppb) for 48 h. Up- and downstream ozone measurements were then repeated.

The ozone was continuously generated in a well-sealed glass box (200 l). Air containing ozone was delivered directly from the outlet of the glass chamber to the intake duct of the test rig via flexible duct. The ozone concentration upstream of the filter sample was held constant at ~75 ppb by a damper situated at the end of the flexible duct. The filter sample was located between two flanges. A frequency converter controlled a variable speed radial fan.

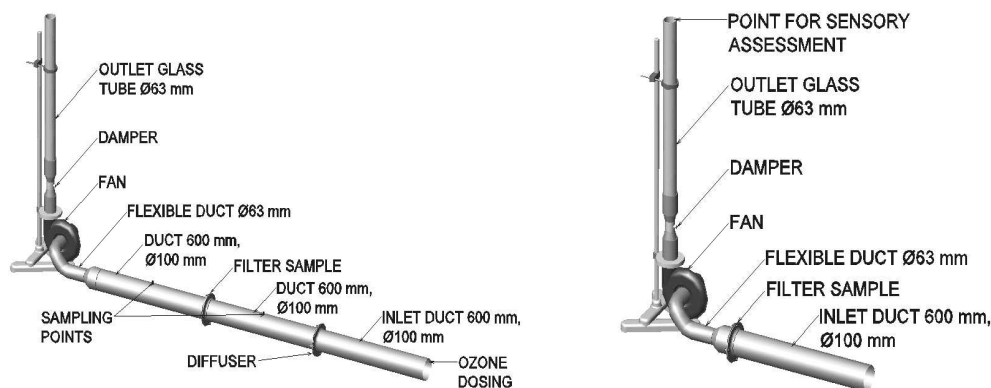


Figure 1 Test rig used for ozone consumption measurements.

Figure 2 Test rig used for sensory assessments by facial exposure

Upstream ozone concentrations were measured with a DASIBI 1003 AH ozone meter and downstream concentrations were measured with a SERES OZ 2000 ozone meter, both located outside the office. The sampling points were in the centre of the duct's cross-section.

For a given sampling time, the ozone removal efficiency (E) was determined as the upstream–downstream concentration difference divided by the corresponding upstream concentration. The upstream concentrations were based on trend-line values to avoid the noise of data collected with the upstream instrument. The initial removal efficiency (E_0) at the beginning of each measurement was based on the average of data collected during the first 72 s in order to reduce the influence of downstream instrument noise. The removal efficiency

at the end of each measurement (E) was based on the average of data collected during last 450 s. The decrease in removal efficiency followed a first order decay. The first order rate constant (k) for this decay slope was derived from plots of $\ln(E - E_0)$ versus time.

Effects on Sensory Assessments

To study the sensory impact of oxidation processes on filters, three identical small-scale test rigs for facial exposure (Figure 2) were built and used for sensory assessments of air flowing through various filter samples. The equipment was placed in a 30m³ stainless steel climate chamber ventilated with outdoor air (1500 m³ h⁻¹). Throughout the experiments the HVAC unit servicing the climate chamber did not contain any filters, and the temperature and humidity were held constant at 22°C and 40% RH. The airflow through the filter samples was adjusted to 1 l s⁻¹. The tested samples were taken from a 0.6 × 0.6 m² EU7 fibreglass filter previously used as outdoor air filter in a suburb of Copenhagen. The filter had been in continuous use (airflow of 3500 m³ h⁻¹) from 31 January until 6 May 2003. The total volume of air that had passed through the filter was 8 × 10⁶ m³.

Three used filter samples (100 mm diameter) were first ventilated in the test rigs for 48 h and then placed for an additional 48 h in separate 200-l glass chambers containing ozone, nitrogen or ambient air. An ozone concentration of around 400 ppb was maintained in the first glass box throughout the period. The second glass box was flushed with nitrogen and sealed after inserting the sample. The third glass chamber contained ambient air. Three sets of sensory assessments were conducted using Center-staff personnel: (1) before treatment in order to ensure that all three samples initially had equivalent effects on perceived air quality; (2) immediately after the treatment; and (3) after air had flowed through the filters for 2 h. Between 14 and 20 human subjects participated in each assessment. All assessments were randomized. The subjects used a continuous acceptability scale to evaluate the air quality. They made assessments one at a time, and there was at least 1 min between each assessment.

RESULTS

Figure 3(a) displays an example of ozone concentration measurements up- and downstream of a filter (sample 4 in Table 1) before and after sitting for 48 h in air. A low airflow (0.2 l s⁻¹) was used in this example. Figure 3(b) displays the corresponding ozone removal efficiency for the same filter sample. Initially, the concentration of ozone downstream was 49% of the upstream value. Over time the concentration difference decreased; the removal efficiency dropped from an initial 51% to approximately 8% after an hour. The filter then sat in air for 48 h. Upon re-evaluation the ozone removal efficiency was found to have increased from 8 to 34%. During the next 1.5 h the removal efficiency decayed to 9%.

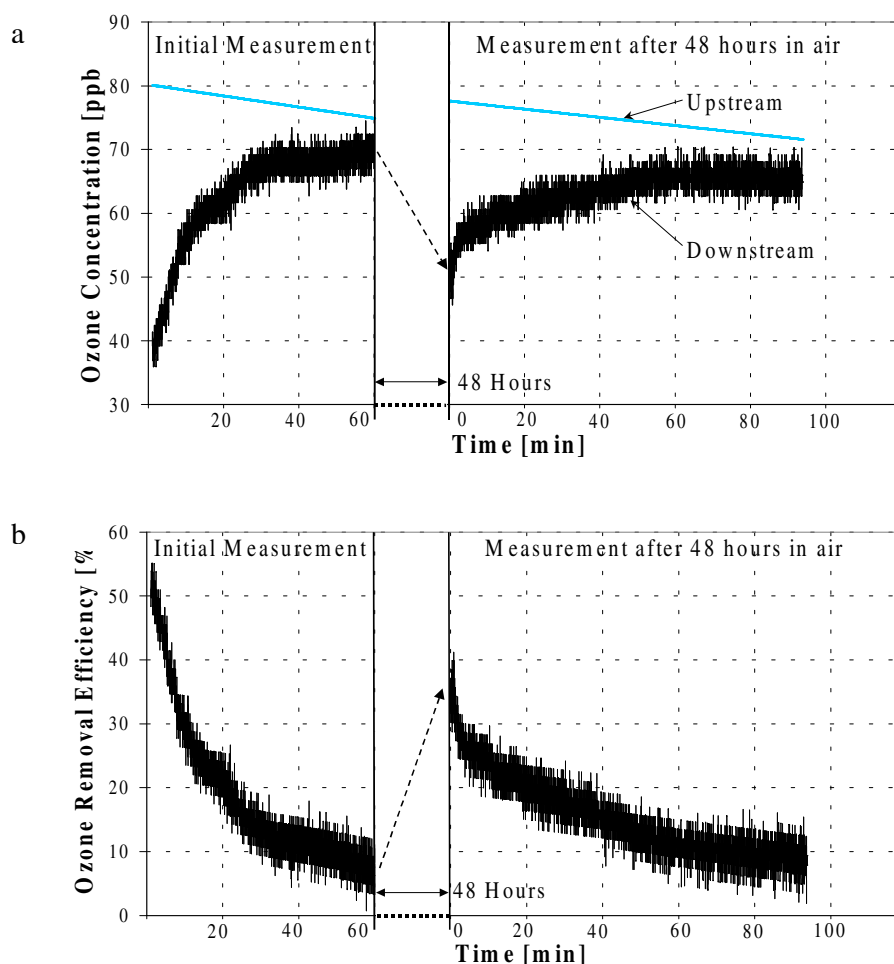


Figure 3 (a) Ozone concentrations upstream (trend line) and downstream of filter sample 4 versus time; airflow = 0.2 l s^{-1} ; after ~60 min the filter sat in air for 48 h before re-evaluation. (b) Corresponding ozone removal efficiency versus time.

Table 1 lists removal efficiencies as well as first order rate constants (k) for the initial decay of the ozone removal efficiencies for all tested filter samples. The average ozone removal efficiency at the beginning of each measurement (E_0) was higher at the low airflow than at the nominal airflow. This was true for both the initial measurements as well as the measurements conducted after the filters had sat for 48 h in air or nitrogen.

Table 1 Ozone removal efficiencies of the four filter samples at the beginning (E_0) and end (E) of the measurements both before and after filter treatment. First order rate constants (k) for the initial decay of the ozone removal efficiency are also listed

Sample	Airflow [L.s ⁻¹]	Initial Measurement			Placed for 48 hours in:	Subsequent Measurement		
		Removal Efficiency [%]		k [s ⁻¹]		Removal Efficiency [%]		k [s ⁻¹]
		Beginning (E ₀)	End (E)			Beginning (E ₀)	End (E)	
1	1	34	6	0,0018	nitrogen	17	4	0,0024
2	1	38	2	0,0014	air	16	2	0,0009
3	0,2	60	11	0,0012	nitrogen	41	13	0,0007
4	0,2	51	8	0,0011	air	34	9	0,0005

Figure 4 shows the results from the sensory assessments of air that had passed through the filters. The distribution of data obtained from the acceptability scales were tested for normality with Shapiro–Wilk's W test. All data were normally distributed and were tested by non-paired and paired t -test, where applicable. Assessments made before treatment revealed no differences among the three samples. In the assessments immediately following treatment the ozonized filter had the greatest impact on the quality of air passing through it. The degradation of perceived air quality was significantly greater than before this filter sample had sat in an ozone atmosphere ($p < 0.01$). Similar results were obtained for the air treated filter sample ($p < 0.05$), whereas the nitrogen treatment did not significantly change the impact of the filter sample on the perceived air quality ($p > 0.05$).

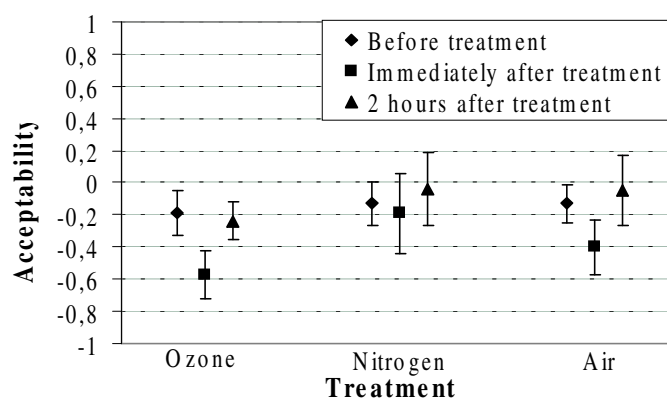


Figure 4 Acceptability of the air downstream of the filter samples; assessments (facial exposure) before, immediately after and 2 h after treatment. The mean value and the 95% confidence interval are shown.

After 2 h of ventilation, assessments of the samples indicated that all the filters had improved in comparison with their assessments immediately following the treatments. However, only in the cases of the ozone ($p < 0.01$) and air treated filters ($p < 0.05$) were the changes significant. The ozonized filter remained the most polluting of the three.

DISCUSSION

Ozone concentrations decreased as air passed through loaded fibreglass filters. This indicates that a combination of ozone consuming chemical reactions and catalysed ozone decomposition occurred on the surface of the loaded filters. Some of the organic compounds associated with the particles collected on the filter contain unsaturated carbon-carbon bonds (e.g., unsaturated fatty acids, terpenes and sesquiterpenes commonly found in plant waxes, pollen and vegetative detritus; Weschler, 2000; Hyttinen *et al.*, 2003). These compounds are likely responsible for a fraction of the observed ozone consumption since they react with ozone much faster than saturated organic compounds. However, ozone consumption is limited by the amount of such compounds on the loaded filter surface. In the depicted example (Figure 3) ozone removal decayed until it reached a steady-state value (after ~1 h). Organic compounds are not only found on the surface of the loaded filter (i.e. the surface of the collected particles) but also within the 'filter cake'. These compounds can neither be oxidized nor desorb from the filter until they have diffused to its surface. The present results suggest that under static conditions in relatively inert atmospheres, organics within the 'filter cake'

diffuse to the surface of the filter, re-generating the filter's ability to remove ozone. It is interesting to consider the results of Mysen *et al.* (2003) in light of this observation.

Sensory evaluations showed significant effects of ozone and air treatments, as well as ventilation, on the filter specimens. Presumably, oxidation products desorbing from the filter samples have a negative impact on perceived air quality. Many of the products of ozone-initiated chemistry are expected to be more sensory offending than their precursors (Weschler, 2000). In a nitrogen atmosphere oxidation processes are minimized.

CONCLUSION

Loaded particulate filters can remove ozone from the air that passes through them. The removal of ozone by a loaded filter decreases over time. However, static conditions promote the regeneration of a loaded filter's ability to remove ozone. Although removal of ozone is desirable, this process appears to be responsible for the generation of products that contribute to the degradation of perceived air quality.

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REFERENCES

- Alm, O., Clausen, G. and Fanger, P.O. (2000). Exposure-response relationships for emissions from used ventilation filters. *Proceedings of Healthy Buildings 2000*, Vol. 2, pp. 245–250.
- Clausen, G., Alm, O. and Fanger, P.O. (2002). The impact of air pollution from used ventilation filters on human comfort and health. *Proceedings of Indoor Air 2002*, Monterey, USA, Vol. 1, pp. 338–343.
- Hytinen, M., Pasanen, P., Salo, J. *et al.* (2003). Reactions of ozone on ventilation filters. *Indoor and Built Environment* **12**, 151–158.
- Mysen, M., Clausen, G., Bekö, G. *et al.* (2003). The influence of typical ways of operating an air-handling unit on the sensory pollution load from used bag filters. *Proceedings of Healthy Buildings 2003*, Singapore (in press).
- Pasanen, P., Teijonsalo, J., Seppänen, O. *et al.* (1994). Increase in perceived odor emissions with loading of ventilation filters. *Indoor Air* **4**, 106–113.
- Pejtersen, J., Bluyssen, P., Kondo, H. *et al.* (1989). Air pollution sources in ventilation systems. *Proceedings of CLIMA 2000*, Sarajevo, August, Vol. 3, pp. 139–144.
- Strøm-Tejse, P., Clausen, G., Toftum, J. (2003). Sensory pollution load from a used ventilation filter at different airflow rates. *Proceedings of Healthy Buildings 2003*, Singapore (in press).
- Wargocki, P., Wyon, D.P. and Fanger, P.O. (2003). Call-centre operator performance with new and used filters at two different outdoor air supply rates. *Proceedings of Healthy Buildings 2003*, Singapore (in press).
- Weschler, C.J. (2000). Ozone in indoor environments: concentration and chemistry. *Indoor Air* **10**, 269–288.
- Weschler, C.J. (2003). Indoor/outdoor connections exemplified by processes that depend on an organic compound's saturation vapor pressure. *Atmospheric Environment* **37**, accepted for publication.

Won, D.Y., Corsi, R.L. and Rynes, M. (2000). New indoor carpet as an adsorptive reservoir for volatile organic compounds. *Environmental Science & Technology* **34**, 4193–4198.

Won, D., Corsi, R.L. and Rynes, M. (2001). Sorptive interactions between VOCs and indoor materials. *Indoor Air* **11**, 246–256.