Ozone Removal, ultra fine particles, and VOC levels on sooty supply air filters in the presence of alpha-pinene

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SUMMARY

Ozone removal, concentration of ultra-fine particles (2 to 64 nm), and VOCs were measured on sooty ventilation filters. A F8 class filter loaded by diesel soot particles in a motor laboratory and a heavily loaded F5 class filter used for 8 months in a bus service terminal were used in the tests. In addition, both filters were saturated with alpha-pinene vapor to examine possible formation of secondary aerosols by heterogeneous reactions. Both filters removed ozone effectively in the beginning. Then, the removal efficiency declined until it reached a steady state level in three hours. Some particle formation was observed on both filters in the beginning of the test. Alpha-pinene disappeared from the air after F5 filter within three hours, whereas, its concentration remained almost on a constant level after the sooty F8 fine filter during the whole four hour test period.

INTRODUCTION

Ozone (O\textsubscript{3}) is a strong oxidation agent in ambient air and it can cause adverse health effects in sensitive people already at low concentrations [1]. Concentration of ambient ozone exceeds health based limit values in several days annually even in Finland where concentrations are lower than in more densely populated southern areas. Ozone reacts on dusty ventilation filters and small fraction of formaldehyde is produced in these reactions [2,3]. Diesel soot increases the removal of ozone. This is beneficial because of toxic effects of ozone. However, more irritating reactive species may form in these reactions.

Ultra fine particles (i.e. secondary organic aerosols, SOA) are formed when VOCs are partially oxidized in air [4]. The reaction products are partially condensed onto existing aerosols and partially form new particles. Ultra fine particles are especially formed in homogeneous reactions between terpenes and ozone in indoor air [5, 6]. These reactions and their health significance are under intensive study.

The aim of the present study is to investigate whether ozone and terpenes can react on sooty supply air filters. Ozone removal and possible formation of secondary aerosols are investigated.

METHODS

A F8 class fine filter loaded by diesel soot particles and a heavily loaded F5 class filter used 8 months in a bus service terminal in Kuopio were used in the tests. Fine (F8) filter materials were made sooty by a vertical 3-cylinder four-stroke turbo-charged 1123 cm\textsuperscript{3} (28.5 kW) industrial diesel-engine (Kubota V1105-TE) in laboratory at constant conditions. The engine
were fuelled with regular low sulfur diesel oil (sulfur content ≤ 8 mg/kg) (Fortum D1K C 0/-10) and lubricated with fully synthetic lubrication oil of quality SAE Diesel turbo 5W-40 (Valvoline). Particle size distributions and mass concentrations of diesel soot in the dilution tunnel were analyzed by L-SMPS (Long-Scanning Mobility Particle Sizer) system consisting of a DMA3071 differential mobility analyzer (size range 15-740 nm) and CPC 3022A condensation particle counter (Thermo Systems Inc.). The sampling time was one hour. The dilution tunnel was designed according to the ISO-8178 standard [7]. Surface areas of the soot/dust samples were analyzed by BET-method (Micromeritec, model 2200) [8].

Filters were exposed in 48 L volume chamber (steel and glass) which contained 3 ml of alpha-pinene (6 petri dishes at the bottom of chamber 0.5 ml of alpha-pinene/dish). Filters were kept in the chamber for a three days to assure their saturation to the model compound.

Sooty filters were installed into a small scale ventilation system using compressed air. Compressed air was first cleaned from VOCs and NOx by activated carbon and Purafil filtration. The face velocity of air was 0.07 m/s on the filter and it was controlled by mass flow meters. Ozone was produced by a UV lamp (5W) and its concentration was adjusted to 100-250 ppb. Ozone was measured continuously (Dasibi 1008-RS) 0.5 m before and after the filters. The accuracy of the O₃ analyzer was reported to be ±0.5 ppb by the manufacturer. The device was calibrated by the Calibration Laboratory of the Finnish Meteorological Institute and its functionality was checked with an in-built calibration system. Data logger (Grant) was used to collect the measured data (Ozone, temperature, and RH).

Particle size distributions were analyzed by TSI (Thermo Systems Inc.) N-SMPS (Nano-Scanning Mobility Particle Sizer) system consisting of a DMA3085 differential mobility analyzer (size range 2-64 nm) and CPC 3025A condensation particle counter. Particle concentrations were measured in the middle of a duct about 0.5 m upstream and downstream of the filters. Sampling location was changed by using a 3-way ball valve. A half minute stabilization and three minute analyzing periods were used for a typical data collection cycle. Transport efficiency of particles undergoing diffusional deposition flowing through a sampling tube was estimated to be over 90% for the particles greater than 10 nm [9].

VOCs (Tenax GR) (sampling time 10-30 minutes) were collected simultaneously 0.5 m upstream and downstream of the filters. Samples were analyzed with an automated thermal desorption coldtrap injector (Perkin Elmer ATD 400) connected to a gas chromatograph (HP 6980) equipped with a mass selective detector (MSD 5973). The ozonolytic decomposition of the sampling cartridges was prevented by potassium iodide coated copper tubes. The analysis method has been described previously [3].

RESULTS

Ozone was removed more effectively on the sooty F8 filter than on the sooty F5 filter. Mean removal of ozone was 44% on the F8 filter and 22% on the F5 filter. Also, unused F8 filter (saturated with alpha-pinene) removed ozone effectively in the beginning of the ozone exposure, but the removal decreased to 12% within two hours and was less than 10% after four hours. Typical ozone removal curves on sooty F8 and F5 filter are presented in figure 1.
Figure 1. Removal of ozone (%) on sooty F8 and F5 filters saturated with alpha-pinene, face velocity during the test was 0.07 m/s. Conditions in F8 test: O$_3$ upstream 182±7 ppb, downstream 103±36 ppb, mean removal of ozone (3 hours) 44±19%, RH 10±1%, temp. 23.5±0.3°C; in F5 test: O$_3$ upstream 198±5 ppb, downstream 156±25 ppb, mean removal of ozone (3 hours) 22±11%, RH 16±4%, temp. 24.0±0.2°C.

Effective surface area of the dust taken from the filters in bus terminal was ca. 4 m$^2$/g of dust whereas soot made in motor laboratory had as large effective area as 100-103 m$^2$/g. Properties of soot also affected to the adsorption of the alpha-pinene onto the surfaces of the sooty filter material. Concentration of alpha-pinene decreased from 12 µg/m$^3$ to undetectable approximately in three hours after the sooty F5 whereas it remained at a relatively constant level of 41±4 µg/m$^3$ after the sooty F8 filter during the whole test period of four hours.

Particle concentrations were slightly higher downstream of the alpha-pinene saturated F5 filter (figure 2). However, there were no clear particle formation peaks during the test period of four hours.
Figure 2. Particle concentrations upstream and downstream of a F5 filter (loaded for 8 months in a bus service terminal) and alpha-pinene concentration downstream of the filter. O₃ concentration 198±5 ppb upstream, 156±25 ppb downstream. Face velocity on the filter was 0.07 m/s.

Particle concentrations behaved similarly upstream and downstream of the sooty F8 filter (saturated with alpha-pinene). Slightly higher concentrations were occasionally observed downstream of the filter. The unused F8 (saturated with alpha-pinene) filter also gave similar results. When there was no ozone present, the particle concentration was negligible, only single particles were detected downstream of the filter and no typical size distribution curves were found. Overall, no clear formation of the ultra-fine particles was detected. However, temporary formation of ultra-fine particles was observed in the beginning of a few tests. An example of such phenomenon is given in figure 3. The duration of the peak was less than 3-4 minutes.
Figure 3. An example of temporary particle formation after sooty F8 filter in the beginning of ozone feeding (saturated with alpha-pinene) (2-64 nm). O₃ concentrations: 115±10 ppb upstream and 103±10 ppb downstream. Temperature 21.6±0.3°C, RH 1.4%.

DISCUSSION

Ozone was removed on sooty filters. In agreement with previous studies [10, 3], the reaction was strong in the beginning and decreased then rapidly during the first few hours. Removal of ozone was also observed on unused F8 filter.

Soot obtained from the bus service terminal had much smaller effective surface area than soot collected in the motor laboratory. This also affected the adsorption and desorption of alpha-pinene and removal of ozone on filters. This is consistent with the fact that effective area is of crucial importance in surface reactions. In addition, bus terminal filters were accumulated 8 months; and ageing of the particles may have changed their reactivity.

Sudden peak emissions of particles were occasionally observed at the start of ozone feeding when filters were still almost saturated with alpha-pinene. The results suggest that formation of secondary aerosols is not practically important on supply air filters. Pinto et al. [11] did not observe any secondary aerosol formation when terpenes were emitted into a test chamber from the plants and ozone concentration was 100 ppb, whereas clear particle formation was observed at higher ozone concentrations (200 and 400 ppb). Concentrations of the six terpenes were 2-15 µg/m³ (alpha-pinene and limonene were the most abundant compounds). It should be noted that average residence time of air in the chamber was about 17 minutes which is much higher than in the present study where possible particle formation time was only a few seconds.
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REFERENCES