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MARKO HYTTINEN

The Formation of Organic Compounds and Subsequent Emissions from Ventilation Filters

Doctoral dissertation

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ABSTRACT

The objective of the study was to investigate the quality and quantity of emissions from used supply air filters by chemical and sensory methods. The effects of temperature, relative humidity (RH), and ozone on the pollutant emissions were examined. In addition, the contribution of diesel soot to the removal of ozone on filters was studied. The formation of organic emissions was investigated with laboratory and field tests.

The sorption capacity of the filter dust was poor in tests made with model compounds at constant conditions. The specific surface area of the dust was also found to be low, which supports the results of the tests. Peak emissions of the model compounds and aromatic hydrocarbons were observed when RH was suddenly increased.

In the thermodesorption tests of the filter dust, the compounds emitted included aldehydes, aliphatic and aromatic hydrocarbons, carboxylic acids, ketones, nitrogen-containing organics, and terpenes. Some emissions occurred already at room temperature, but the emissions increased substantially when temperature exceeded 100°C. Among the compounds emitted, aldehydes and carboxylic acids have low odor threshold values and they probably contribute to the perceived stuffy odor originated from the used filters.

The supply air filters removed a fraction of ozone (O₃). No removal of O₃ was observed in clean pre-filters; however, some O₃ was removed in unused fine filters. Dust which had accumulated on the filters increased the removal. The removal of O₃ was highest at the start of exposure but then reached an almost steady state value within a few hours, typically 5-10% of the maximum removal. Ozone was removed effectively on sooty filters with simultaneous production of formaldehyde. The formation of acetaldehyde and some longer aldehydes was also observed during O₃ exposure. With high RH of air, the removal of O₃ increased on the filters.

The pre-filter was the main odor source in air handling units. However, a sudden increase in the RH increased the odor emissions mainly from the fine filter. The effect of the elevated air humidity was again temporary and the intensity of the odor decreased to the initial value within 30 to 60 minutes.

The sorption phenomenon is negligible at constant conditions in air handling unit. The formation of odorous compounds probably occurs mainly by oxidative processes. The chemical analyses suggest that aldehydes especially contribute to odor emission. The effect of RH on the emissions is short-term but it might lead to odor emissions when the weather changes. Removal of the O₃ on ventilation filters is beneficial, since O₃ has toxic effects. However, this benefit is at least partially lost due to the reactive and potentially harmful oxidation products formed in the reactions.

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CAB Thesaurus: air quality; air pollution; air pollutants; buildings; ventilation; air filters; odours; dust; ozone; organic compounds; volatile compounds; temperature; relative humidity; sorption; desorption; oxidation; aldehydes; carboxylic acids



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Kuopio, 2007

Marko Hyttinen

ABBREVIATIONS AND DEFINITIONS

Adsorption	A physical process in which a molecule of a vapor or gas (adsorbate) is condensed on and taken up by the surface of the porous material (adsorbent) such as silica gel or activated carbon
AHU	Air handling unit
Air filter efficiency	The ability of a filter to remove particles from the air, expressed in terms of the contaminant concentrations upstream and downstream of the filter. It may be obtained by a) Weight test, b) Dust spot test, c) Arrestance test, or d) Particle counting.
ASHRAE	American Society for Heating, Refrigerating and Air-conditioning Engineers
Average arrestance (Am)	Ratio of the total amount of loading dust retained by the filter to the total amount of dust fed up to final pressure drop. Average arrestance is used for classification of G-filters (expressed in %)
Average efficiency (Em)	Weighted average of the efficiencies for the different specified dust loading levels up to final pressure drop. Average efficiency is used for classification of F-filters (expressed in %)
CO	Carbon monoxide
CO ₂	Carbon dioxide
DEHS	Liquid DiEthylHexylSebacate for generating the test aerosol
Desorption	The process of removing a sorbed substance by the reverse of adsorption or absorption.
DNPH	2,4-dinitrophenylhydrazine
Dust holding capacity	The amount of dust, by weight, retained by a filter under a standard test such as EN779.
EC	Elemental carbon
EPA	Environmental Protection Agency
EXPOLIS	Air pollution exposure distributions within adult urban populations in Europe - study.
F6	Fine filter, average (Em) efficiency (0.4µm), 60% ≤ Em < 80% according to the EN 779:2002

F7	Fine filter, average (Em) efficiency (0.4µm), 80% ≤ Em < 90% according to the EN 779:2002
F8	Fine filter, average (Em) efficiency (0.4µm), 90% ≤ Em < 95% according to the EN 779:2002
G3	Pre-filter, average (Am) arrestance (synth. dust), 80% ≤ Am < 90% according to the EN 779:2002
G4	Pre-filter, average (Am) arrestance (synth. dust), 90% ≤ Am according to the EN 779:2002
HEPA	High efficiency particulate air filter
HPLC	High performance liquid chromatography
HS-GC-MS	Headspace - gas chromatography - mass spectrometer
HVAC	Heating, ventilating and air-conditioning
IAQ	Indoor air quality
MSD	Mass selective detector
NO _x	Nitrogen oxides
OC	Organic carbon
O ₃	Ozone
PAH	Polycyclic aromatic hydrocarbons
PAP	Perceived air pollution
PD	Percentage of dissatisfied
PM _{2.5} , PM ₁₀	Particulate matter (with aerodynamic cut size diameter smaller than 2.5, 10 µm). Particles consisting of solid and liquid materials, suspended in the air
RH	Relative humidity of air (%)
SVOC	Semi volatile organic compound, boiling-point range 240-260°C to 380-400°C
TCT-GC-MS	Thermodesorption/cold trap - gas chromatography - mass spectrometer
TVOC	Total volatile organic compounds
VOC	Volatile organic compound, boiling-point range 50-100°C to 240-260°C
VVOC	Very volatile organic compound, boiling-point range <0 to 50-100°C

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications, referred to the text by their Roman numerals.

- I Marko Hyttinen, Pertti Pasanen and Pentti Kalliokoski, 2001, Adsorption and desorption of selected VOCs in dust collected on air filters, *Atmospheric Environment*, 35, 5709-5716.
- II Marko Hyttinen, Pertti Pasanen, Jutta Salo, Marko Björkroth, Matti Vartiainen and Pentti Kalliokoski, P, 2003, Reactions of ozone on ventilation filters, *Indoor + Built Environment*, 12, 151-158.
- III Marko Hyttinen, Pertti Pasanen and Pentti Kalliokoski, 2006, Removal of ozone on clean, dusty and sooty supply air filters, *Atmospheric Environment*, 40, 315-325.
- IV Marko Hyttinen, Pertti Pasanen, Marko Björkroth and Pentti Kalliokoski, 2007, Volatile organic compounds and odors released from the ventilation filters, *Atmospheric Environment*, 41, 4029-4039.



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1 INTRODUCTION

The purpose of a ventilation system is to ensure good indoor air quality by providing fresh air and diluting the air pollutants produced indoors. Minimum allowed ventilation rates are specified in national and international building codes and guidelines. Human bioeffluents, usually characterized by carbon dioxide, have conventionally been the main criterion for the minimum ventilation rates. In addition, ventilation is needed for controlling other indoor air pollutants such as volatile organic compounds (VOCs) emitted from building materials, cleaning agents, furniture. Moreover, VOCs are formed by human activities (e.g., cooking and smoking).

Ventilation can be achieved naturally, without a fan, or mechanically. The main parts of a typical mechanical supply air ventilation system used in public buildings are an outdoor air intake, filtration unit, heating and cooling coils, supply air fan, duct work, and terminal device. Filtration is needed to keep the ventilation unit clean. Without effective filtration of supply air, particles and dust in ambient air would soil the air handling unit and possibly cause a malfunction. Naturally, the removal of particles is also beneficial for indoor air quality (IAQ).

Filtration has usually been accomplished in public buildings by mechanical filters including at least F7- or F8-class fiberglass fine filters. In addition, a two-stage filtration technique where a pre-filter (G3 or G4 class polymer based filter) has been added before the fine filter to remove coarse particles is common in urban environments. The efficiency of an unused G4 pre-filter is ca. 65% for 1-5 μm particles, and that of a F7 filter is ca. 80% for smaller particles from 0.4 to 1 μm (Hagström et al., 1996). The use of high efficiency particulate air filter (HEPA) or even gas filtration is sometimes justified in spaces where extremely clean air is needed (e.g., hospitals and laboratories) in spite of the high energy costs involved.

Although a ventilation system is essential for improving indoor air quality, many studies have found that it is a cause of unpleasant odor and discomfort (Fanger et al., 1988; Finke and Fitzner, 1993; Björkroth et al., 1997c). The prevalence of non-specific symptoms has been reported to be higher in buildings with mechanical ventilation than in naturally ventilated buildings. Dusty supply air filters are usually the main source of odors (Hujanen et al., 1991,

Finke and Fitzner, 1993; Pasanen et al., 1994; Björkroth et al., 1997a). The odors released from the filters have been found to increase rapidly during the first three months after installing new filters and then level off (Pasanen et al., 1994). In addition, dusty and oily ducts increase the odor load of the ventilation system (Björkroth et al., 1997b). As a result of problems associated with the poor indoor air quality more attention has started to be paid to the hygienic aspects of HVAC systems.

Filter dust contains a complex mixture of inorganic and organic components, some of which are odorous and irritating. It is not yet certain which particular compounds are main causes of the odors (Björkroth et al., 1997a; Hyttinen et al., 2003). In general, reactive VOCs such as polar and unsaturated hydrocarbons cause more sensory effects than non-reactive compounds (Wolkoff et al., 1997; Wolkoff et al., 2006).

Chemical reactions occur on ventilation filters, for example diesel soot accumulated on the filter reacts with ozone (Metts et al., 2005). It has been suggested that chemical reactions between ozone, other reactive gases (such peroxides and OH radicals) and impurities inside the ventilation unit can decrease the supply air quality (Fick et al., 2002; 2003; Bekö et al., 2006). The concentration of troposphere ozone has increased in the past decades and nowadays exceeds the health-based limit value of 120 ppb, even in a northern and relatively non-polluted country like Finland, on several days annually. Ozone can cause health effects in sensitive people at even lower concentrations (US EPA, 1996).

The main source of indoor ozone is generally outdoor air, though laser printers and copy machines may also generate it. The indoor ozone concentration is only around 20-70% of the outdoor air concentration because of its reactions on interior surfaces (Sabersky et al., 1973; Weschler, 2000). The formation of secondary aerosols due to reactions between ozone and terpenes in indoor air has also been detected. In spite of the large surface area involved, the removal of ozone is reported to be negligible on ventilation ducts (Morrison et al., 1998).

The focus of the present work is on the emissions and oxidative reactions occurring on supply air filters used in public buildings. The effects of temperature and relative humidity (RH) on the emissions of organic compounds and on the reactions of ozone on dusty and sooty filters were also studied. The reasons for stuffy odors emitted from the used filters were evaluated.

2 REVIEW OF THE LITERATURE

2.1. Ventilation system

Ventilation of buildings can be achieved naturally or mechanically. Natural ventilation operates without a fan and is based on the indoor-outdoor pressure difference. The tightness of the building and weather greatly affect the air change rate, so it is difficult to control the performance of natural ventilation (Seppänen, 1996), and mechanical ventilation is required in all public buildings in Finland (D2-2003).

A fan is used to move air in a mechanical ventilation system. Air conditioning is a mechanical ventilation system where the temperature (especially if cooling is provided) and humidity of the air can be controlled. A more extensive term for all mechanical ventilation systems is heating, ventilation, and air conditioning (HVAC). Such a system typically consists of an outdoor air intake, filtration unit, heating and cooling coils, supply air fan, duct work, and terminal device. In some cases, HVAC also includes a humidification or dehumidification unit and an air recirculation system. In addition, the thermal energy of the exhaust air is usually transferred to the supply air by a regenerative or recuperative heat exchanger.

The location of the outdoor air intake is important for supply air quality because it largely determines to what extent pollution from traffic and other sources is transferred to the supply air. According to the Finnish building code (D2), the minimum distance from the air intake to the pollution sources such as parking lots or garbage cans is eight meters, and the minimum height of the air intake is two meters above ground level.

Heating and cooling coils located usually after the filters, are used to control the temperature of supply air. In cooling coils, water, brine or glycol are used as chilled liquids. Water condensed from the air is collected into a drain pan under the coil. Humidifiers are sometimes installed into the air handling unit and they are used in cold climates during the heating season. Steam, a heated pan, spray, and atomizing humidifiers can be used. To avoid contamination of the humidifiers, they need regular and careful maintenance.

A supply air fan is located after the filtration, temperature and humidity controlling units. A sound attenuator is usually installed after the fan. It can be made of mineral or glass fibers and if improperly installed or maintained, it may transport fibers to occupied areas and cause irritation symptoms (Ludwig, 2001).

2.2. Ventilation filters

To keep the ventilation unit and indoor air clean, supply air needs to be filtrated. Filtration has usually been accomplished by mechanical filters. Filters can be made of glass fibers, synthetic plastic fibers, natural cellulose, or combinations of these. Glass fibers and synthetic plastic fibers (polyester, polypropylene, polyamide and polycarbonate) are the most commonly used filter materials. In addition, galvanized and stainless steel has been used for making reusable coarse filters. Pressure drop over the filters and particle collection efficiency are the most important performance parameters for filters (McDonald and Ouyang, 2001). As particles attach on the filter media, they increase the pressure drop and energy cost, but also participate in the collection of other particles.

Filters are categorized as coarse and fine filters. Coarse or pre-filters collect large particles and are used to increase the life span of the more expensive fine filters. Coarse filters are made of thick fibrous material and are usually flat panels or bag-filters. The air velocity is high, 0.2-2 m/s, and the pressure drop over the coarse filter is typically 25-250 Pa depending on the air flow rate and on the dust loading on the filter (Seppänen, 1996).

Fine filters can be bag, pocket, or pleated filters. The diameter of the fiber is thin (a few micrometers), and the distance between fibers is about 10 μm . To ensure tightness, the filter pockets are usually glued to the frame. The efficiency of the filter depends on the diameter of the fiber, the compactness of the material, and the air velocity. Collection efficiency can be enhanced by using small fibers and a slow air velocity. The depth of the filter is 50-1000 mm and the air velocity through the filter media is 0.02-0.1 m/s. The pressure drop is 12-250 Pa for clean filters, and 125-500 Pa for dirty ones (Seppänen, 1996). The filters must be replaced when the pressure loss reaches a specified final pressure loss or after a maximum operating period of 8760 hours (Eurovent/Cecomaf, 1999). However, the most economical final pressure drop is much lower than those used in the classifications. A life cycle cost analysis gives a final pressure drop of 100-200 Pa as optimum (Gustavsson, 2002). Typically, filters are changed at least once a year. For hygienic reasons, it is recommended to change filters

after the dusty season (spring dust, pollen, spores) in the fall (Eurovent/Cecomaf, 1999). For higher hygienic demands, it is also advisable to change filters after the heating season in the spring to eliminate odors from combustion products (Eurovent/Cecomaf, 1999).

2.3.1 Classification of filters

Filters are ranked according to their particle collection efficiency. In the revised EN 779 method, fine filters are classified in terms of the penetration of liquid diethylhexylsebacate (DEHS) particles of 0.4 μm diameter (EN 779: 2002). Filters with an average efficiency value less than 40% are classified as coarse (symbols G1-G4). The classification of coarse filters is based on their average arrestance with the loading dust. Fine filters (symbols F5-F9) have an from 40% to over 95% for 0.4 μm diameter particles. The filter classification according to the EN 779 method is presented in Table 1.

Table 1. Classification of filters (EN 779:2002)

Filter type	EN 779 class	Average (Am) arrestance (synth. dust), %	Average (Em) efficiency (0.4 μm), %	Initial* / Final P loss, Pa
Coarse Filters	G1	$50 \leq Am < 65$	-	- / ≤ 250
	G2	$65 \leq Am < 80$	-	- / ≤ 250
	G3 (synth)	$80 \leq Am < 90$	-	40 / ≤ 250
	G4	$90 \leq Am$	-	45-65 / ≤ 280
Fine Filters	F5	-	$40 \leq Em < 60$	50-73 / ≤ 450
	F6	-	$60 \leq Em < 80$	65-74 / ≤ 450
	F7 (synthetic and glass fiber)	-	$80 \leq Em < 90$	75-109 / ≤ 450
	F8 (synthetic and glass fiber)	-	$90 \leq Em < 95$	115-142 / ≤ 450
	F9 (glass fibre)	-	$95 \leq Em$	142 / ≤ 450

The method used to determine the performance criterion of the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE 52.2 standard) is similar to the European test methods. Corresponding European and American filter classifications are presented in Table 2. The earlier Eurovent 4/9 classification is also presented in the table.

Table 2. Filter classification by three different methods

	EUROVENT 4/9 class	EN 779 class	ASHRAE 52.2
Coarse filters	EU1	G1	MERV 1
	EU2	G2	MERV 2-4
	EU3	G3	MERV 5
	EU4	G4	MERV 6-7
Fine filters	EU5	F5	MERV 8-11
	EU6	F6	MERV 11-12
	EU7	F7	MERV 13-14
	EU8	F8	MERV 14-15
	EU9	F9	MERV 15-16

Filters are selected so that they fulfill the demands for indoor air quality and the legislative guidelines. According to the Finnish D2 building code, the particle efficiency should be at least 80% for the particles of 1 μm diameter in urban areas (D2-2003). In practice, this is accomplished by a fine filter ranked as F7. The use of G4 filters is sufficient outside the urban and industrial areas.

2.4 Oxidative reactions (Ozone)

2.4.1 Properties of ozone

Ozone (O_3) is a colorless gas and reactive oxidant. It plays an important role in the formation of reactive hydroxyl (OH) and nitrate radicals (NO_3) and secondary aerosols in the atmosphere (Atkinson, 2000; Jacob, 2000; Wainman et al., 2000). Ozone has a pungent odor with a threshold value of 40-70 ppb (Devos et al., 1990). The main sources of ambient ozone include air streams from the stratosphere to the troposphere and photochemical reactions between nitrogen oxides and VOCs (Jacob, 2000). Especially as a consequence of the later reason, ambient O_3 concentration has increased from 10-15 ppb to 30-40 ppb during the last hundred years (Seinfeld and Pandis, 1998). Recent measurements show that there has been an approximately 0.5-2% rise per year in O_3 concentration in the northern hemisphere (Vingarzan, 2004). The development of combustion technology and fuels has decreased NO_x emissions in the western world. However, traffic and industry are increasing very fast especially in Asia, so it is expected that tropospheric ozone concentrations will remain high.

In Finland, O_3 concentration has been monitored by round-the-clock measurements in several places. The highest one hour mean concentrations of O_3 have been 145-188 $\mu\text{g}/\text{m}^3$ (73-94

ppb) in the spring and summer in Helsinki, whereas the concentration has been typically 19-62 $\mu\text{g}/\text{m}^3$ (10-31 ppb) in winter (Myllynen et al., 2006).

2.4.2 Health effects

Ozone may have adverse health effects even at low concentrations (EPA, 1996). When inhaled, it can irritate the respiratory system and damage the lungs. It may also worsen chronic respiratory diseases such as asthma. In addition, many products formed in the reactions between ozone and VOCs are more irritating than their precursors (Wolkoff et al., 1999; 2000; Weschler, 2000). A health-based limit value of 120 $\mu\text{g}/\text{m}^3$ (60 ppb) has been presented by the WHO, and the Finnish occupational exposure limit value is even lower, 100 $\mu\text{g}/\text{m}^3$.

2.4.3 Ozone in ventilation system

The change in the concentration of ozone due to ventilation ducts is usually negligible: a decrease of 0.1% has been reported (Morrison et al., 1998). Nevertheless, exposure to ozone has been reported to increase the emissions of aldehydes from a duct liner, duct sealing caulk, and a neoprene gasket (Morrison et al., 1998).

Ozone removal in a fiber glass-lined duct (a resin coating was applied to attenuate noise) was measured to be 9% in the beginning, but only 4% after ten days. Dusty ventilation filters can also be a site for oxidative reactions. Supply air filters can contain up to 1000 grams of dust, and in spite of the low specific surface area of the dust, it provides a medium for ozone to react.

Diesel soot particles are commonly present in ambient urban air and are filtrated from the supply air by fine filters. Soot particles have an agglomerate structure and a large specific surface area. Soot reacts effectively with ozone, but the reaction mechanism is not fully understood (Metts et al., 2001). The decomposition of ozone on soot has been suggested to consist of a fast surface reaction followed by slow catalytic destruction, and finally surface passivation of the soot particles (Kamm et al., 1999). In these oxidation reactions, carbon dioxide is of the main product (Disselkamp et al., 2000). In addition, the formation of non-volatile surface oxidation products has been detected as the mass increases (Smith and

Chughtai, 1996). Mass increase is probably related to the functional groups which have been formed on the surface of the soot, in a similar fashion as on the surface of the activated carbon while exposed to ozone (Lee and Davidson, 1999).

2.5 Sensory methods for air quality evaluation

Olfactory methods have been used to evaluate the acceptability and intensity of odors inside the buildings and ventilation systems (Fanger et al., 1988; Bluysen, 1990; Pejtersen et al., 1991; Björkroth et al., 1997a,b,c.). Odor perception is a complicated process which is influenced by several variables including the concentration and properties of the odorous compounds, and human physiology. The perceived odors indoors or in ventilation air are usually caused by tens to hundreds of different compounds, and every odorant molecule activates several odorant receptors (Buck and Axel, 1991). The "odorant pattern" formed is the basis for our ability to recognize and remember approximately 10 000 different odors (Buck and Axel, 1991). The human nose is sensitive and can detect odors at concentrations below the detection limits of most chemical analyzers. Therefore, chemical methods may not reveal anything unusual in the indoor air even though something clearly appears in a sensory evaluation. However, the repeatability of sensory methods may be poor because the sensitivity and accuracy of the olfaction system vary with time. These problems can be reduced by using a trained sensory panel and standardized methods or an untrained panel with a high number of panelists.

2.5.1 Odor threshold value

The odor threshold value is the lowest concentration of a substance which can be smelled. It is measured by diluting the sample with clean air until half the members of a sensory panel no longer detect the odor or irritation (ECA, 1999, Report no 20). However, the method does not give any information on the perceived intensity above the threshold level. In addition, the results vary with the measurement technique, purity of the chemical substances, quality of the olfactometer, and the number and individual differences of the panelists. Therefore, a high number of panelists is needed to obtain reliable results. Because of these problems, there is a large variation in odor threshold values for single compounds reported in the literature.

2.5.2 Trained panels

Panelists have been selected for a trained sensory panel according to their performance in an odor detection test and they have been instructed to evaluate the odors using the same scale. Panelists are expected to remember the odor scale, but a sensitive olfaction system is not necessary. Panelists "calibrate" their noses with a series of concentrations of a reference solvent (usually acetone) before the sensory evaluations. Discussion of the results with other panelists is not allowed during the evaluation. Before each judgment, the panelists should be exposed to pure air (i.e., fresh outdoor air) for some minutes to avoid adaptation effects. The method was originally developed by Ole Fanger who also coined the term "olf" to express the emission rate of air pollutants (bioeffluents) from a standard person (Fanger, 1988). One decipol is the pollution caused by one standard person (one olf) when ventilated by 10 L/s of unpolluted air. The basic aim is to evaluate perceived air pollution (PAP), i.e., how annoying the odor is. Fanger (1988) also determined the percentage of dissatisfied panelists out of 168 as a function of the perceived air pollution (in decipols) based on the bioeffluents from more than one thousand occupants. Figure 1 shows the connection between the perceived air quality and proportion of dissatisfied evaluators. Although the method is practicable, it might be difficult for the panelists to distinguish between intensity, quality, and acceptability. For example, cultural and individual differences influence the annoyance of the odor. It was also assumed that emissions are additive, but this is not necessarily so (see 2.4.2). Consequently, the method was later modified in the AIRLESS project so that the panel was only instructed to evaluate the odor intensity. Otherwise, the same acetone scale was still used. The upper limit value is 20 in the new method, whereas there was no maximum limit value in the original version: the number of panelists was typically 12-14 subjects in the AIRLESS project.

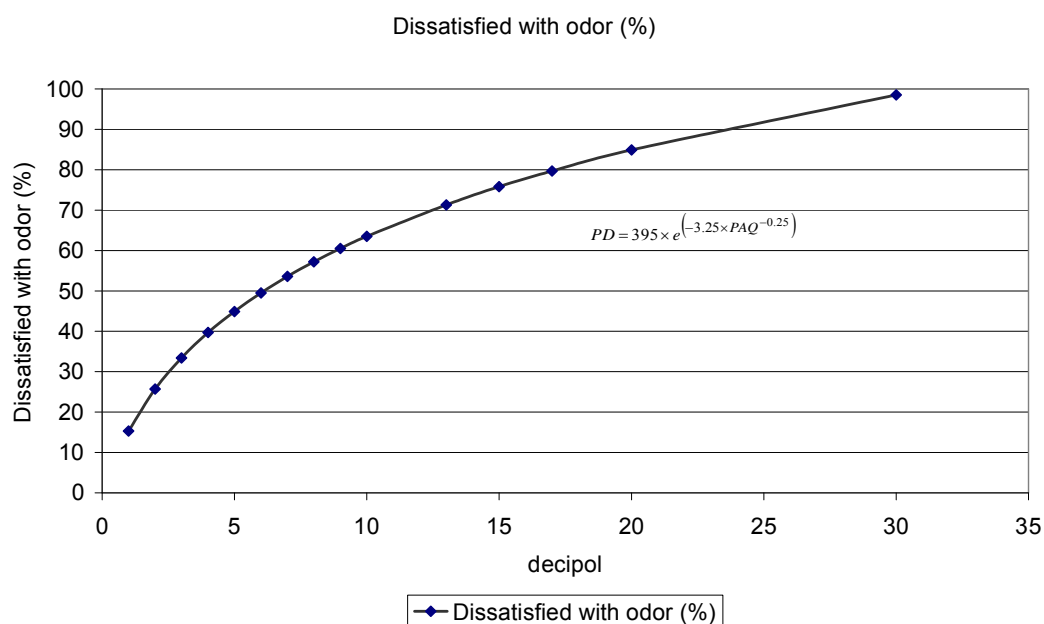


Figure 1. Influence of the odor (decipol) on the proportion of panelists dissatisfied with it

2.5.3 Untrained panels

Training panelists is time consuming and expensive, so untrained panels have also been used. Untrained panel must be bigger than trained ones to obtain representative results. According to Bluysen et al. (1996), as many as 280 untrained panel members are required to match a trained panel of 12 persons, whereas in Data Base research forty members were considered sufficient for an untrained panel, and an acceptable accuracy could already be obtained by using an untrained panel of 15 persons (Björkroth and Kukkonen, 2002). However, untrained panels need some guidance, and careful selection of the panelists is recommended. According to a large European study (Clausen and Fernandes, 1997), members of an untrained panel should pass a two-stage test: they should be able to distinguish and put in order four different butanol concentrations and recognize the quality of eight different odors using three reference samples.

2.5.4 Properties of the odorous VOCs

In general, oxygenated compounds such as alcohols, aldehydes, carboxylic acids, and ketones have low odor threshold values (Devos et al., 1990). Aldehydes have been found to be the most prevalent and predominant odorous compounds in new residences (Hodgson et al., 2000).

VOCs are usually present in the air as complex mixtures. When sensory responses to single and mixed VOCs were compared, both produced similar responses and the adaptation rates were also similar (Prah et al., 1998). Olfactory intensity was highest at the beginning of the test, and it gradually declined to ca. 40% of the initial value at the end of six hour exposure. In some studies, mixtures of VOCs have been hypoadditive, i.e., the combined odor intensity was less than the sum of the single odor intensities (Berglund and Olsson, 1993; Laing et al., 1994; ECA, 1999). However, it seems that the concentration levels of the mixtures have a strong influence on the sensory response. Cometto-Munich et al. (2003) observed a complete dose addition at low detectability levels but no more in higher concentrations when using butyl acetate and toluene as test compounds. In some cases, hyper addition is also suggested to be possible (Bluyssen, 1990). The perceived quality of the odor can also vary according to the concentration of the odorous compound (Malnic et al., 1999). For example, indole, which has a putrid odor at high concentrations, is perceived as floral when diluted.

2.5.5 Odors in ventilation systems

Pejtersen et al. (1991) showed with a trained sensory panel that ventilation systems are significant sources of odors, besides materials and occupants in kindergartens, schools, offices, and assembly halls. The perceived quality of supply air has been found to decrease inside the air handling units in several other studies (Fanger et al., 1988; Pejtersen et al., 1989; Fink and Fitzner, 1993; Björkroth et al., 1997a). Used supply air filters have usually been the most odorous ventilation system components (Finke and Fitzner, 1993; Pasanen et al., 1994; Björkroth et al., 1997a; Bluyssen et al., 2003). Air downstream of dusty filters has been reported to be stuffy and unpleasant. In addition, rotary heat exchangers and humidifiers have emitted odors into the supply air (Pejtersen et al., 1989). Pasanen et al. (1994) reported that perceived air quality started to decrease rapidly after the installation of a new filter. The percentages of dissatisfied evaluators were 0.7 - 28.5% after 6 weeks and 27.4 - 46.2% after

13 weeks use of the F6 fine filters in a one-stage filtration system. The corresponding values were 8.6 - 23% and 19.4 - 25.9% in a two-stage filtration unit (pre-filter G3 and fine filter F6). The highest odor emission source was the G3 pre-filter. In most cases, the perceived air quality continued to decrease for 19 weeks but after that it reached a fairly constant level. No clear correlation was found between the pressure drop and the odor emissions of the filters (Pasanen et al., 1994). The odor intensity of the unused air filters was negligible.

The quality and quantity of the filtrated dust affect the odor emissions. The pre-filter, which collected the coarse particle fraction, caused the highest odor emissions (Pasanen et al., 1994). This was confirmed later by a study where the coarse fraction ($>10 \mu\text{m}$) of particles in ambient air caused the highest odor emission per mass (Pasanen et al., 1995). The amount of dust correlated with the odor emissions (Bluyssen, 1990; Pejtersen, 1996). It has also been found that the odor emissions depend on the total air volume and location of the air handling unit (Hujanen et al., 1991). In Helsinki, the odor emission was highest from the filters located in the downtown area. On the other hand, no clear correlation between odor and the total air volume was found in filters taken from less polluted areas in Kuopio, in central Finland. The percentage of dissatisfied panelists reached as high as 40%, when the amount of dust was 30 g or more than 20 g/m^2 on the filter (Pasanen et al., 1994).

After a dusty season in the fall, odor emissions from the filters were higher than in the winter (Pasanen et al., 1994). Seasons may also influence the odor emission from the collected particles. Outdoor air particles collected during the heating season caused a significant odor emission (Pasanen et al., 1995). Smoke-like odorous compounds were then detected from the particles originated from the combustion processes.

Microbial growth in porous dusty filters may contaminate the air downstream (Kemp et al., 1995). However, this required long-term continued high humidity (RH 90%) (Kemp et al., 1995). In static storage conditions, high humidity caused the formation of microbial-related alcohols and ketones from the dusty filters faster (Pasanen et al., 1995). In addition, endotoxins have been found on supply air filters (Möriz et al., 1999). The concentrations of endotoxins were higher on pre-filters than on fine filter and were not related to how long the filters had been in use.

It is obvious that compounds emitted from dusty air filters cause sensory pollution. However, when concentrations of volatile organic compounds have been compared upstream and downstream of the filters, usually no clear differences have been detected (Björkroth et al., 1997; Hyttinen et al., 2003). Also, no correlations between the concentration of VOCs and odor have been reported (Bluyssen, 1990; Torkki, 1995; Björkroth et al., 1997a). It might be that the concentrations of compounds which are mainly responsible for sensed odor are very low and the dominating VOCs have high odor threshold values. In addition, it is difficult to compare chemical and sensory analyses because the intensity of odors follows the concentration of impurities not linearly but in a logarithmic scale.

2.6 How air quality changes when it goes through a ventilation system

2.6.1 Supply air quality

In urban areas, outdoor air contains complex mixtures of impurities such as particles, very volatile organic compounds (VVOCs), VOCs, semivolatile organic compounds (SVOCs), inorganic gases (NO_x , SO_x , CO , CO_2 , O_3), and radicals (OH , H_2O_2 , O^\cdot).

The particle size range from 0.01 to 0.1 μm is known as the ultra fine mode, which contains most (in numbers) of the ambient particles (Koutrakis and Sioutas, 1996). The fine mode consists of particles in the size range of 0.1-2.5 μm . Fine particles originate mainly from combustion processes, and the carbonaceous fraction can be as much as 70% of the total mass of particulates in polluted urban areas (Heintzenberg, 1989; Hall et al., 1999).

Organic matter, sulfate, and nitrate have been reported to dominate $\text{PM}_{2.5}$ and PM_{10} mass concentrations in rural, near-city, and urban background areas (Hueglin et al., 2005).

Typically, atmospheric $\text{PM}_{2.5}$ and PM_{10} particles are a complex mixture of elemental (EC) (5-18%) and organic carbon (OC) (16-30%), ammonium (NH_4^+) (4-11%), nitrates (NO_3^-) (7-17%), sulfates (SO_4^{2-}) (8-30%), mineral dust (5-15%), trace elements (2-6%), and water (13-23%). It has been reported that in Helsinki, SO_4^{2-} (21-25%), NO_3^- (11-12%), NH_4^+ (9-10%), diacids (0.9%), metals (0.4%), sea salt (Mg^{2+} , Na^+ and Cl^-) (2.5-3.3%) among others (estimated to be mainly water and organic compounds) (39-43%) were the main constituents in fine particles ($\text{PM}_{2.3}$) (Pakkanen et al., 2001). The mean mass concentration of fine particles ($\text{Dp} < 2.3 \mu\text{m}$) was 8.4 $\mu\text{g}/\text{m}^3$ in the outskirts and 11.8 $\mu\text{g}/\text{m}^3$ in downtown Helsinki.

Vehicle exhaust was concluded to be the most important local emission source (Pakkanen et al., 2001). The mean concentration of black carbon was $1.5 \mu\text{g}/\text{m}^3$ on work days, $1.2 \mu\text{g}/\text{m}^3$ on Saturdays, and $1.0 \mu\text{g}/\text{m}^3$ on Sundays. On work days, 63% of black carbon was estimated to be from local traffic, and the highest mean concentration, $2.7 \mu\text{g}/\text{m}^3$, was measured during the morning rush hour. The background concentration was estimated to be $0.4 \mu\text{g}/\text{m}^3$ (Pakkanen et al., 2001).

Higher concentrations of elemental black carbon have been measured in urban areas in London and Birmingham (Harrison et al., 2004). Mean EC content was as high as $9.2 \mu\text{g}/\text{m}^3$ (25.8% of PM_{10}) and $8.4 \mu\text{g}/\text{m}^3$ (35.3% of $\text{PM}_{2.5}$), respectively, in busy roadside samples.

Typically, soot content (mainly EC) is $1\text{-}10 \mu\text{g}/\text{m}^3$ in big cities near roads with heavy traffic (Kamm et al., 1999). Solvent extraction of $\text{PM}_{2.5}$ yielded 46-80% fatty acids, 10-34% alkanes, 4-21% alkanols, and 1-6% PAHs in Hong Kong (Zheng et al., 2000). Fatty acids are ubiquitous in the troposphere, and they dominate the fraction especially in summer measurements, and have been suggested to originate from microbial sources, combustion processes, oxidative reactions, and vegetable, and animal metabolic processes (Zheng et al., 2000). Polycyclic aromatic compounds (PAHs), some of which are carcinogenic, are mainly formed in incomplete combustion, and their main source is traffic. Usually, PAHs are attached to the particulate matter.

Even if the filtration of particles from the supply air is effective, there can be emission of VOCs (and SVOCs) from the particles which are attached to the filters. Gaseous compounds are of both anthropogenic and biogenic origin. The main biogenic emissions comprise alcohols, aldehydes, carboxylic acids, and terpenes. Isoprene and monoterpene emissions are the predominant VOC emissions from plants. Spatial and seasonal variations can be huge in biogenic VOC emissions (Guenther, 1997). In most urban environments, gaseous compounds originate mainly from combustion processes and include aldehydes, and aliphatic and aromatic hydrocarbons. The distribution of ambient air pollutants between the gas and particle phases determines their transport inside the ventilation unit. Compounds with low vapor pressure stay in the particle phase.

At constant air flow conditions, VOC profiles have been similar upstream and downstream of used filters (Björkroth et al., 1997a; Hyttinen et al., 2003). However, the concentrations of

light carbonyls have been found to increase when the air passed through heavily loaded ventilation filters in field and laboratory experiments (Pasanen et al., 1995). Concentrations decreased later when air flow was kept constant.

Although outdoor air and ventilation systems can be significant sources of VOCs, usually the contribution of indoor sources dominates VOC concentrations of indoor air. This was clearly seen in the extensive EXPOLIS (Air Pollution Exposure Distributions within Adult Urban Populations in Europe) study, where VOC concentrations were measured in six European cities (Saarela et al., 2003). Even the concentrations of the most commonly found VOCs, which were associated with traffic and combustion processes, were higher indoors than outdoors, demonstrating the presence of strong additional indoor sources such as building materials and consumer products. Toluene ($16.3 \mu\text{g}/\text{m}^3$), xylenes ($8.7 \mu\text{g}/\text{m}^3$), d-limonene ($8.5 \mu\text{g}/\text{m}^3$), hexanal ($6.8 \mu\text{g}/\text{m}^3$), and alpha-pinene ($6.5 \mu\text{g}/\text{m}^3$) were the most commonly found personal VOCs in Helsinki (Edwards et al., 2001). Formaldehyde (18.7 ppb), acetone (8.8 ppb), and acetaldehyde (6.8 ppb) were the most commonly found personal carbonyl compounds, and their concentrations were indoors systemically higher than in outdoor samples (Jurvelin et al., 2003). Limonene correlated negatively with formaldehyde, acetaldehyde, benzaldehyde, and heptanal. This may be due to indoor air reaction between terpenes and ozone (Jurvelin et al., 2003).

2.6.2 Quality and quantity of dust particles inside the ventilation unit

An air handling unit may contain various inorganic and organic impurities. A significant amount of the impurities originates from outdoor air. In addition, ventilation systems contain dust and oil residues from the manufacturing process and construction work (Pasanen et al., 1995; Björkroth et al., 1997c).

In office buildings in Helsinki and Kuopio, the mean surface density of dust has been reported to be $13.2 \text{ g}/\text{m}^2$ (from 1.2 to $158 \text{ g}/\text{m}^2$) in the supply air ducts and its average yearly accumulation was $1.8 \text{ g}/\text{m}^2$ (Pasanen, 1995).

The mean surface density of materials originating from the building construction time has been reported to be $5 \text{ g}/\text{m}^2$ (Pasanen et al., 1995). The Finnish Classification of Indoor Climate 2000 contains guidelines for the cleanliness of a HVAC system (Holopainen et al.,

2000). In the cleanliness class P1, the amount of dust must be less than 1.0 g/m² in a new ventilation system, and it needs to contain two-stage filtration with efficiency requirements of G3 for pre-filter and F8 for a fine filter. In class P2, the maximum dust content is 2.5 g/m² and the filtration unit should contain at least one F7 fine filter.

Typically, dust inside the ventilation unit contains pollen and microbes, soil-derived particles, inorganic salts, and particles formed in combustion processes. Some common particles found in ventilation system and their size ranges are presented in Table 3.

Table 3. Size ranges of particles present in supply and indoor air (McDonald and Ouyang, 2001)

Particle	Diameter, μm
Mold and pollen spores	2-200
Dust mite	50
Visible dust and lint	>25
Resuspended dust	5-25
Street dust	>10
Mite allergen	5-10
Mineral fibers	3-10
Fungal spores**	0.5-30
Outdoor fine particles (sulfates, metals)	0.1-2.5
Diesel soot	0.01-1
Tobacco smoke	0.1-0.8
Bacteria*	0.05-0.7
Fresh combustion particles	<0.1
Ozone- and terpene formed aerosols	<0.1
Viruses*	<0.01-0.05

* Occur in larger droplet nuclei, **Nevalainen et al., 1992

Typically, 75-87% of the particles in a ventilation unit consist of inorganic material (Laatikainen et al., 1991; Fransson et al., 1995; Pasanen et al., 1995). Silicon (7-22%), iron (5-15%), zinc (1-10%), aluminum (2-4%), sodium (2-4%), and elemental carbon (EC) (7%) have been reported to be the most abundant elements in the inorganic fraction of dust collected from ventilation systems (Fransson et al., 1995). The carbon content varies, being highest in urban areas. Dust taken from filters located in the outskirts of Helsinki contained 7-42% of carbon (Hyttinen et al., 2002). The mean contents of organic and elemental carbon were 6% and 3%, respectively.

3 AIMS OF THIS STUDY

The overall objective of this thesis work was to investigate adsorption and desorption of impurities and their reactions with ozone on air filters and how these affect supply air quality. Tests were carried out both in the laboratory (a small scale dynamic test apparatus) and in the field (real ventilation units).

The detailed aims of the study were:

1. To examine the sorption capacity of filter dust for gaseous compounds (Paper I, laboratory tests).
2. To characterize VOC emissions from the dust attached to the filter media (Papers: I and IV, laboratory and field tests).
3. To investigate the reactions of ozone on unused and used (dusty) ventilation filters (Papers II and III, laboratory and field tests).
4. To study the effect of diesel soot on the removal of ozone (Paper III, laboratory tests).
5. To find out how odor changes when air passes through ventilation filters (Paper IV, laboratory tests in full scale ventilation unit).
6. To clarify the reasons for the release of stuffy odor from used filters (Paper IV, laboratory tests).

4 MATERIALS AND METHODS

4.1 Supply air filters

Supply air filters were collected from urban office buildings located in Helsinki and Kuopio. The filters included G3 and G4 pre-filters and F5 to F8 fine filters, and they had served their normal period of use (6-12 months). When the filters were removed from the air handling unit, they were transported to the laboratory, and stored in their original cardboard boxes and in glass chambers in a clean room. Information about the supply air filters used in the study is presented in Table 4.

Table 4. Information on the filters. Filtration classes G3-4 are pre-filters and F6-8 are fine filters. Air handling units (AHU) are presented with the letters A to F (paper I) and a to g (papers III and IV).

Filter class	Location	Operating time	Amount of air (m ³)	Paper (AHU or test)
F7	Outskirts of Helsinki	6 months, 18h/day	2.8×10 ⁷	1 (A) and 2 (test 4)
F7	Outskirts of Helsinki	12 months, 15h/day	2.15×10 ⁷	1 (B) and 2 (test 2)
F6	City of Helsinki	12 months, 12h/day	1.7×10 ⁷	1 (C) and 2 (test 3)
F8	City of Helsinki	12 months, 12h/day	1.7×10 ⁷	1 (C)
F8	City of Kuopio	12 months	not available	1 (D) and 2 (test 1)
F5	City of Kuopio	7 months	not available	1 (E) and (test 7)
F7	Outskirts of Helsinki	6 months	1.6×10 ⁷	1 (F)
F6	Outskirts of Helsinki	12 months	not available	2 (test 5)
F7	Outskirts of Helsinki	12 months	not available	2 (test 6)
F7	City of Kuopio	12 months	not available	2 (test 8)
F5	City of Kuopio	12 months	not available	2 (test 9)
F8	Motor laboratory, University of Kuopio	1 day	Soot content (7.9-11.0 g/m ²)	3
G3	Outskirts of Helsinki	6 months	not available	3
G3	Outskirts of Helsinki	6 months	not available	3
F8	Outskirts of Helsinki	6 months	not available	3
G3	Helsinki, downtown	6 months, 12h/day	estimation 0.8×10 ⁷	4 (a) ^{1,2}
F8	Helsinki, downtown	6 months, 12h/day	estimation 0.8×10 ⁷	4 (a) ^{1,2}
G3	Helsinki, downtown, Allergy building	5-6 months	not available	4 (b) ¹
F7	Helsinki, downtown, Allergy building	5-6 months	not available	4 (b) ¹
G3	Outskirts of Helsinki	6 months	not available	4 (c) ¹
F7	Outskirts of Helsinki	6 months	not available	4 (c) ¹
F8	Outskirts of Helsinki	6 months	1.2×10 ⁷	3 and 4 (d) ^{2,3}
F8	Outskirts of Helsinki	6 months	1.6×10 ⁷	3 and 4 (e) ^{2,3}
G4	Outskirts of Helsinki	6 months, 12h/day	estimation 1.8×10 ⁷	4 (f) ²
F7	Outskirts of Helsinki	6 months, 12h/day	estimation 1.8×10 ⁷	4 (f) ²
G3	Outskirts of Helsinki	6 months, 18h/day	estimation 1.7×10 ⁷	4 (g) ²
F7	Outskirts of Helsinki	6 months, 18h/day	estimation 1.7×10 ⁷	4 (g) ²

¹Odor evaluation and VOC measurements in the ventilation unit ²TCT analyses ³HS analyses

Unused pre- and fine filter materials were obtained from the manufacturer. The pre-filter, classified as G3, was made of polyester, and the fine filters, classified as F8, were made of fiberglass. The tested fine filters were made by two different manufacturers (A and B). Information about the adhesive and resin content of the filters was not available. Filter material A was obtained several months before testing. Filter material B was tested immediately after delivery.

4.2 Adsorption and desorption

Adsorption and desorption phenomena were examined in a small-scale dynamic test apparatus. The air used in the system was cleaned by activated carbon and its relative humidity (RH) was adjusted by mixing dry air and air moistened by bubbling it through ultra-high quality water. The dust samples were loaded with the model compounds either by adsorption from a constant concentration in an air flow generated by diffusion vials (PN19C, VICI Metronics Inc.) or by direct injection into the dust. Compounds were selected to represent typical indoor air pollutants with different aromaticity and polarity: alpha-pinene, ethylbenzene, nonane, and hexanal were used in the tests. Air samples were collected from both sides of the chamber using Tenax GR adsorbent. The method is described in more detail in Paper I.

4.3 Dust analyses

Filter dust samples were collected from the filter media, and they were stored in glass canisters before the tests. In the thermodesorption analysis, the filter dust samples (10-50 mg) were put into empty Tenax tubes, and analyzed using an automatic thermodesorption / cold trap (TCT) device (Perkin Elmer, ATD 400) connected to a gas chromatograph (HP, 6890 GC with HP, 5973 MSD). Dust samples were desorbed at 50 to 250°C for 10 minutes with constant helium flow. The compounds emitted were collected in a cold trap (-30°C) containing Tenax TA adsorbent. The desorption temperature of the coldtrap was 220°C. The column was HP-5MS (column length 50 m, film thickness 0.5 µm), and the identification of the compounds was accomplished by retention times, standard compounds, and GC-MS data library. The concentrations were determined as the sum of the areas of compounds compared with the area responses of known amounts of toluene.

Headspace (HS) measurements were made by a headspace analyzer (Agilent, G1888 HS) connected to the gas chromatograph (Agilent, 6890GC) and mass spectrometer (Agilent, 5973N inert MSD). Analyses were made at temperatures of 120, 160, and 200°C. The amount of dust varied from 100 to 380 mg per 20 ml HS vial. The heating period was 15 minutes. The specific area of dust samples was determined by the BET method in the Technical University of Lappeenranta.

4.4 Ozone and nitrogen oxide measurements

Ozone was produced by the generator of an ozone calibrator (MGC 101, S.A. Environment) or a UV lamp (5W) and its concentration was adjusted to 20-220 ppb. Compressed air was cleaned from VOCs and NO_x (excluding first tests) by activated carbon and Purafil (potassium permanganate impregnated alumina). The temperature of the air was 21-23°C, and the relative humidity was adjusted to 20-80%.

Ozone was measured continuously (Dasibi, 1008-RS) upstream and downstream of the tested filters. The detection limit of the O₃ analyzer was reported by the manufacturer to be 2 ppb, and the accuracy to be ±0.5 ppb. Nitrogen oxides were measured continuously with a direct reading monitor (Environment, AC3M for nitrogen oxides). A data logger (Grant) was used to collect the measured data (Ozone, NO_x, temperature, and RH).

4.5 Air samples

Air samples were collected simultaneously upstream and downstream of the filters. Volatile organic compounds (VOCs) were collected onto Tenax GR adsorbent (sampling rate 100-200 mL/min, time 30–60 min) and analyzed with a gas chromatograph (HP, 6890 GC) equipped with a mass selective detector (MSD 5973) after thermal desorption (Perkin Elmer, ATD 400). The procedures of the Tenax GR analyses are presented in detail in paper I. The concentrations of single and total VOCs (TVOC) were determined as toluene equivalents. This has been common practice in TVOC measurements and also in the single VOC quantifications when the reference compounds are not available (ISO 16000-6, 2004). However, the use of toluene standards underestimates the true concentrations of the polar compounds (especially aldehydes). Therefore, correction coefficients for aldehyde concentrations calculated as toluene equivalents were determined by comparing the ratios of the total ion chromatogram areas of thirteen parallel toluene and aldehyde (butanal to decanal)

standards. The standards were made in methanol (Rathburn HPLC grade) and injected (1 μ L) to the clean Tenax GR tubes, and they were analyzed by the same way as the samples. The results are presented in Table 5. Breakthrough volume for butanal is relative low, therefore its concentration might be underestimated in field measurements (Scientific Instrument Services, 1995).

Table 5. Correction coefficients for aldehyde concentrations calculated as toluene equivalents.

Aldehyde	Correction coefficient \pm standard deviation
Butanal	2.0 \pm 0.2
Pentanal	1.9 \pm 0.2
Hexanal	1.6 \pm 0.2
Heptanal	1.4 \pm 0.2
Octanal	1.5 \pm 0.1
Nonanal	1.6 \pm 0.2
Decanal	1.9 \pm 0.5

Carbonyl compounds were collected onto 2,4-dinitrophenylhydrazine (DNPH) cartridges (Waters Sep-Pak) and analyzed by HPLC (HP 1050) with a UV detector. Carboxylic acids (sampling time 360-480 minutes and air flow 1.0-1.2 L/min) were measured in some experiments. They were collected on alkaline-impregnated C₁₈ cartridges (coated with potassium hydroxide) and analyzed by HPLC (HP 1050) (Zhang et al., 1994).

The ozonolytic decomposition of the sampling cartridges (C₁₈, DNPH, and Tenax) was prevented by potassium iodide-coated copper tubes.

4.6 Odor evaluation

The quality of the air was evaluated by a trained sensory panel of 7–14 young adults. Odor evaluations were made in full scale ventilation units located in the outskirts of and downtown Helsinki. The panelists estimated the odor intensity before and after the fan, filters, heating coil, and humidifier. Evaluation was made in random order controlled by the panel's technical manager. Before and after every evaluation, panelists "refreshed" their senses in a room where the windows were open. Ventilation air flow rate was 0.36 m³/s during the evaluations (face velocity 1 m/s). Tests were conducted at a low (23–32%) and high (58–61%) RH of air. The humidity of air was adjusted by a cold water spray humidifier, and the enthalpy of air was maintained at a constant level by lowering the temperature at the high RH. One field test was

made at the ambient (55 ppb) and elevated ozone concentration (80-111 ppb). The HVAC unit was located in downtown Helsinki and was equipped with three-stage filtration (G3 pre-filter, F7 and F8 fine filter). Air flow was 0.5 m³/s during the sensory evaluations (face velocity 1.4 m/s).

Panelists did not have background knowledge on the function of the air handling unit or what components it contained. They reported time, site, and intensity of odor. The panel evaluated odor intensity on a scale from 0 to 20 using acetone as the reference compound. The evaluation method was otherwise the same as described by Fanger (1988) and Bluysen and Walpot (1993) but instead of evaluating perceived air pollution, i.e., how annoying the odor is, the panel was instructed to evaluate odor intensity only. Distributions of the odor evaluations were tested for normality with the Shapiro-Wilk's test, and the significance of the differences between the odor evaluations was analyzed with the independent sample t-test (SPSS 14.0).

5 RESULTS

5.1 Adsorption and desorption of selected VOCs in filter dust

The specific surface area of filter dust was relatively low, $\sim 1 \text{ m}^2/\text{g}$, and this was also seen in the tests where model compounds were introduced into the air stream over the chamber covered with filter dust. At constant air flow and RH, the sorption of the model compounds to the dust was negligible. When the model compounds were added directly to the filter dust, the emission of the compounds decreased with time. However, there was a notable peak emission of the compounds when the RH was suddenly increased. The increase in RH also caused VOC emissions from dusty F7 filters without adding any model compounds. The concentrations of aromatic hydrocarbons were higher downstream of the filter, and the increase in RH caused peak emissions. Aldehydes were also emitted from the dusty filters in the air handling unit when the humidifier was turned on. Some aldehydes were detected already upstream of the filters. In particular, the source of nonanal before the filters remained unknown. The influence of RH on the emissions of impurities from the filters was perceived clearly by sensory methods in the same field tests.

5.2 Content of organic compounds in the filter dust

In thermodesorption tests made at 50°C and 70°C , slight emissions of VOCs were detected. Aldehydes (hexanal, heptanal, octanal, nonanal and decanal) and aromatic hydrocarbons (toluene and ethyl benzene) were the main emission products. The emission of aromatics was observed already at room temperature (see previous section). However, emissions increased substantially when temperatures were higher (over 100°C). The maximum emission at 150°C was approximately 0.2% of the mass of the filter dust. The number of emitted VOCs from the dust samples was substantially over 150; however, not all individual compounds could be identified reliably. The main compounds emitted were alcohols, aldehydes, aromatics, carboxylic acids, nitrogen-containing organic compounds, phthalates, and terpenes.

Emissions were lower at static conditions (headspace measurements) than in the dynamic thermodesorption measurements with a constant helium flow over the dust samples. In both methods, emissions increased with increasing temperature. Figure 2 shows TVOC emissions of two different fine filter dusts (air handling units d and e) at different temperatures analyzed

by HS-GC-MS. The higher fraction of inorganic compounds in filter dust taken from AHU e than AHU d was presumably the reason for the difference in emission results.

The compounds emitted were similar in both methods. However, more organic nitrogen compounds were found when analyzed by HS-GC-MS than TCT. The main compound groups detected by both methods at 160°C (HS) and at 150°C (TCT) are presented in Figure 3.

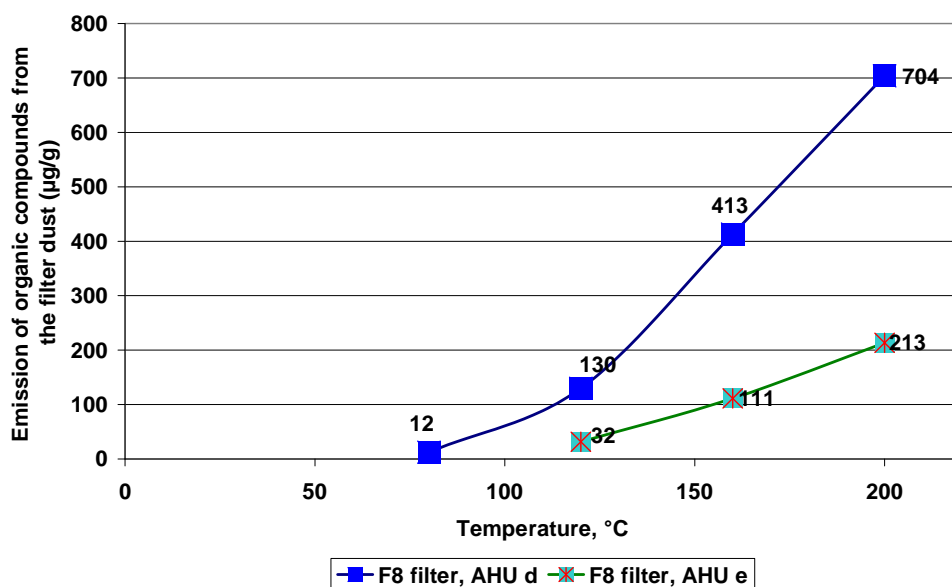


Figure 2. Total emission of VOCs ($\mu\text{g/g}$) from the F8 fine filter dust samples (air handling units d and e, paper IV) at different temperatures.

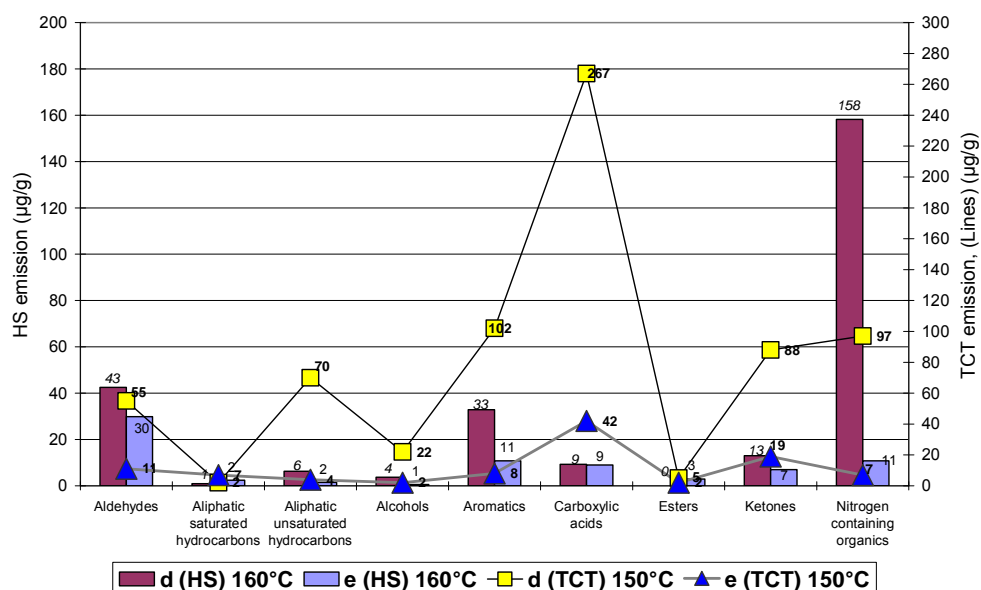


Figure 3. The main compound groups from the F8 filter dust samples (air handling units d and e, paper IV) at 160°C (HS) and 150°C (TCT). HS emission is shown on the left axis and TCT emission on the right axis.

5.3 Ozone reactions

Removal of ozone was negligible on unused coarse (G3) and F5 class fine filter. In contrast, unused fine filters (F7 and F8) removed ozone, but two tested materials reacted differently with ozone. Material B reacted with ozone more effectively than material A at the beginning of the test; mean removals were 6% (material A) and 19% (material B) during the first hour of O₃ exposure. Removal of O₃ became negligible within one hour (below 2%) with material A, but the same low level was achieved only after 16 hours with material B (O₃ concentration 230 ppb). A slight recovery of reactivity occurred in the unused F8 filter made of material B during O₃ exposure breaks (16-18 h, air flow remained unchanged).

Low concentrations of nitrogen oxides (NO_x) were measured in the first experiments when there was no Purafil filtration, and some NO_x remained in the air in spite of the filtration. The concentrations were 0.5-12 ppb for NO and 7-30 ppb for NO₂. The contribution of NO to the removal of O₃ varied from negligible to 5.7%. Some additional formation of NO₂ was observed during most of the experiments.

Dust load increased the removal of O₃ on the pre-filter, and it also extended the removal period. The pre-filters (G3) which had been used in an air handling unit for 6 months, removed 12% (amount of dust 5 g/m²) and 35% (amount of dust 36 g/m²) of O₃ during the first hour. The O₃ loss decreased to 3% and 16% during the second hour of O₃ exposure. The fine filters contained less dust than the pre-filters, and the influence of the dust load on the O₃ removal did not appear as clearly as in the case of the pre-filters. Soot clearly increased and extended the removal of O₃. The specific surface area of soot measured by the BET method was 100-103 m²/g. Removal of O₃ increased when the RH and ozone concentration increased. On the other hand, the air velocity (0.11-0.21 m/s) did not have any effect on the removal of O₃.

Increased formaldehyde concentrations were detected after the used filters during the O₃ feeding. Mean formaldehyde production was 15.1 µg/h at the elevated O₃ concentration on the used filters. When the area of the filter was taken into account, the specific emission rate of formaldehyde from the filter material was around 750 µg/m²h. Emissions of the acetaldehyde were also observed at elevated O₃ concentrations in some of the tests. The influence of ozone on the concentrations of other aldehydes (C₃-C₁₀) on the used filters remained negligible.

Tests made with sooty fine filters showed that the production of formaldehyde was clearly elevated at the start of O₃ feeding, but it decreased to the initial level within 150-360 minutes. In addition, the production of acetaldehyde and higher aldehydes (C₃-C₁₀) was also occasionally observed. The formation of acetaldehyde, formaldehyde, propanal, and higher aldehydes (C₄-C₁₀) and the removal of ozone on a sooty fine filter are presented in Figure 4. Formaldehyde production was highest at the start of O₃ feeding when the removal of O₃ was also the highest. Higher aldehydes behaved similarly, although less of these than of formaldehyde was formed. Acetaldehyde was not detected when there was no O₃ present, but its level remained almost constant during the O₃ exposure. The concentration of acetone also seemed to increase during the O₃ exposure. However, it was also found upstream of filters and when there was no O₃ present.

Formic acid was detected in some of the tests but its concentration was always near the detection limit in spite of the long sampling time used (6-9 hours). A maximum concentration of 7 µg/m³ was observed in the presence of O₃.

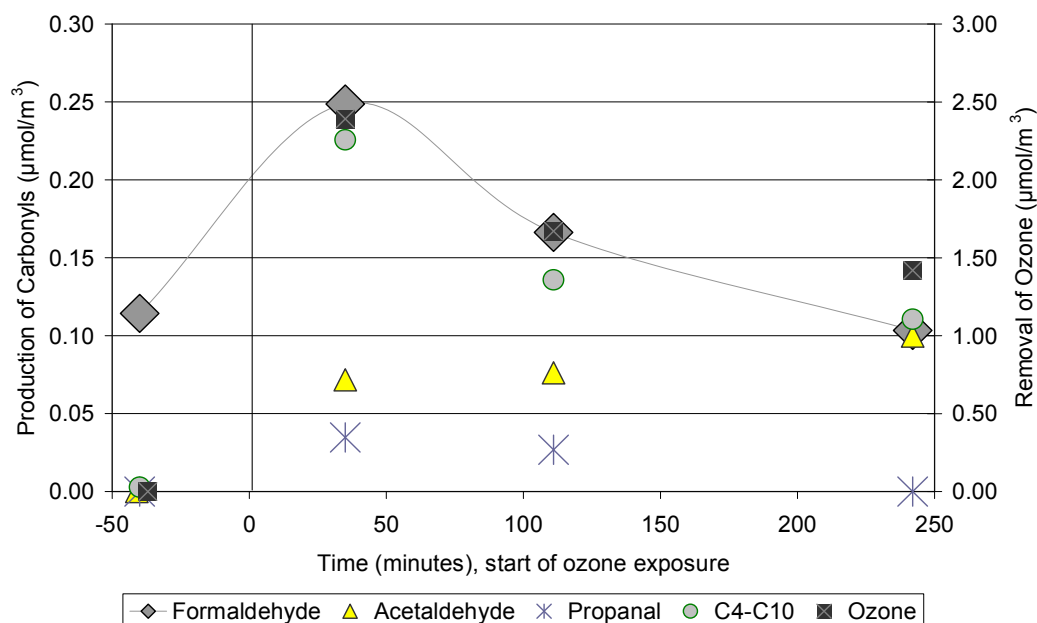


Figure 4. Production of carbonyls and removal of ozone ($\mu\text{mol}/\text{m}^3$) on a sooty F8 filter (amount of soot ca. $11\text{g}/\text{m}^2$). Ozone concentration upstream of the filter was 90 ± 6 ppb, RH $34\pm 0.3\%$, and temperature $24.0\pm 0.4^\circ\text{C}$. Carbonyls were sampled with DNPH cartridge and analyzed with HPLC.

The VOC profiles were similar upstream and downstream of the used filters, and no clear effect of ozone was observed. However, an increase in the concentration of TVOC was detected after the sooty fine filters. The concentration was $4\text{--}21\ \mu\text{g}/\text{m}^3$ upstream and $8\text{--}40\ \mu\text{g}/\text{m}^3$ downstream of the filter. The concentrations of ($\text{C}_5\text{--}\text{C}_{10}$)-aldehydes were also higher downstream than upstream of the filters: $\text{nd}\text{--}3.6\ \mu\text{g}/\text{m}^3$ before and $0.3\text{--}6.7\ \mu\text{g}/\text{m}^3$ after. Aliphatic (branched) hydrocarbons were the most abundant group of VOCs emitted from the sooty filters. Aromatic hydrocarbons were also observed in all the measurements and their concentrations were $0.5\text{--}5.5\ \mu\text{g}/\text{m}^3$ upstream and $0.7\text{--}6.2\ \mu\text{g}/\text{m}^3$ downstream of the filter.

5.4 VOCs and the odor emissions on supply air filters

The pre-filter was the main odor source in the ventilation unit, but when the humidifier was turned on odor was released mainly from the fine filter. The difference in odor intensity was significant after the fine filter during the first 31 minutes ($p < 0.0005$). The mean intensity of odors in all the three tests at low and high RH (first two evaluations after start of the humidification) is presented in Figure 5.

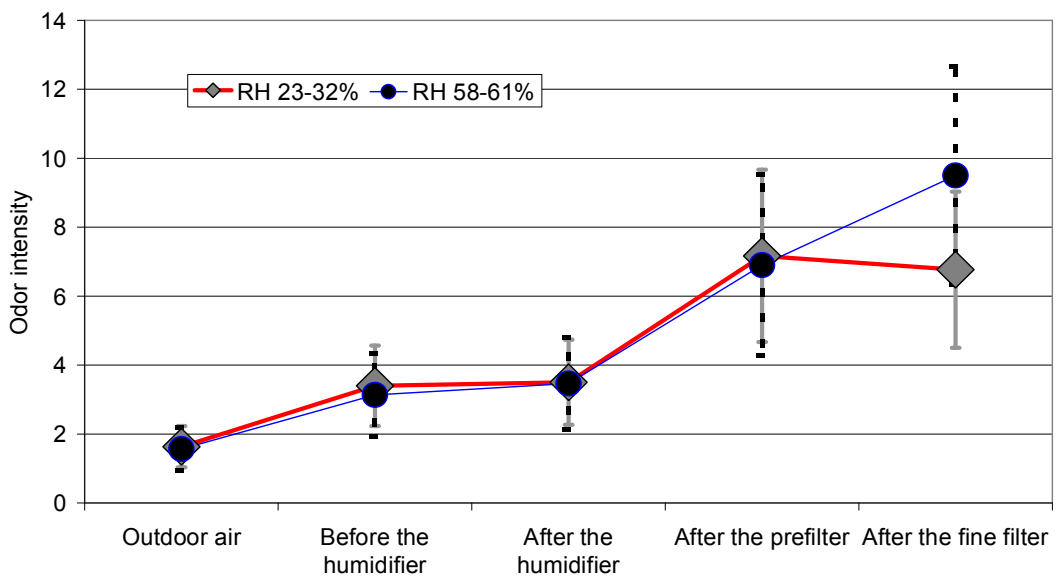


Figure 5. Intensity of odor in the air handling unit at low and high RH (average values of three tests). Filters G3 + F7/F8 had been used for 6 months. The number of the panelists was 7-14.

However, the effect of RH was only temporary, and odor fell back to the same level as sensed before humidification within 30 to 60 minutes. The alteration in the odor intensity during the one test is presented in Figure 6.

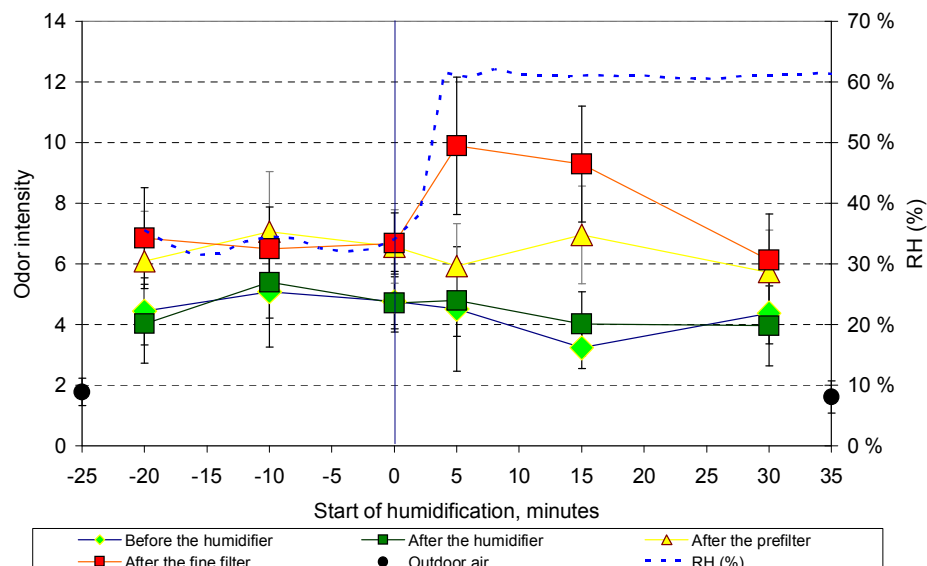


Figure 6. Intensity of odor before and after a G3+F7 filter. The number of panelists was 14.

TVOC concentration upstream and downstream of the filters varied from 30 to 58 $\mu\text{g}/\text{m}^3$ and it was not clearly affected by the filtration. When the humidifier was turned on the proportion of higher aldehydes ($\text{C}_4\text{-C}_{10}$) increased already before the filters, whereas an increase in the concentration of the shorter aldehydes was observed only after the filters. The total mean concentration level of the aldehydes was 9.9 $\mu\text{g}/\text{m}^3$ upstream and 15.8 $\mu\text{g}/\text{m}^3$ downstream of the filter at the low RH, and correspondingly, 17.1 $\mu\text{g}/\text{m}^3$ and 21.5 $\mu\text{g}/\text{m}^3$ at the high RH.

When the effect of elevated ozone concentration was tested in a real ventilation unit in downtown Helsinki, the mean intensity of the odor was 2.6 ± 1.5 upstream and 4.3 ± 1.6 downstream of the three-stage filtration before additional ozone feeding (ambient ozone level was 55 ppb). When additional ozone was introduced into the system (the concentration was 111 ppb upstream of the filters and 84 ppb downstream), it masked the other odors and no differences before and after the filters were observed. The mean intensity of the odor was 5.4 ± 1.6 upstream and 5.4 ± 2.0 downstream of the filters.

In Table 6, the most odorous compounds are presented according to their emissions in thermodesorption analysis (at 150°C) divided by their odor threshold values. Bolded

compounds were also present in the real air handling units and their maximum concentrations downstream of the air filters are presented in the table.

Table 6. VOC emissions from the dust samples at 150°C calculated as toluene equivalent ($\mu\text{g/g}$) and their possible effect on odor per 1 gram of the dust and 1 m^3 of supply air, and their maximum concentration downstream of the filters in field measurements.

Compound	Odor threshold ($\mu\text{g/m}^3$) ^a	Vapor pressure at 25°C (mmHg) ^b	Bp (°C)	Maximum concentration in air handling unit after filters ($\mu\text{g/m}^3$)	Thermodesorption $\mu\text{g/g}$ (AVG)	STDEV	VOC (AVG)/(odor threshold)
Nonanoic acid	12.6	0.0087	254	nd	22.95	46.89	182.14 %
Nonanal	13.4	0.53	185	10.0	10.08	9.38	75.22 %
Acetic acid	43	14	118	1.8	31.81	49.27	73.98 %
Dodecanoic acid	20	0.00066	296	nd	9.98	22.25	49.90 %
Decanal	5.9	0.21	207	4.1	1.75	1.88	29.66 %
Octanal	7.2	2.1	171	1.7	1.71	2.03	23.75 %
Butanal	28	96	76	0.6	3.11	3.27	11.11 %
Butanol	90	8.52	118	0.2	8.9	21.88	9.89 %
Pulegone	21	0.093	220	nd	1.99	2.86	9.48 %
Hexanal	58	10.9	131	4.8	5.08	3.71	8.76 %
Heptanal	23	3.85	153	2.0	1.8	1.59	7.83 %
Pentanal	22	31.8	103	1.9	1.63	1.42	7.41 %
Hexanoic acid	60	0.16	202	0.6	3.8	4.16	6.33 %
3-methylbutanal	8	49.3	90	0.6	0.5	0.48	6.25 %
Octanoic acid	24	0.022	240	nd	1.4	2.51	5.83 %
Benzaldehyde	186	1	179	1.4	5.46	13.85	2.94 %
2-pentanedione	132	6.8	140	nd	2.04	5.76	1.55 %
Butanoic acid	14	1.35	164	0.5	0.21	0.39	1.50 %
Propanoic acid	110	4.23	141	nd	0.91	1.4	0.83 %
Trimethylbenzene	776	2	170	nd	4.44	12.55	0.57 %
Pyridine	275	22.8	115	nd	1.24	2.45	0.45 %
Styrene	36	6.21	145	4.5	0.16	0.16	0.44 %
2-ethyl-1-hexanol	500	0.21	183	1.4	0.84	1.04	0.17 %
4-methyl-2-pentanone	2290	18.2	117	nd	2.23	5.57	0.10 %
2-heptanone	676	4.73	150	nd	0.15	0.39	0.02 %
2-pentanone	5500	38.6	100	nd	0.98	1.88	0.02 %
Furfural	3162	2.23	167	nd	0.54	1.01	0.02 %
Toluene	5888	27.7	111	21.5	0.7	1.42	0.01 %
Limonene	2500	1.54	176	0.7	0.28	0.78	0.01 %
					$\mu\text{g/g}$ (AVG)		Σ 516.2 %

Dust samples were collected from the eight filters (paper IV), nd = not detected, ^aDevos et al. (1990) (odor threshold valuer, ^bDatabases SciFinder Scholar (vapor pressures)

6 DISCUSSION

Specific surface area is a dominating factor for adsorption capacity of materials (Ong and Lion, 1991; Lin et al., 1994; Ruiz et al., 1998). A low specific surface area of the filter dust also appeared as poor adsorption of the model compounds from the air stream into the filter dust at constant test conditions. When the model compounds were injected directly into the dust samples, the emission of the compounds also decreased fast. However, when the RH of air was suddenly increased there was a substantial increase in the concentration of the model compounds. The same phenomenon was observed with dusty ventilation filters without adding any model compounds. Peak emissions of aromatic hydrocarbons were found downstream of dusty fine filters when the RH was suddenly increased. Similar effects of the RH on the adsorption and desorption phenomenon have been observed in studies made with soil minerals (Chiou, 1985; Thibaud and Akgerman, 1993; Petersen et al., 1995; Ruiz et al., 1998) and in sorbent trapping analyses (Harper, 2000). Water molecules compete with VOCs for the adsorption sites and replace them from the adsorbent (Chiou, 1985).

VOC emissions were relatively low in thermodesorption tests at 50°C and 70°C, but they increased substantially when temperature was elevated to 100°C and 150°C. The maximum emission of VOCs at 150°C was around 0.2% of the mass of the dust. This is much less than the carbon content of the dust, which varies from 7-42% (Hyttinen et al., 2002). Aldehydes, aromatic hydrocarbons, carboxylic acids, nitrogen-containing organics, terpenes, and many unidentified compounds were released from the filter dust during the heating. More than 150 compounds were emitted. The great numbers of compounds make it difficult to estimate the reason for the odor perceptions of the dusty filters. In addition, filter dust also contains a high proportion of compounds with high boiling points, which cannot be detected by conventional analyzing methods (Hyttinen et al., 2002). Nonanal and nonanoic acid as well other aldehydes and carboxylic acids were the most odorous compounds emitted from the dust when the thermodesorption results were divided by their odor threshold values (Table 6). Origin of the compounds is not clear. It is possible that unsaturated long chain fatty acids which have been found from atmospheric aerosols, e.g., oleic acid could be precursors for them (Guo et al., 2003). These polar organic compounds are also emitted directly from various sources including traffic, biomass burning and cooking, and formed in photochemical oxidation processes (Oliveira et al., 2007).

Polar organic compounds have also earlier been supposed to be one of the reasons for irritation and odor problems of indoor air (Wolkoff et al., 1997; Wolkoff et al., 1999). Additive or even synergistic effects of the mixtures of organic compounds have also been found to exist when concentrations are low. Cometto-Muniz et al. (2003, 2005) observed that odorous compounds have a complete dose addition at low concentrations, but not at higher concentrations. With an assumption of additive odor effect, the observed concentrations of aldehydes exceed the odor threshold, and thus they can explain why air becomes odorous while passing through filters.

VOCs are usually measured as toluene equivalents, and this is one of the reasons why concentrations of polar compounds have often been underestimated. The real concentrations of the aldehydes were approximately 1.4-2.0 times higher than the toluene equivalent concentrations. In addition, carboxylic acids and many nitrogen-containing organics (e.g., amines) have low odor thresholds but they are difficult to determine by the conventional VOC analytical techniques (Wolkoff and Nielsen, 2001).

Organic compounds in aerosols are partially oxidized in ambient air, where O₃ is one of the most important oxidants. In addition, oxidation reactions continue on the supply air filter. Unused pre-filters did not remove O₃, but O₃ removal was observed on unused fine filters. However, the removal of O₃ was lower on unused filters than on used dusty filters and became negligible within hours. Zhao et al. (2007) also noticed that the removal of O₃ was greater on loaded than unloaded filters. Unexpectedly, the two fiber glass materials tested reacted differently with O₃. The different resin content of the materials might be the one reason for the results. Similar observations have also been made elsewhere (Bekö et al., 2006; Zhao et al., 2007).

All the dusty ventilation filters removed O₃, although they had been exposed to high amounts of ambient O₃ already during their service time. Simultaneous emissions of formaldehyde and on some occasions formic acid and longer aldehydes were observed. These findings are supported by those of other studies where the formation of aldehydes, ketones, or organic acids were detected when O₃ reacted with various building materials and organic pollutants in indoor environments (Weschler and Shields, 1997; Wolkoff et al., 1997; Morrison et al., 1998; Fick et al., 2004; Aoki and Tanabe, 2007). Ozone removal was highest in the beginning of O₃ exposure and it rapidly decreased, reaching a fairly constant value. Similar results have

been obtained elsewhere (Bekö et al., 2003; 2006; Zhao et al., 2007). In addition, the loading of the pre-filter affected the removal of O₃. Dust loading did not affect the removal of O₃ in fine filters when tests were made at low RH. At high RH, the removal of O₃ was highest on the most loaded fine filter.

Sooty fine filters removed ozone more effectively than normally used dusty filters. Loss of ozone has been observed previously on soot (Smith and Chughtai, 1996; Gao et al., 1998; Kamm et al., 1999; Chughtai et al., 2002). However, the observed final removal of O₃ on soot was higher in the present study than in the tests made by Metts et al. (2005). In the present study, filter type and age affected the removal of O₃. Sooty F8 filter material B reacted more effectively with O₃ (over 20% removal after 72 hour exposure, amount of soot ca. 11g/m²) than sooty F8 material A (below 10% removal after 4 hour exposure, amount of soot ca. 8g/m²). In addition, the OC/EC ratio was estimated to be lower and the loadings of the soot higher in the present study than in the study made by Metts et al. (2005). A higher production of formaldehyde and, on some occasions, longer aldehydes were detected on sooty than on dusty filters. Surprisingly, formaldehyde was emitted from the sooty filters even when there was no O₃ present. It might have been formed during the combustion process when soot was sampled. However, the production of carbonyls (especially formaldehyde) was most dominant at the beginning of O₃ exposure and it became insignificant in 150 minutes indicating limited amount of reactive sites on the surface of soot particles. Soot and dust were not the only source of formaldehyde but it was also detected from the unused fine filter materials when O₃ exposure started. Reason for that could be the resins used in manufacturing processes of the filter materials.

The removal of O₃ increased with the increasing RH. The result is consistent with those of previous studies (Chughtai et al, 2002; 2003). Water uptake was found to increase on particles as soot surface oxidation increases (Chughtai et al., 2002). Ozone increases the hydrophilic nature of soot, and this increases the attendance of water molecules. It is well known that O₃ is highly reactive in water (Gunten, 2003).

As in previous studies, the reactivity of soot with O₃ decreased with time (Kamm et al., 1999). However, the removal of O₃ lasted longer on sooty filters than on dusty filters. The reaction capacity of dust has been reported to return partially during the breaks in ozone exposure (Bekö et al. 2006, Zhao et al. 2007). This was also observed in the present study when the

reactions of ozone were studied with unused and sooty fine filters. In particular, regeneration of the ozone removal capacity was detected on sooty filters during the ozone exposure break. A possible reason for this phenomenon on the filter dust might be the diffusion of reactive species from the inside of the dust layer to the external surface during the break (Bekö et al., 2006). Another mechanism has been suggested to occur with soot: the recovery of reactive sites occurs spontaneously when gaseous oxidation products (CO, CO₂) are released from the surface of the soot (Kamm et al., 1999).

The detected odor intensities were 5.7 - 9.6 downstream of the filters which correspond to levels where 50-60% of the persons would be dissatisfied. The used pre-filter was the main odor source in the air handling unit at constant conditions. It seems that odor emission is related especially to the compounds emitted from coarse particles. This was also found in a previous study in which the coarse particle fraction caused higher odor emission than the finer fraction (Pasanen et al., 1995). Reason for that might be simply the higher amount of dust on pre-filter than on fine filter. However, the particles (in the size range of 50-300 nm) released from the dusty pre-filters during the sensory evaluation were not the reason for the perceived odor (Hyttinen et al., 2003). Filtration slightly increased TVOC concentration but it was low in all the tests, 20-50 µg/m³. When the RH of air was increased, odorous compounds were released mainly from the fine filters but again the phenomenon was temporary and returned to the initial level in 30-60 minutes. Often a sudden increase of the RH also increased concentrations of aldehydes downstream of the filters.

These results suggest that oxidized VOCs and SVOCs released from the ventilation filters are an important reason for the stuffy odor emitted from the filters. Ozone increased the formation of these VOCs and SVOCs. The study confirms that an increase in RH significantly affects both the release and formation of odorous compounds and also the removal of O₃. The effect of RH on emissions is short-term but it might lead to odor emissions when the weather changes.

7 SUMMARY AND CONCLUSIONS

The adsorption capacity of filter dust was low at constant conditions. However, the dust contained a huge number of VOCs, which were detected during the thermodesorption analyses. It seems that the adsorption of these organic compounds into the dust has partially occurred already in ambient air. In addition, oxidation reactions occur on the filter media due to exposure to ambient oxidants (O_3 and O_2). This appeared as high fractions of aldehydes and carboxylic acids in filter dust.

Besides aldehydes and carboxylic acids, aromatic hydrocarbons, nitrogen-containing organics, and ketones were the main compounds emitted from the dusty filters. Aldehydes and aromatic hydrocarbons were emitted already at relative low temperatures, but the emissions increased substantially when the temperature exceeded 100°C . A sudden increase in the RH caused a temporary peak emission of VOCs. This was observed both in laboratory and field tests. Also, peak emissions of model compounds were detected when the RH was suddenly increased. In addition, emissions of aromatic compounds were observed from the dusty filters. In field tests, emissions of aldehydes were also observed.

Removal of O_3 occurred on the dusty supply air filters. Also, unused new fine filter materials removed O_3 at the beginning. Higher removal of O_3 was observed in summer tests (high RH and temperature) than in winter. In all the tests, the highest removal of O_3 occurred at the beginning of O_3 exposure. Typically, the final removal of O_3 remained at 5-10 % of the supply air filter. The main reaction product was formaldehyde, but some observations of longer aldehydes were also made. Time of exposure, RH, and soot particles influenced the removal of O_3 on the filters. The effect of soot on ozone removal also increased when the RH was increased. During the O_3 breaks, partial O_3 removal recovery occurred on the sooty and also on the dusty filter.

Soot obtained from the motor laboratory reacted effectively with O_3 . In contrast to the case with dusty filters, it remained reactive for a long time. The high specific surface area of the soot (over $100\text{ m}^2/\text{g}$) compared with the area of filter dust ($1\text{-}2\text{ m}^2/\text{g}$) explains this difference. Since O_3 has toxic effects, its removal is beneficial, but more irritating oxidizing products can be formed at the same time.

Pre-filter, which collects the coarse fraction of the particles, was the major odor source in air handling unit, but when the RH suddenly increased odorous compounds were released mainly from the fine filters. Although, the effect of the RH was temporal and decayed within 30 to 60 minutes, this may lead to peak emissions of odorous compounds from filters after sudden weather changes.

Overall, it seems that odor released from used filters is related to polar organic compounds. Aldehydes, carboxylic acids and nitrogen-containing compounds contribute the odor emitted from the filters. These compounds have been analyzed from the filtered dust and they have low odor threshold values. In addition, the results support the previous findings that the critical point of air quality control is the pre-filter, which should be changed regularly.

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