PhD thesis
Anni Vibenholt

Measurements of selected air pollutants in Danish homes and ozone interaction with floor dust
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Submitted:  01/11/2013
PhD thesis – Measurements of selected air pollutants in Danish homes and ozone interaction with floor dust

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Institution: Det Nationale Forskningscenter for Arbejdsmiljø (NFA)

Udgiver: Det Nationale Forskningscenter for Arbejdsmiljø (NFA)

Udgivet: Januar 2014

ISBN: 978-87-7904-277-3
Preface

The topic of this thesis is chemical exposure in indoor air in homes, and is a part of a larger collaboration of the Centre for indoor air and health in dwellings (CISBO). The results obtained are divided into three sections:

Part I: "Laboratory studies: Chemical properties of house dust in the FLEC"

This section presents laboratory based experiments on the interaction between indoor floor dust and ozone investigated in a small climate chamber (FLEC). The results from this section is presented in paper I: "Ozone reaction characteristics of indoor floor dust examined in the emission cell “FLEC”"

Part IIa: "Field campaign"

This section presents the data obtained in a 5-home field sampling campaign performed in collaboration with the Danish Technical University and the Danish Building Research Institute, Aalborg University, within the framework of the Center for Indoor air and Health in dwellings (CISBO). Passive ozone samplers have been collected by SBi in relation to a 60-home intervention study and the samplers have been analyzed as a part of this thesis.

Part IIb: "Low Temperature Plasma ionization-MS on filter samples"

This section focuses on the use of a new ionization technique (Low Temperature Plasma – LTP) for direct MS-analysis of PM$_{2.5}$ filters sampled during the 5-home field campaign in section IIa. Some of the work in this section is presented in paper II: "Direct quantitative analysis of PAHs, phthalates and fatty acids on Teflon filters using Low Temperature Plasma ionization MS"
Acknowledgements

This thesis could not have been completed without the help, collaboration and support from a number of people, to whom I owe great thanks!

First of all I would like to thank my supervisors at the National Research Centre for the Working Environment (NRCWE) Peder Wolkoff and Per Axel Clausen for always being there for questions, discussions or just good ideas and for believing in me through this whole long process. Also a special thanks to Asger Nørgaard, who introduced me to NRCWE more than 7 years ago for my master thesis, and who have since been a great advisor in both mass spectrometry and whisky, as well as a great travel companion for a number of courses and conferences during my time at NRCWE. Our fantastic laboratory technician at NRCWE Vivi Kofoed Sørensen has been a great practical help in the lab and deserves a great thanks for support on professional as well as personal level. I also thank my supervisors at the University of Copenhagen, Merete Bilde and Ole John Nielsen.

A great thank goes to Ulla Vogel for great support and loving kicks when needed, and to Lars Andrup for believing in me.

Thanks to all of the CISBO project members, especially Mika Frankel, Gabriel Bekö, Sine Gustavsen, Marie Frederiksen, Barbara Kolarik and Michal Spilak for the many hours spent together and with the field measurements. Also, Anne Mette Madsen, Geo Clausen, Jørn Toftum and Torben Siggaard have been very helpful in the planning and execution of the CISBO projects. Special thanks goes to the five families in the field study, for letting us into their homes and being so patient with all our bulky, noisy and disturbing instruments.

Also great thanks to the rest of the “chemical and physical guys” (Brian Hansen, Yahia Kembouche, Ismo Koponen, Marcus Levin, H.C. Budtz and Jacob Kudal) for numerous interesting discussions during coffee breaks and Friday beers. How could I live without that knowledge.....?

I thank the “bread and cake club” at NRCWE for great cakes and good bread and for creating such a nice atmosphere at work.

Finally I thank Marcell Olsen for joining me in this crazy ride finishing a PhD thesis, for coping with the weird working hours and in general just for being you and for being there. Great new adventures are awaiting us in the future.

This PhD study has been funded by the REALDANIA foundation, University of Copenhagen and The National Research Centre for the Working Environment.

[2]
Publications and proceedings

Publications included in this thesis:


Publications not included in this thesis:


Conference proceedings:


Summary
Section I: Laboratory studies: Chemical and sorption properties of indoor floor dust in FLEC:

Ozone reacts with C-C double bonds in common indoor VOCs and SVOCs contained in indoor dust and may be catalytically degraded on dust surfaces. The reaction between floor dust and ozone was investigated in the Field and Laboratory Emission Cell (FLEC) at different ozone concentrations and relative humidities (0, 25, and 50 % RH). One gram of dust was spread on a clean stainless steel plate which was placed in the FLEC. Steady state reaction rate (k_{Dust}) at 2.2 ppm ozone was determined for four different floor dust samples collected in Danish homes and offices. This high concentration was necessary in order to measure and determine the consumption of ozone in the outlet air from the FLEC. Measurements were corrected for FLEC wall effects by subtraction of the steady state reaction rate between ozone and a FLEC on a stainless steel plate without dust (k_{FLEC}). The composition of organic compounds in the dust was analyzed by pressurized liquid extraction and thermal desorption GC-MS before and after ozone exposure.

K_{FLEC} was independent of the ozone concentration and the reaction was treated as first order. The same was indicated for K_{Dust} since it remained unchanged at 2.2 and 1.6 ppm ozone for one dust sample. However, the measured K_{Dust} in the FLEC should be considered an average rate constant due to the FLEC geometry. K_{Dust} was trice higher at 25% RH than at 50% RH and 6 times higher than at 0 % RH.

The major identified compounds before and after ozone exposure included aldehydes, saturated and unsaturated linear alkanoic acids, benzoic acid and their methyl esters, dimethyl esters, phthalates and traces of α-pinene and limonene. Substantial increase of C_7-C_9 aldehydes was observed after ozone exposure.

Section IIa: Field study

Field measurements were carried out inside and outside of five Danish homes throughout a year, with four measurement campaigns in each home, representing four seasons: Spring, Summer, Fall, and winter. Ozone, NO_2 and aldehydes were measured outdoor for comparison with indoor measurements. Seasonal variation of indoor ozone, NO_2, aldehydes, particles (0.75-15 µm), ultrafine particles (<1 µm) was investigated. The parameters measured as part of this thesis was compared, to search for correlations. Temperature, relative humidity and air exchange rates, obtained in other parts of the CISBO-project, were also investigated with regard to seasonal variation and correlation with the parameters found as a part of this thesis. Volatile organic compounds were analyzed qualitatively.

Correlations were found between indoor and outdoor absolute humidity; opening of windows and air exchange rate; indoor aldehydes and outdoor ozone; and, indoor aldehyde and air exchange rate.
A total of 85 VOCs was identified from sampling on Tenax TA in the five homes during the fall season.

**Section IIb: Direct Low Temperature Plasma ionization-MS analysis of air sampling filters**

The quantitative properties of a new ionization technique for mass spectrometry (Low Temperature Plasma ionization – LTP) were investigated for analysis of Teflon air sampling filters. Standards of free fatty acids (lauric, myristic, palmitic, oleic, and stearic acid), phthalates (dimethyl, diethyl, dibutyl, benzylbutyl and bis(2-ethylhexyl) phthalate) and PAHs (including naphthalene, fluorene, anthracene, and pyrene) were used for the quantification and linear calibration curves were obtained within a limited concentration range. Free fatty acids and phthalates were determined on Teflon air sampling filters obtained in the field study. The results were compared to a direct thermal desorption (TD) GC-MS method of sampled filters. Advantages and disadvantages as well as possible improvements of the LTP-MS method are discussed together with principal component analysis (PCA) of the sampled filters.

**Dansk resume**

**Del I: Laboratorie studie: Kemiske og sorptionsegenskaber af husstøv målt i FLEC**

Ozon reagerer med C-C dobbeltbindinger i almindeligt forekommende organiske forbindelser i husstøv og kan også nedbrydes katalytisk på overflader. Reaktionen mellem ozon og støv blev undersøgt i en emission celle (FLEC) ved forskellige ozonkoncentrationer og relative luftfugtigheder (0, 25 og 50%). Et gram støv blev spredt på en rustfri stål plade, som fungerede som bund i FLECen. Hastighedskonstanten ved ligevægt ($k_{Dust}$) ved 2.2 ppm blev bestemt for fire forskellige prøver af husstøv indsamlet i danske boliger og kontorer. Den høje ozonkoncentration var nødvendig for overhovedet at kunne måle ozon i udgangsluften fra FLECen og dermed kunne bestemme forbruget af ozon over støvet. Målingerne blev korrigeret for absorption af ozon af FLECens overflade ved at fratrække ligevægts hastighedskonstanten for en tom FLEC ($K_{FLEC}$).

$k_{FLEC}$ var uafhængig af ozon koncentrationen og reaktionen kunne derfor behandles som en førsteordens reaktion. Den samme uafhængighed blev indikeret for $k_{Dust}$, som forblev uændret ved en sænkning af ozonkoncentrationen fra 2.2 til 1.6 ppm. $k_{Dust}$ skal betrages som en gennemsnitlig konstant over hele støvoverfladen på grund af geometrien og luftstrømmene i FLECen. Ved 25% relativ luftfugtighed var $k_{Dust}$ 3 gange højere end ved 50% og 6 gange højere end ved 0%.

De primære identificerede reaktionsprodukter for og efter ozon eksponering inkluderede aldehyder, mættede og umættede linære syrer, benzosyre og disse methylestre samt methylestre, phthalater samt spormængder af α-pinene og limonen. Efter ozoneksponering indeholdt støvet en væsentlig højere koncentration af C$_7$-C$_9$ aldehyder.
Del IIa: Feltstudie

Der blev foretaget feltmålinger i 5 danske hjem gennem et år med fire målekampagnen i hvert hjem. Kampagnerne var planlagt så de fire sæsoner blev repræsenteret (forår, summer, efterår og vinter). Ozon, NO₂ samt aldehyder blev også målt udenfor for sammenligning med indendørs målinger. Sæson variation af indendørs ozon, NO₂, aldehyder, partikler (0.75-15 µm) samt ultrafine partikler (<1 µm) blev undersøgt. De målte parametre blev sammenlignet for at teste for korrelationer. Temperatur, relativ luftfugtighed og luftskifte blev målt i andre dele af CISBO-projektet og blev også undersøgt med hensyn til årstidsvariation og korrelation med de parametre, som blev undersøgt som en del af denne these. Flygtige organiske forbindelser blev karakteriseret kvalitativt.

Der blev fundet korrelationer mellem indendørs og udendørs absolut luftfugtighed; åbning af vinduer og luftskifte; indendørs aldehyder og udendørs ozon samt mellem indendørs aldehyder og luftskifte. 85 flygtige organiske forbindelser blev identificeret udfra prøvetagning på tenax TA i de fem hjem i efterårrsæsonen.

Del IIb: Direkte lavtemperatur plasma ionisering af luftprøver på Teflon filtre

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### Abbreviations

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-DNPH</td>
<td>2,4-Dinitrophenylhydrazine</td>
</tr>
<tr>
<td>AER</td>
<td>Air Exchange Rate (ventilation)</td>
</tr>
<tr>
<td>BBP</td>
<td>Benzyl butyl phthalate</td>
</tr>
<tr>
<td>CI</td>
<td>Chemical Ionization</td>
</tr>
<tr>
<td>CISBO</td>
<td>Centre for Indoor Climate and Health in dwellings</td>
</tr>
<tr>
<td>DBP</td>
<td>Dibutyl phthalate</td>
</tr>
<tr>
<td>DEHP</td>
<td>Di-2-ethylhexyl Phthalate</td>
</tr>
<tr>
<td>DEP</td>
<td>Diethyle phthalate</td>
</tr>
<tr>
<td>DMP</td>
<td>Dimethyl phthalate</td>
</tr>
<tr>
<td>DTU</td>
<td>Danish Technical University</td>
</tr>
<tr>
<td>EI</td>
<td>Electron Ionization</td>
</tr>
<tr>
<td>EIC</td>
<td>Extracted Ion Chromatogram</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray Ionization</td>
</tr>
<tr>
<td>FLEC</td>
<td>Field and Laboratory Emission Cell</td>
</tr>
<tr>
<td>I/O</td>
<td>Indoor to Outdoor ratio</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit of Detection (3xSD)</td>
</tr>
<tr>
<td>LOQ</td>
<td>Limit of Quantitation (10xSD)</td>
</tr>
<tr>
<td>LTP</td>
<td>Low Temperature Plasma ionization</td>
</tr>
<tr>
<td>MALDI</td>
<td>Matrix Assisted Laser Desorption Ionization</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass to charge ratio</td>
</tr>
<tr>
<td>MTBH</td>
<td>3-methyl-2-benzothiazolinone hydrazone hydrochloride</td>
</tr>
<tr>
<td>NEDA</td>
<td>N-(1-naphthyl)-ethylenediamine dihydrochloride</td>
</tr>
<tr>
<td>NRCWE</td>
<td>National Research Centre for the Working Environment</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
</tr>
<tr>
<td>PLE</td>
<td>Pressurized Liquid Extraction</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>rt</td>
<td>Retention time</td>
</tr>
<tr>
<td>SBi</td>
<td>Statens Byggeforskningsinstitut/Danish Building Research Institute</td>
</tr>
<tr>
<td>SIM</td>
<td>Selected Ion Monitoring</td>
</tr>
<tr>
<td>SVOC</td>
<td>Semi Volatile Organic Compound</td>
</tr>
<tr>
<td>TD-GC-MS</td>
<td>Thermal Desorption Gas Chromatography Mass Spectrometry</td>
</tr>
<tr>
<td>TIC</td>
<td>Total Ion Chromatogram</td>
</tr>
<tr>
<td>TVOC</td>
<td>Total Volatile Organic Compounds</td>
</tr>
<tr>
<td>$v_d$</td>
<td>Deposition velocity</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>WP</td>
<td>Work Package</td>
</tr>
</tbody>
</table>
1 General introduction and theory

1.1 The CISBO project

The work in this thesis is a part of the CISBO research center funded by the REALDANIA foundation (Center for indeklima og sundhed i boliger/Centre for Indoor Climate and Health in Homes) (Siggsgaard et al., 2011); a collaboration between NRCWE (National Research Centre for the Working Environment), DTU (Technical University of Denmark, Department of Civil Engineering), SBi (University of Aalborg, Statens Bygge-forskningsinstitut), KU-SUND (University of Copenhagen, Faculty of Health and Medical Sciences) and AU (Aarhus University, Department of Public Health, Institute of Environmental and Occupational Medicine).

The project consists of four work packages (WP), all with a focus on air quality and health effects in Danish homes. This thesis contributes to CISBO WP 1.1 and CISBO WP 4.1.

1.1.1 CISBO Work Package 1 - Pilot Study

This WP is concerned about indoor environmental exposure in Danish homes and was divided into three sub tasks. CISBO WP 1.1 was a pilot study, investigating five homes during a period of one year. The main objectives were to investigate seasonal changes in the air exchange rate and the temporal and spatial behavior of selected chemical-, biological and particulate pollutants in homes. The pilot study was also used to evaluate different dust sampling methods and different air exchange rate measurements techniques. A major part of this thesis is founded in the chemical aspects of CISBO WP 1.1 and will be described in further details. CISBO WP 1.2 was a cross sectional study investigating a few easily accessible exposures in 60 homes during a heating season. The objective was to deliver data based on few easily accessible methods to CISBO WP 1.3, where the objective was to develop a model to predict indoor exposure. The present thesis contributed with analysis of passive ozone samplers in the 60-homes study.

1.1.2 CISBO Work Package 2 - Population based study of health effects of indoor air

CISBO WP 2 combined existing cohort data and monitoring of indoor air and selected biomarkers and physiological functions to investigate associations between indoor air in homes and related health effects.

1.1.3 CISBO Work Package 3 - Indoor environment exposures in Danish residences

The objective of CISBO WP3 was to investigate the effect of interventions in private homes. In CISBO WP 3.1 the intervention was removal of indoor particles via a specially designed re-circulating particle filtration unit. The objective was to investigate if the intervention had positive impact on cardiovascular and respiratory health among elderly people. CISBO WP 3.2 investigated if increased ventilation, and thus air exchange rates, had positive impacts on health of asthmatic children and children allergic to house dust mites.

1.1.4 CISBO Work Package 4 - Emission testing and exposure experiments carried out under controlled conditions at low and high humidity.

This WP consisted of three different sub tasks: CISBO WP 4.1 investigated dust particle dynamics in air and on surfaces with focus on deposition, re-suspension, SVOC uptake and re-emission and
chemical degradation. This thesis works on emission of VOCs and ozone exposure of house dust. Other projects within this subtask were influence of temperature on the emission of DEHP from PVC flooring and emission and uptake of gas phase DEHP by floor dust. CISBO WP 4.2 investigated the release and inflammatory potential of microbiological contaminants at different conditions such as airflow, humidity and the infested material surface. CISBO WP 4.3 investigated biological effects such as inflammation, sensitization, lung effects, and cardiovascular effects of targeted air pollutants. These factors were both assessed via an animal bioassay and controlled human exposures.

1.2 Volatile and Semi volatile Organic Compounds

The air we breathe contains thousands of different volatile and semi volatile organic compounds (VOCs and SVOCs) with both natural and anthropogenic sources. Some of these compounds are harmless, some might influence how we perceive the air quality due to their odors and some have adverse health effects. Some might not be problematic in themselves but reactive towards gasses such as ozone, and thus form reaction products which can be of greater concern; e.g. formation of ozonides and aldehydes from reaction between terpenes and ozone (Wolkoff et al., 1999; Nørgaard et al., 2006). Thus a complete characterization of organic compounds in air is complex, but knowledge about concentrations and understanding of chemical processes are fundamental for the assessment of indoor air quality.

The general definition of a VOC is an organic chemical compound present in the gas phase under normal indoor conditions of temperature and pressure. This definition is however not precise, since “normal” conditions may vary on geography, season and building type. Another more precise definition by WHO utilizes boiling points (World Health Organization, 1987). According to this definition VVOCs (Very Volatile Organic Compounds) are compounds with boiling point <29 °C e.g. formaldehyde; VOCs in the range 50-260 °C e.g. monoterpenes, acetone, ethanol and hexanol; SVOCs in the range 260 -400°C e.g. pesticides, flame retardants, PAHs, and plasticizers such as phthalates.

Indoor VOCs and SVOCs are mostly released into the air from use of VOC/SVOC containing products such as cleaning products or released from building materials such as phthalates from plastic. VOCs can also be released as products from reactions such as hydrolysis or oxidative degeneration. Over the past half century there has been a major change in the emission profiles in buildings as a consequence of changes in indoor sources such as composite wood, synthetic carpets, polymeric floorings, scented cleaning agents etc. (Weschler, 2009)

For assessment of indoor VOC pollution the total VOC concentration (TVOC) can be used. TVOC concentration is defined as the total concentration of all compounds within the range of a chromatogram between hexane (b.p. 68 °C) and hexadecane (b.p. 287 °C) (Seifert, 1999). However, a sum of the major VOCs within this range is often used to estimate TVOC, but due to different selection of analyzed VOCs, different studies are generally not comparable (Mølhave et al., 1997, Andersson et al., 1997). Without the knowledge of the amounts of the individual VOCs included in
TVOC, assessment of health effects is impossible, since different VOCs might have different effects (Andersson et al., 1997).

VOC exposures has been considered to cause symptoms similar to those of sick building syndrome, which is defined as a group of symptoms including irritability, sleepiness, inability to concentrate, and other health hazards (Mølhave, 2003; Nielsen et al., 2007).

1.2.1 Selected organic compounds
The following section will give an overview of the different compounds investigated in this thesis. It is not to be seen as a comprehensive list of chemicals encountered in indoor environments. Major and well established health effects will be mentioned, but detailed a discussion are beyond the scope of this thesis.

1.2.1.1 Aldehydes
A range of common aldehydes and their boiling points are summarized in Table 1. With the low boiling points formaldehyde and ethanal are VVOCs and the remaining aldehydes in the table are VOCs.

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Formula</th>
<th>Molar mass [g/mol]</th>
<th>b.p. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>CH₂O</td>
<td>30.03</td>
<td>-19</td>
</tr>
<tr>
<td>Ethanal</td>
<td>C₂H₄O</td>
<td>44.05</td>
<td>20</td>
</tr>
<tr>
<td>Propanal</td>
<td>C₃H₆O</td>
<td>58.08</td>
<td>49</td>
</tr>
<tr>
<td>Butanal</td>
<td>C₄H₈O</td>
<td>72.11</td>
<td>75</td>
</tr>
<tr>
<td>Isovaleraldehyde</td>
<td>C₅H₁₀O</td>
<td>86.13</td>
<td>90</td>
</tr>
<tr>
<td>Pentanal</td>
<td>C₅H₁₀O</td>
<td>86.13</td>
<td>102</td>
</tr>
<tr>
<td>Hexanal</td>
<td>C₆H₁₂O</td>
<td>106.18</td>
<td>130</td>
</tr>
<tr>
<td>Heptanal</td>
<td>C₇H₁₄O</td>
<td>114.18</td>
<td>153</td>
</tr>
<tr>
<td>2-Furaldehyde</td>
<td>C₅H₉O₂</td>
<td>96.08</td>
<td>162</td>
</tr>
<tr>
<td>Octanal</td>
<td>C₈H₁₄O</td>
<td>128.21</td>
<td>171</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>C₇H₈O</td>
<td>106.12</td>
<td>178</td>
</tr>
<tr>
<td>Nonanal</td>
<td>C₉H₁₄O</td>
<td>142.24</td>
<td>195</td>
</tr>
<tr>
<td>Decanal</td>
<td>C₁₀H₁₄O</td>
<td>156.27</td>
<td>208</td>
</tr>
</tbody>
</table>

Aldehydes in indoor air can originate from both primary and secondary emissions (e.g. Gall et al. 2013; Morrison & Nazaroff 2002; Nicolas et al. 2007). Many common household and personal products contains aldehydes as fragrances (Rastogi et al., 2001). Aldehydes are also a common oxidation product from ozonolysis of other organic compounds in e.g. homes (Wang and Morrison, 2010; Rancière et al., 2011), building materials (Gall et al., 2013), and human hair (Pandrangi and Morrison, 2008), but they are also released directly from the human body (Ellin et al., 1974; Goetz et al., 1988).
One of the most common aldehydes is formaldehyde, a product of incomplete combustion of carbon containing compounds (Dias et al., 2012) and a precursor to materials such as a number of resins, used e.g. as adhesives in plywood and carpeting, which causes primary emission especially in new or recently renovated homes.

Formaldehyde has been regulated for its carcinogenic properties (WHO, 2010) and aldehydes may cause sensory irritation and influence the perceived indoor air quality due to their generally low odor thresholds (Wolkoff, 2013).

### 1.2.1.2 Phthalates

One common group of SVOCs is phthalates, which were found to dominate the indoor samples in this thesis.

Phthalates are esters of phthalic acid and since the 1930s, they have been used as plasticizers to enhance the flexibility of polyvinylchloride (PVC). They are used in consumer products, building materials, cars, clothing, food packaging, children’s products and medical devices and may be present at concentrations as high as 10-60% (w/w) (Rudel and Perovich, 2009; Schettler, 2006). Other common phthalates include dimethyl-(DMP), diethyl- (DEP), di-n-butyl-(DBP), and butylbenzyl phthalate (BBP) (Figure 1).

![Figure 1: General structure of phthalate esters and boiling points of selected phthalates.](image)

<table>
<thead>
<tr>
<th>Phthalate</th>
<th>Formula</th>
<th>Molar mass [g/mol]</th>
<th>Boiling point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMP</td>
<td>C₁₀H₁₀O₄</td>
<td>194.18</td>
<td>283</td>
</tr>
<tr>
<td>DEP</td>
<td>C₁₂H₁₄O₄</td>
<td>222.24</td>
<td>295</td>
</tr>
<tr>
<td>DBP</td>
<td>C₁₆H₂₂O₄</td>
<td>278.34</td>
<td>340</td>
</tr>
<tr>
<td>BBP</td>
<td>C₁₉H₂₀O₄</td>
<td>312.36</td>
<td>370</td>
</tr>
<tr>
<td>DEHP</td>
<td>C₂₄H₃₈O₄</td>
<td>390.56</td>
<td>385</td>
</tr>
</tbody>
</table>

Phthalates embedded in a polymer matrix are not chemically bound, and a slow emission will occur from the products to the air. The emission from the material is coupled to a constant diffusion of phthalate through the material, and not only limited to whatever might be present at the surface at a given time. This release is often slow enough to last throughout the entire product use phase. As a result phthalates are one of the most abundant semi-volatile compounds in indoor air (e.g. Clausen et al., 2003; Rudel et al., 2003). Similar to other (SVOCs), they are strongly adsorbed onto surfaces (Clausen et al., 2010).
A source of phthalates in indoor air may also be re-suspension of sedimented dust (Oie et al., 1997). DEHP concentrations measured in the indoor climate are often the sum of gas phase and particle phase. About 80% of the total airborne DEHP in indoor settings are associated with particles suspended in the air (Weschler, 2003). Inhalation and skin deposition from re-suspended dust might therefore be a major exposure route (Xu et al., 2009). As opposed to phthalates embedded in a building material, dust can be removed by frequent cleaning, which should reduce exposure (Clausen et al., 2004).

A number of studies have suggested that phthalates might possess adjuvant effects to enhance the health damaging potential of common allergens (Jaakkola et al., 1999; Larsen et al., 2001).

1.2.1.3 Free fatty acids
Free fatty acids were found to dominate indoor samples obtained in this thesis. With boiling points similar to the phthalates they are also expected to be found mainly condensed on particles or other surfaces (Table 2).

<table>
<thead>
<tr>
<th>Free fatty acid</th>
<th>Formula</th>
<th>Molar mass [g/mol]</th>
<th>b.p. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric acid (C12:0)</td>
<td>C_{12}H_{24}O_{2}</td>
<td>200.32</td>
<td>299</td>
</tr>
<tr>
<td>Myristic acid (C14:0)</td>
<td>C_{14}H_{28}O_{2}</td>
<td>228.37</td>
<td>326</td>
</tr>
<tr>
<td>Palmitic acid (C16:0)</td>
<td>C_{16}H_{32}O_{2}</td>
<td>256.42</td>
<td>351</td>
</tr>
<tr>
<td>Stearic acid (C18:0)</td>
<td>C_{18}H_{36}O_{2}</td>
<td>284.48</td>
<td>376</td>
</tr>
<tr>
<td>Oleic acid (C18:1 cis 9)</td>
<td>C_{18}H_{34}O_{2}</td>
<td>282.46</td>
<td>360</td>
</tr>
</tbody>
</table>

*: Unsaturated.

Human skin contains free fatty acids (Nicolaides et al., 1972); human debris and emission from the human body are thus a major source (Ellin et al., 1974; Goetz et al., 1988), but also emission from cooking contributes (Rogge et al., 1991; Schauer et al., 2001). The most common free fatty acids contain an even number of carbon atom, due to the way they are synthesized in biological processes (Haslam and Kunst, 2013).

Unsaturated free fatty acids containing one or more C-C double bonds are reactive towards ozone, thus they have the potential to be a source of new compounds, e.g. aldehydes, which might impact the indoor air quality, but they are in themselves of no health concern.

1.2.1.4 Polycyclic Aromatic Hydrocarbon (PAH)
Polycyclic aromatic compounds (PAHs) are complex organic chemicals with compounds with a fused ring structure containing at least 2 benzene rings. The structures of 16 common PAHs are given in App. D.

PAHs are atmospheric pollutants which are found naturally in oil, coal and tar, and are formed by incomplete combustion of carbon-containing compounds such as diesel and wood. The major source
is heavy traffic but they can also be formed during cooking. Thus they are often found in higher concentrations outdoor than indoor (Ravindra et al., 2008; Kliucininkas et al., 2011), thus, they are mainly considered outdoor pollutants, and are not expected to be found in substantial amount in the indoor samples. The structures and chemical properties of 16 common PAHs are summarized in App. D. High molecular PAHs with 5 or more rings have low vapor pressure and are largely bound to particular matter. Low molecular PAHs with 2-3 rings are predominantly found in the gas phase, whereas the 4-ring containing are present both in the gas phase and on particles in ambient air depending on the temperature (Scrogi, 2007).

PAHs are not found in any of the indoor samples in this thesis, but the LTP-MS method in section IIb includes them in the evaluation of quantitative properties for a possible future use of the method to outdoor samples.

Most PAHs are recognized as being carcinogenic in humans (WHO, 2010).

1.2.2 Ozone

Ozone is important due to its reactivity with a number of VOCs and SVOCs. Section I investigates the interaction between dust and ozone. Indoor and outdoor ozone concentrations in homes are reported in Section IIa.

The concentration of indoor ozone depends on a number of factors including outdoor concentration, air exchange rates, indoor sources, surface removal rates and removal by reactions with other compounds in the air. The half-life of indoor ozone is typically between 7 and 10 min, and is controlled mainly by surface removal and air exchange (Weschler, 2000). Though ozone reacts with a number of indoor relevant VOCs and SVOCs, the reaction rates for most of these reactions are too slow to compete with the air exchange. The reactions with fast enough reactions rates to occur include compounds with unsaturated C-C bonds e.g. in terpenes (Weschler, 2000). Unsaturated fatty acids and esters thereof can also react with ozone (Pryor et al., 1976), and are common constituents of indoor dust from skin lipids (Clausen et al., 1998). Two other polyunsaturated compounds (squalene and cholesterol), which are expected to scavenge ozone, are shed from human skin and in a previous study found in 97% of dust samples collected from bedrooms and daycare centers in Denmark (Weschler et al., 2011).

There are two sides of the aspect of ozone and health. Ozone itself is potentially deleterious to human health even in trace levels (U.S. Environmental Protection Agency, 2006) and its reaction with relatively harmless compounds can result in formation of airway irritants (e.g. Wolkoff et al., 1999; Wolkoff et al., 2006).

Typical indoor air only contains trace elements of ozone (typically 10-100 ppb) and typical recommended limits for indoor ozone are around 80-100 ppb (Weschler, 2000). Most studies on long term effects of ozone suggest health effects, but are inconclusive (U.S. Environmental Protection Agency, 2006).
The photochemical ozone production outdoors involves a complex set of reactions involving vapor phase organic compounds, nitrogen oxides, carbon monoxide, and sunlight and will not be covered further here. As a consequence of these factors, the outdoor ozone levels tend to be highest in densely populated areas with intense sunshine.

Indoor sources of ozone are typically caused by electronic equipment such as photocopiers, laser printers, and electrostatic filters and precipitators (Leovic et al., 1996), but the major source is infiltration from outdoor air (Weschler, 2000).

Ozone is reactive toward a number of organic compounds containing C-C double bonds via ozonolysis (Figure 2), e.g. in the reaction with terpenes (Criegee, 1975). A number of carbonyl products such as aldehydes, ketones, and carboxylic acids can be formed, depending on the R-groups on the double bond. Some of these compounds might have other properties such as a larger irritation potential than the reactants (Wolkoff et al., 1999), thus ozone can have an indirect effect of perceived air quality and health effects of indoor air.

\[
\begin{align*}
  \text{O}_3 + \text{CH}_2=\text{CH}_2 &\rightarrow \text{CH}_2=\text{CH}-\text{CO}+2\text{O}_2 \\
  \text{O}_3 + \text{CH}_3\text{CH}=\text{CH}_2 &\rightarrow \text{CH}_3\text{CH}=\text{CH}-\text{CO}+2\text{O}_2
\end{align*}
\]

Figure 2: Cycloaddition of ozone to C-C double bond, formation of primary ozonide and breakdown to carbonyl product and unstable Criegee intermediate.

1.2.3 \textbf{NO}_2

Nitrogen dioxide (NO₂) is a part of the NOx family (NOx=NO+NO₂), which is associated with combustion sources, e.g. from traffic (IPCC, 2001). Thus high indoor NO₂ is often correlated with proximity to heavy traffic (e.g. Kimbrough et al., 2013), though indoor sources such as burning of candles, tobacco smoke, and wood- and gas stoves can also be substantial.

During combustion 90-95% of the NOx is released as NO, which under ambient conditions is rapidly oxidized in air to NO₂ by any available oxidants (oxygen, ozone and VOCs), thus NO₂ is usually considered the primary pollutant, though the oxidation reaction is slower in indoor conditions (Arashidani et al., 1996).

The WHO guidelines for NO₂ concentration are 200 µg/m³ (1 h average; 106 ppb) and 40 µg/m³ (annual average; 21 ppb) (WHO, 2010). Typical urban/suburban outdoor NO₂ concentrations are in the range 10-1000 ppb and only 0.2-10 ppb in rural areas (Seinfeld and Pandis, 2006).

1.3 \textbf{Particles}

Airborne particles consist of a number of different components including organic chemicals, metals, soil and biological particles e.g. pollen or mold spores (Owen et al., 1992). Particles can be characterized by their size distribution, either given by their number or mass distribution. A plot of the number distribution will favor small particles, whereas a mass distribution favors the larger and
thus heavier particles. For most calculations of particle size distributions a spherical shape of the particles is assumed. This is often true for aerosols, which are tiny droplets of condensed compounds in the liquid phase, but not necessarily for e.g. dust or sand particles which are solids. An overview of the sizes of different types of particles is given in Figure 3. The major source of indoor particles <2.5 µm (PM$_{2.5}$) in non-smoking homes is cooking, while that of coarse particles (2.5-10 µm) is cooking and/or resuspension of particles from cleaning or people’s movement (Abt et al., 2000).

In this thesis particles are of interest since they can act as condensation nuclei for SVOCs and thus cause compounds with low vapor pressures, such as phthalates, to be air-borne. The floor dust samples examined in section I are particles, but without any knowledge about size distribution. Ambient particles are diverse in both composition and size and so are the possible health effects. Two main factors determine the possible health effects:

- How far the particle size allows the particles to penetrate into the respiratory tract (Figure 4). Particles >10 µm mainly deposits in the upper airways, and are thus mainly at risk to irritate nose and throat, whereas smaller particles can reach deeper into the lungs, and thus have a greater risk of crossing into the bloodstream and influence the cardiovascular system (Nelin et al., 2012). For environmental measurements of particles PM$_{2.5}$ and PM$_{10}$ is often used; i.e. the total amount of particles below 2.5 and 10 µm respectively.
- If the particle, or any compounds adsorbed to the surface, is harmful. Thus not only the size, but also the chemical composition and morphology of the particle is important to characterize with regard to health effects.

![Figure 4: Particle deposition within the respiratory tract as a function of particle size. From Golin et al., 2013.](image)

However, controlled human exposure studies with indoor particles have not shown any significant health effects, though some effects have been observed with combinations of particles and ozone or NO₂. However effects from field intervention studies can be difficult to assign to particles alone, since other parameters might also be changed by the intervention (Wolkoff, 2013).

### 1.4 Mass spectrometry

Throughout this thesis, mass spectrometry has been used for analysis of different samples. The following sections will cover the relevant background for the methods used.

A mass spectrometer consists of 5 components: Sample inlet, ion source, mass analyzer, detector and a data treatment system (Figure 5).

![Figure 5: Principle components of a mass spectrometer. From www.premierbiosoft.com](image)

Especially for the ion source and the mass analyzer a number of different methods exists, which can be combined to suit the analyte. Those relevant to the work in this thesis will be described in the following sections. Other methods will just be mentioned briefly.
1.4.1 Ionization techniques

The key step in successful performance in mass spectrometry is the ionization of the analytes. Through the ionization process the analyte molecules become either positively or negatively charged and may therefore be influenced by electrical fields and introduced into the mass spectrometer.

A number of different ionization techniques are in use in labs around the world today. They can coarsely be divided into three groups: Ionization techniques that require vacuum; techniques that function at atmospheric pressure under controlled conditions and those that function at ambient conditions.

1.4.1.1 Vacuum ionization techniques

Electron impact is utilized for the analysis of extracts of dust samples in section I; for analysis of VOCs in indoor air sampled on Tenax TA in Section IIa and for TD-GC-MS of Teflon air filter samples in Section IIb.

The most common vacuum ionization technique is electron ionization (EI), where analyte molecules are subjected to a flux of electrons from a heated filament. The electrons typically have energies of 70 eV. The impact between analyte molecule (M) and electron causes ionization of the analyte molecule by ejection of one electron:

\[ M + e^- \rightarrow M^{+} + 2e^- \]

The resulting radical cations (M^{+}) will often have excess internal energy from the collision with the high-energy electrons and may thus fragment. A fragmentation results in fragment ions (X^{+}), radicals (Y^{+}), radical ions (Z) or neutrals (N):

\[ M^{+} \rightarrow X^{+} + Y^{+} \]

\[ M^{+} \rightarrow Z^{+} + N \]

The fragment ions might still contain enough excess energy to break down in secondary fragmentations. The fragmentation is characteristic for each molecule and relatively reproducible between instruments if the same ionization energy is used. It can therefore be used for identification of unknown products. The EI identification is further strengthened by years of compiling spectra of different compounds, which is searchable in the e.g. NIST Mass spectral Library (NIST, 2011). Even though the high degree of fragmentation can be useful for identification of unknown compounds, it also has a drawback, namely that the molecular mass is often not seen in the mass spectrum due to extensive fragmentation. EI requires that the analyte molecules are already in the gas phase when they enter the ionization source. This requirement limits the possible analytes to volatiles and semi volatiles. At the same time it makes this ionization technique compatible with gas chromatography (GC).
1.4.1.1 Thermal Desorption Gas Chromatography Mass Spectrometry (TD-GC-MS)
TD-GC-MS is used in three different applications in this thesis: Injection of extracts from dust onto Tenax TA in Section I, desorption of VOCs in indoor air adsorbed to Tenax TA in Section IIa, and desorption of VOCs and SVOCs from Teflon air sampling filters in Section IIb.

Tenax TA is a porous polymer resin based in 2,6-diphenylene oxide. It adsorbs organic compounds from air or liquids, and is thus useful for sampling of VOCs and SVOCs from air. For TD-GC-MS active sampling, where a pump delivers a flow of sample air through the adsorbent, is used.

The analytes on the Tenax TA or on the filter is released by heating the sampling tube, with a stream of helium in the opposite direction of the sampling flow. If this flow was connected directly to the GC-MS, it would result in broad chromatographic peaks, since the release from the adsorbent material does not occur instantly. Thus the analytes are collected in a cryo-trap, from where it can be released fast via flash heating and injected onto the GC column.

One disadvantage of the method is, that once a sample has been desorbed it cannot be analyzed again, opposed to on-column injection, where a small amount (typically 0.5-1 µl) of an extract are injected onto the GC-column.

1.4.1.1.2 Ambient ionization techniques
Over the recent years a number of techniques for ionization at ambient conditions have been developed. These take advantage of the interfaces developed for electrospray and its ability to act as a gate between the atmospheric pressure just outside the mass spectrometer and the high vacuum within and to transport ions without compromising the high vacuum.

Desorption electrospray ionization (DESI) (Takats et al., 2004) and direct analysis in real time (DART) (Cody et al., 2005) was developed in 2004 and 2005 and they were the first ionization techniques to enable mass spectrometric analysis of virtually any substance or surface under ambient conditions. Complex liquids such as blood or urine could also be spotted on a surface and evaporated to dryness and analyzed without further sample cleanup and with minimal risk of contamination or clogging of the mass spectrometer. Inspired by the concepts of these techniques a new field in mass spectrometry has risen and a number of related techniques have been presented (Alberici et al., 2010; Chen et al., 2009; Venter et al., 2008; Chipuk and Brodbelt, 2008; Haddad et al., 2006; Harper et al., 2008; Haddad et al., 2008; Harris et al., 2011). The ultimate goal of these ambient ionization techniques is to develop a portable ionization source, which can desorb and ionize analytes simultaneously directly from a surface with little or no sample pretreatment.

1.4.1.1.2.1 LTP
LTP is used for analysis of Teflon air sampling filters in section IIb.

Among the new ambient ionization techniques is low temperature plasma ionization (LTP) (Harper et al., 2008), presented as an ionization method capable of direct analysis of biological samples such as living skin surfaces. In this method a cold plasma (~30°C) is utilized for the ionization of liquids, solids and compounds in the gas phase. The plasma is generated inside a small glass tube by an alternating high voltage applied to an outer electrode wrapped around the glass tube and a low flow
(< 0.3 l/min) of discharge gas (He, Ar, N₂ or air). The exit of the glass tube is pointed towards the sample and the plasma ionizes the compounds at the surface (Figure 6). Depending on the polarity of the mass inlet both positive and negative ions can be analysed. In the LTP setup used for the experiments in this thesis, He was used as discharge gas. Relatively long lived high energy metastable helium (Heₘ) is formed in the plasma region, which could lead to Penning ionization of analytes (M) (Chan et al., 2011b):

\[
He_m + M \rightarrow M^{**} + e^- 
\]

However neither the presence of Heₘ in the ionization region nor the direct involvement of Heₘ in the analyte-ionization has been experimentally verified for any plasma based ambient ionization source, but formation of He₂⁺ in the plasma region has been reported (Chan et al., 2011b). He₂⁺ carries energy from the discharge area to the ionization area in the open atmosphere, where N₂⁺⁺, O₂⁺⁺ and subsequently protonated water clusters, [(H₂O)_n+H]⁺ are formed by charge transfer reactions (Chan et al., 2011b). Any analyte with a higher proton affinity than the water clusters can be ionized via proton transfer. Thus, LTP ionization probably resembles DART, where similar ions are formed (Chan et al., 2011a; Cody et al., 2005; Cody, 2009). In positive mode, LTP ionization usually yields protonated molecules, [M+H]⁺, but radical cations (M⁺⁺) and various adduct ions may also be formed (Garcia-Reyes et al., 2011; Harper et al., 2008).

In negative mode O₂⁻ and clusters containing water and oxygen are formed. These are probably the major ions leading to the formation of [M-H]⁻, M⁻ and various adduct ions under ambient conditions (Cody et al., 2005; Garcia-Reyes et al., 2009).

The desorption mechanism of LTP is governed by thermal processes to liberate analytes from surfaces (Chan et al., 2011b) and the method is therefore most suited for volatile and semi-volatile compounds and heating of the sample may improve the sensitivity for compounds of low volatility.

Figure 7 shows the He-plasma and the tip of the LTP probe positioned close to the MS inlet for analysis of a filter surface as analyzed in this thesis.
1.4.2 Ion modes
A chromatogram can contain a large number of peaks of different intensity. If only the major peaks are of interest, the total ion chromatogram (TIC) can be sufficient to identify the peaks, but if the compounds of interest are minor compounds it can be useful to obtain some kind of filtration of the data. Extracted ion chromatograms (EIC), where the ion-trace of one or more ions is plotted, can often be used to find these minor peaks. If the ion is characteristic for the compound of interest, the area of the EIC-peak can be used for quantification. It is however important that the detector is not saturated by ions from other compounds in the same time. If a minor peak co-eludes with a major peak it can be difficult to quantify the minor peak at low concentration without reaching detector saturation due to the signal from the major peak. This can be solved by use of selected ion monitoring (SIM) during the recording of the spectrum. During SIM only selected ions reach the detector during a specified time. This method is often useful to improve the detection limit, both because of the eliminated interference with other peaks and because the intensity of the SIM ion is improved since the detector is dedicated to the detection of relevant peaks instead of scanning the whole mass range. The last argument is only valid for scanning type analyzers such as quadrupoles. The drawback of SIM is that it must be done during the actual analysis of the sample and that the retention times and the mass spectra of the analytes must be known. The method is therefore more suited for quantitative analysis of specific compounds and not for screening of a complex sample.

Screenings of complex samples can often be aided by GC-MS or LC-MS software. A simple approach is an automated search and comparison of EIC traces to determine which ions peak at the same time and therefore can be expected to originate from the same compound. This approach is used by the Automated Mass Spectral Deconvolution and Identification System (AMDIS) developed at NIST, which extracts individual mass spectra thus enables comparison with compounds in the NIST MS database (NIST, 2011).

1.5 T-test
Throughout this thesis t-test has been used for the comparison of data-sets to determine whether they differed significantly. The calculations have been performed by the function in Excel. If nothing else is stated a 2-sided t-test assuming equal variance in the sample sets have been used.

A t-test can be used compare analytical results from different data sets. The t-test investigates whether the means of the two data sets differs significantly from zero. The null hypothesis to be tested is, $H_0: \mu_1 = \mu_2$, thus, if the sample means $\bar{x}_1 - \bar{x}_2$ differ significantly from zero. The statistic t can be calculated from the following equation:

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s_{\text{pooled}} \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

Eq. 5:
\[ \bar{x}_1 \text{ and } \bar{x}_2 : \text{ Sample mean of each of the two data sets} \]

\[ n_1 \text{ and } n_2: \text{ The number of samples in each of the two data sets} \]

\[ s_{\text{pooled}}: \text{ A pooled estimate of the standard deviations of the two data sets.} \]

When \( s_{\text{pooled}} \) is used, it is assumed that the samples in the data sets are drawn from populations with equal standard deviation, which will often be the case for different sets of samples analyzed with the same analytical method and for the same samples analyzed with two different methods. \( s_{\text{pooled}} \) can be calculated from:

\[
\text{Eq. 6} \quad s_{\text{pooled}}^2 = \frac{(n_1 - 1) \cdot s_1^2 + (n_2 - 1) \cdot s_2^2}{n_1 + n_2 - 2}
\]

The t-value can be used to determine the probability (p) that the difference between the samples are only caused by random errors. For a 5% significance level a p value below 0.05 shows that the null hypothesis can be rejected and hence that the two sample sets are significantly different.

A paired t-test is used to determine if a parameter measured in e.g. bedroom and living room are significantly different. In this case the data set is paired and the difference, d, between each pair is calculated. The null hypothesis to be tested is \( \mu_d=0 \), i.e. there is no difference between each of the data pairs, in order to test this hypothesis it is tested whether \( \bar{d} \) differs significantly from 0 by using the statistic t:

\[
\text{eq. 7} \quad t = \frac{\bar{d}}{\sqrt{n}/s_d}
\]

Similar to the normal t-test, the t-value can be used to determine the probability (p) that the difference between each data pair are only caused by random errors.
2 Section I: Laboratory studies: Chemical properties of indoor floor dust in FLEC

2.1 Introduction
As described previously, this section is a part of the CISBO WP 4.1 which aimed to characterize house dust with regard to chemical properties such as reaction with ozone and sorption of e.g. phthalate plasticizers. Paper I investigates the reaction between ozone and four different floor dust samples from a schools, offices and homes with regard to steady state reaction rate and formation and reaction of organic compounds during the ozone exposure.

2.1.1 Controlled laboratory experiments – ozone and dust (CISBO work package 4.1)
Field sampling can give valuable information on exposures in the real world that have an influence on all of us. At the same time the control over a number of conditions are lost; the system is often more complex and can be influenced by unknown factors, thus complicating the interpretation. A deeper understanding of the mechanisms behind a phenomenon can be obtained by well-defined experiments in the laboratory. The optimal experiment tries to imitate realistic conditions as close as possible, but often it is also necessary to work with experimental conditions far outside realistic ranges.

2.1.2 Field and Laboratory Emission Cell (FLEC)
The Field and Laboratory Emission Cell (FLEC) was developed as a portable, user-friendly micro emission cell with the possibility for non-destructive field testing of e.g. building materials (Wolkoff, 1996). The technical specifications are summarized in Table 3.

<table>
<thead>
<tr>
<th></th>
<th>Volume [m³]</th>
<th>Max exposed test surface area [m²]</th>
<th>Inlet slit [mm]</th>
<th>Diameter [mm]</th>
<th>Height (centre) [mm]</th>
<th>Maximum material loading [m²/m³]</th>
<th>Airflow rate [l/min]</th>
<th>Air exchange rate (n) [h⁻¹]</th>
<th>Air velocity (slit) [m/sec]</th>
<th>Area specific flow rate [m³/(s·m²)]</th>
<th>Reynolds number</th>
<th>Wall surface micro structure (Rw)</th>
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<tr>
<td></td>
<td>3.5·10⁻⁵</td>
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<td>507</td>
<td>0.100</td>
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<td>0.1</td>
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<td></td>
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<td></td>
<td></td>
<td>1.400</td>
<td>2400</td>
<td>≈0.05</td>
<td>=0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.800</td>
<td>4800</td>
<td>≈0.1</td>
<td>=0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The cell consists of a circular stainless steel (SS) body with an inner diameter of 150 mm and a maximum height of 18 mm. The volume of the cell chamber is 35 cm³ and the surface of the test material area is 0.0177 m² resulting in a loading factor of 507 m²/m³, which ensures a high analytical sensitivity. Stainless steel is preferred for its robustness, and large thermal capacity, which improves temperature control, and for its negligible specific emissions and negligible sinks. For further minimization of adsorption sites, the inner surface is hand polished in order to achieve a uniform microstructure.
The cell is supplied with clean humidified air from an air supply control unit. The humidity can be varied from 0-100% RH. If required, other gases or reagents, such as ozone, can be introduced. The airflow is distributed from a circular slit over the material surface into the center, where it exits the FLEC outlet (Figure 9). Samples of VOCs and monitoring of O₃ is performed at the outlet.

In previous studies, the FLEC has been used for investigation of DEHP emission and sorption in dust (Clausen et al., 2004), and the emission of DEHP from vinyl flooring as a function of the air flow rate (Clausen et al., 2010), humidity (Clausen et al., 2007) and temperature (Clausen et al., 2012).

Calculation of reaction rates using the FLEC assumes a constant air velocity over the whole FLEC surface, but as for most other test chambers a completely homogenous airflow is not achieved (Uhde et al., 1998; Zhu et al., 2007) For test materials evenly distributed over the whole surface the effect will average out, thus for the results presented in paper I, a constant air velocity over the whole FLEC surface is assumed.

The experimental setup used for the ozone-exposure of dust in the present study is outlined in Figure 9 and described in further details in paper I.

Ozone is generated by UV photolysis of oxygen by the Chapman mechanism (Seinfeld and Pandis, 2006), where UV-light ($\lambda<242$ nm) dissociates O₂ to two oxygen radicals (Eq. 8). One oxygen radical reacts with O₂ in the presence of a third molecule M (e.g. N₂ or O₂) (Eq. 9).

\begin{align*}
\text{Eq. 8:} & \quad O_2 + h\nu \rightarrow 2O^* \\
\text{Eq. 9:} & \quad O^* + O_2 + M \rightarrow O_3 + M
\end{align*}
2.1.3 Ozone consumption until steady state

The removal of ozone in the FLEC can be considered as a combination of two different types of processes:

1: Chemical reactions with organic compounds in the dust

2: Catalytic degradation of ozone on the dust and stainless steel surfaces.

The determination of $k_{\text{dust}}$ corrects for the catalytic degradation in the FLEC.

Two hypotheses on the system can be formulated:

A: At steady state, the reactive compounds have been removed by ozonolysis. Thus the ozone consumption at steady state is only caused by catalytic breakdown

B: At steady state, accessible and reactive compounds have been removed, but are replenished by diffusion from within the dust to the surface. Thus the ozone consumption at steady state is still a combination of chemical reactions and catalytic breakdown.

To investigate these two hypotheses the amount of ozone consumed until steady state was calculated as indicated in Figure 10 ($C_{\text{inlet}}=2200$ ppb). The calculated area is marked in blue. The difference between $C_{\text{outlet}}$ (at any given time) and $C_{\text{dust}}$ (at steady state) was summated from the beginning of the exposure until steady state by Eq. 10 to obtain the ozone consumption until steady state.

\[
\text{Eq. 10: } O_3-\text{ozonolysis}_{\text{steady state}} = \sum_{\text{Exposure start}}^{\text{steady state}} (O_3-\text{measured} - O_3-\text{measured})
\]

To compare the consumed amount of ozone to consumption of organic compounds in the dust, the concentration in ppb was converted to molecules/cm$^3$. The relation between these is a function of the ideal gas law and is therefore dependent on the temperature. A concentration of 1 ppb (volume) means that there is 1 molecule for every $10^9$ molecules of air. The volume occupied by the air is given by Eq. 11.

\[V_{\text{air}} = \frac{nRT}{p} = \left(\frac{10^9}{N_A}\right) \left(\frac{RT}{p}\right) = \left(\frac{10^9 \text{ molecules}}{6.023 \cdot 10^{23}}\right) \left(\frac{0.082 L \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) \left(\frac{T}{1 \text{bar}}\right) \left(\frac{1000 cm^3}{1.0 L}\right)\]

\[\text{Eq. 11: } V_{\text{air}} = \frac{nRT}{p} = \left(\frac{10^9}{N_A}\right) \left(\frac{RT}{p}\right) = \left(\frac{10^9 \text{ molecules}}{6.023 \cdot 10^{23}}\right) \left(\frac{0.082 L \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) \left(\frac{T}{1 \text{bar}}\right) \left(\frac{1000 cm^3}{1.0 L}\right)\]

\[\text{Eq. 12: } C_{\text{ozon}} \left[\frac{\text{molecules}}{cm^3}\right] = C_{\text{ozon}} \left[ppb\right] \frac{V_{\text{air}}}{C_{\text{ozon}} \left[ppb\right]}\]
At 20°C and 1 bar the conversion factor is thus: 

\[
\text{Eq. 13: } C_{\text{ozone}} [\text{molecules/cm}^3] = \frac{C_{\text{ozone}} [\text{ppb}]}{3.99 \times 10^{11}}
\]

Figure 10: Principle for determination of total ozone consumption

If hypothesis A is true, the ozone consumption until steady state should be comparable to the amount of organic compounds removed by the ozonolysis as determined by TD-GC-MS of the extracted dust samples before and after ozone exposure.

2.1.4 The rate of ozone/dust reaction in the FLEC at steady state

The concentration of ozone at the outlet of the FLEC (\(C_{\text{outlet}}\)) is given as a function of the air exchange rate and the ozone reaction rate in the system. The general equation is given in Eq. 14 (Kleno et al., 2001). More than one mechanism can contribute to the ozone reaction rate, thus what we measure here is therefore a sum of each of the individual processes, such as ozone reaction with the stainless steel surface of the FLEC and reaction with the dust.

\[
\text{Eq. 14: } C = \frac{R_i}{E_x + \sum k}
\]

Where:

\(R_i\): Ozone generation rate [ppb/s]

\(E_x\): Air exchange rate [s\(^{-1}\)]

\(k\): Ozone reaction rate [s\(^{-1}\)]

The specific equations for the steady state concentrations of ozone from a blank FLEC and dust in a FLEC are given in Eq. 15 and Eq. 16. For a dust sample placed in the FLEC, ozone reaction occurs both in the sample, and on the surface of the FLEC, and it is necessary to know the steady state ozone concentration of a blank FLEC.
Eq. 15: \[ C_{FLEC} = \frac{R_i}{E_x + k_{FLEC}} \]

Eq. 16: \[ C_{dust} = \frac{R_i}{E_x + k_{dust} + k_{FLEC}} \]

If the same ozone generation rate \((R_i)\) is used for both the blank FLEC and the dust FLEC, the two concentrations can be combined to Eq. 17.

Eq. 17: \[ \frac{C_{dust}}{C_{FLEC}} = \frac{E_x + k_{FLEC}}{E_x + k_{dust} + k_{FLEC}} \]

Which can further be rearranged to Eq. 18:

Eq. 18: \[ k_{dust} = \left( \frac{C_{FLEC}}{C_{Dust}} - 1 \right) \cdot (E_x + k_{FLEC}) \]

Since \(R_i\), which is the ozone concentration delivered from the ozone generator \((C_{inlet})\) will be known in the experiment, \(k_{FLEC}\) can be defined by rearranging Eq. 15:

Eq. 19: \[ k_{FLEC} = \left( \frac{C_{inlet}}{C_{FLEC}} - 1 \right) \cdot E_x \]

By substitution of Eq. 19 for \(k_{FLEC}\) in Eq. 18 the final equation for calculation of \(k_{dust}\) from experimental known parameters can be obtained:

Eq. 20: \[ k_{dust} = \left( \frac{1}{C_{dust}} - \frac{1}{C_{FLEC}} \right) \cdot C_{inlet} \cdot E_x \]

The \(k_{dust}\) found in Eq. 20 is a first order rate constant for the reaction between the material and ozone with the unit \(s^{-1}\).

### 2.1.5 Sampling of VOCs on Tenax in presence of ozone

A method to analyze volatile reaction products from the ozone/dust reaction, would be sampling of the FLEC outlet air on Tenax TA during exposure, but as described in the following, it is not well suited for the conditions used in this study.

Tenax is a synthetic polymer consisting of 2,6-diphenyl-p-phenylene ether used for sampling of VOCs with boiling points above 50°C. It is thermally stable in the absence of \(O_2\) and has a low chromatographic background. Nitrogen oxides (NO₂) and ozone (O₃) degrade Tenax. A large number of degradation products have been reported in TD-GC-FID (Kleno et al., 2002).

The major products from ozone degradation of Tenax TA are benzoic acid and phenylmaleic anhydride (DPHQ). Furthermore, monoterpenes are known to
undergo ozonolytic decomposition during sampling on Tenax with residue ozone concentrations as low as 8-150 ppb (Calogirou et al., 1996). If the C-C double bond of the monoterpenes reacts under these conditions it can be assumed that this would also occur in other unsaturated compounds, such as unsaturated fatty acids. The sampling rate is crucial to minimize the degradation; a shorter sampling time will decrease the time for ozonolysis of Tenax TA and adsorbed reactive compounds.

2.1.6 Dust samples
Four dust samples (Dust 1-4) have been collected in previous studies and characterized in the present study. Their origins and collection methods are described below.

2.1.6.1 Dust 1
Dust 1 was collected and partly characterized in the study “Damos - Changes in airway mucosal membranes after experimental exposures to dust containing glucan and volatile organic compounds” conducted in 2003 (Mølhave et al., 2003).

The dust was collected in office buildings and institutions in the Aarhus area. None of the buildings had any known indoor climate problems. Each building was vacuumed once each week during 4-8 weeks using normal cleaning procedures. The vacuum cleaners used to collect the dust samples were not used for unusual situations, such as cleaning of ashtrays, tilted pot plants etc.

The dust bags were collected and the dust homogenized according to a standard procedure. This included opening of the dust bag and removal of large items (clips, insects etc.), treatment in a food processor (Robot 2 Coupe 700W) to remove larger textile fibers, since these would tangle up into a ball which could be removed. The remaining dust was sieved through a 1.0 mm sieve. During the sieving, fractions from different vacuum cleaner bags were combined to ensure homogeneity in the bulk dust.

Visual inspection of the dust showed that it mainly consisted of fibers and no sand-like particles were observed. There was some tendency for the fibers to tangle, which made it difficult to spread completely homogeneously on FLEC surface.

2.1.6.2 Dust 2
Dust 2 was collected and characterized in the study “Sensitization of occupants of water damaged buildings – Does house dust from water damaged buildings cause stronger responses among occupants than dust from buildings without water damage?” conducted in 2006 (Mølhave et al., 2006).

The dust was collected in schools in the Aarhus and Copenhagen area in buildings either classified as dry or damp. Damp building had to show at least three of the following signs of dampness: Repeatedly severe water damage without remediation; SBS-type of complaints from a large fraction of occupants; visible damage or fungal growth or condensation on windows during winter. Dry buildings showed none of these signs.

The dust was collected and processed as described for Dust 1.
Visual inspection of the dust revealed some sand-like particles in the dust, but the major fraction consisted on fibers, which had less tendency to tangle compared to Dust 1.

2.1.6.3 Dust 2
Dust 3 was collected as a part of the study “Controlled Human Exposure to Indoor air dust and Ozone” conducted at the Institute of public health, Department of Environmental and Occupational Medicine, University of Aarhus as a part of CISBO WP 4. The dust was obtained from vacuum cleaner bags collected from private homes in the period ultimo 2012-primo 2013 and has not yet been characterized further. Three selection criteria of applicable homes were defined: There should be no visible/known moisture or mold problems, no furbearing pets such as dog or cat, and no smokers in the homes. The dust from all the collected vacuum cleaner bags were combined and processed as described for Dust 1.

By visual inspection the fibers in the dust seemed smaller than in the other dust samples and it contained no sand-like particles as opposed to Dust 2. It was the sample that could be spread most evenly on the FLEC surface.

2.1.6.4 Dust 4
Dust 4 was collected with a standard industrial vacuum cleaner (Clausen et al., 2003). Fibers were cut by use of scissors and the dust was homogenized by sieving (500 µm, 12 DIN). Large objects, such as clips were discarded. A particle and a fiber fraction were obtained with the particle to fiber ratio 1:4 (w/w). For the experiments in this thesis only the particle fraction was used. Visual inspection of the dust revealed no sand-like particles, and a tendency for the fibers to tangle. It was the sample that was most difficult to spread evenly on the FLEC surface. Pictures of 1 g of each of the four dust samples spread on the SS FLEC bottom plate is given in Figure 11.

![Figure 11: Four dust samples spread as evenly as possible over the FLEC surface prior to ozone exposure. Dust 1 is shown with the template ring used to place dust only within the sampling area of the FLEC.](image)

2.2 Results and discussion

2.2.1 Ozone consumption until steady state
To test, whether hypothesis A or B (as presented in 2.1.3) is valid, the amount of consumed ozone until steady state was determined for the four dust samples and the empty FLEC (see Table 4). The consumption from the empty FLEC was substantially lower than for a FLEC loaded with dust (Table...
4). The concentrations of two reactive compounds (octadecenoic acid and its methyl ester) in the dust samples before exposure (see paper I for details) are summarized in Table 4. Comparison of the ozone consumption until steady state with the amounts of just 2 reactive compounds shows that the amount of ozone calculated in this manner is not sufficient to deplete the reactive compounds; thus hypothesis B must be valid, i.e. chemical reactions still occur at steady state.

<table>
<thead>
<tr>
<th>Table 4: Comparison ozone consumption until steady state and total concentration of octadecenoic acid and octadecenoic methyl ester in unexposed samples.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dust 1</td>
</tr>
<tr>
<td>Ozone consumption [µmol/g]</td>
</tr>
<tr>
<td>Octadecenoic acid + methyl ester [mmol/g]</td>
</tr>
</tbody>
</table>

It should be noted that since this calculation only takes two reactive compounds into account, the total amount of reactive compounds must be even larger, since the dust are expected to contain non-volatile reactive compounds, which are not detected with the TD-GC-MS method.

2.2.2 Summary of paper I – Ozone reaction characteristics of indoor floor dust examined in the emission cell "FLEC"

Paper I investigated the interaction between ozone and four indoor floor samples. The reaction rate at steady state (k_{Dust}), the maximum reaction rate (max d[O₃]/dt) as well as the chemical composition of extractable volatile organic compounds before and after exposure was investigated. For the investigation of chemical composition dust samples before and after ozone exposure were extracted by pressurized liquid extraction (PLE). The following sections will summarize as well as elaborate on the results obtained in this paper.

Our hypothesis was that the degradation of ozone in the FLEC is caused both by chemical reactions with unsaturated organic compounds on the dust surface and by catalytic degradation by the dust and SS surfaces. Chemical reactions consume readily available reactive organic compounds on the surface of the dust in the beginning of the exposure. From the determination of ozone consumed until steady state, it was determined that chemical reactions also occurred at steady state, thus we assume that reactive organic compounds are continuously replenished to the dust surface via mass transport from the core of the dust. At steady state the consumption and mass transport is expected to be in equilibrium. The catalytic degradation is more constant, but the decomposition of reactive compounds at the surface of the dust might generate new catalytic active sites.

Thus, the maximum reaction rate (max d[O₃]/dt) reflects the amount of readily available reactive compounds on the surface of the dust at the beginning of the exposure. A high maximum reaction rate indicates a fast consumption of the available reactive compounds. The steady state reaction rate characterizes the amount of catalytic reactive sites on the surface as well as mass transport of reactive chemical compounds from within the dust to the surface. A high steady state reaction rate

[36]
indicates either a high number of catalytic sites or a high total concentration of reactive organic compounds.

2.2.2.1 Steady state reaction rate and maximum reaction rate

It was shown that \( k_{\text{FLEC}} \) was independent of \( C_{\text{inlet}} \) in the range 145-2200 ppb (0.11±0.01 s\(^{-1}\)); i.e. \( k_{\text{FLEC}} \) was constant over the whole concentration range (see Figure 12). The empty FLEC was used for this investigation due to the much shorter time to reach steady state compared to the FLEC/dust system (ca. 40 compared to ca. 60 h). For one dust sample (Dust 2) \( k_{\text{Dust}} \) was also determined at 1600 ppb to test for dependency on \( C_{\text{inlet}} \). \( k_{\text{Dust}} \) at 1600 ppb was slightly, but not significantly, lower than at 2200 ppb (p=0.18), however it could not be completely ruled out that significant differences would be found at even lower \( C_{\text{inlet}} \).

![Figure 12: Steady state reaction rate in an empty FLEC as a function of \( C_{\text{inlet}} \).](image)

The monitoring of \( C_{\text{outlet}} \) during ozone exposure of the dust yielded an ozone absorption time profile as in Figure 13. It is clear that the dust consumed much more ozone than the empty FLEC and the time until steady state was reached was much longer. Close to steady state, \( C_{\text{outlet}} \) only rose slowly, and the slope of the ozone absorption time profile was used to determine the time for steady state (\( d[O_3]/dt = 0 \)) as shown in the example in Figure 14. The maximum reaction rate (max \( dt[O_3]/dt \)) was determined as the maximum of the 30 min running average in the plot of \( d[O_3]/dt \) as indicated.

![Figure 13: Typical time vs. measured ozone concentration from ozone exposure of Dust 4 at \( C_{\text{inlet}}=2.2 \) ppm compared to an empty FLEC cell.](image)

![Figure 14: Slope of the linear regression of 30 min (\( d[O_3]/dt \)) as a function of exposure time. The line shows the running average of 30 min.](image)
The ozone absorption time profiles for the four different dust samples are given in Figure 15. From this, it can be seen that the dust samples differ both in the amount of ozone consumed at steady state, the time to reach steady state and the maximum slope of the absorption curve (max d[O₃]/dt). These differences are reflected in the data obtained on the dust samples summarized in Table 5.

![Figure 15: Comparison of ozone time profiles of floor dust samples (2.2 ppm ozone. The standard deviation for 3 different exposures for each dust sample is indicated with shaded areas.](image)

<table>
<thead>
<tr>
<th>Dust #</th>
<th>Source</th>
<th>Reference</th>
<th>Collection year</th>
<th>Organic fraction [mass %]</th>
<th>Surface Area [m²/g] (n=3)</th>
<th>k_{Dust} [s⁻¹ per g dust] (n=3)</th>
<th>Deposition velocity (ν₆) [cm/s] (n=3)</th>
<th>Max d[O₃]/d(t) [s⁻¹ pr. g dust] (n=3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Offices</td>
<td>1</td>
<td>1999</td>
<td>45.5±0.2 (n=2)</td>
<td>0.52±0.05</td>
<td>0.070±0.007 (n=3)</td>
<td>0.014±0.001 (n=2)</td>
<td>1.7±0.3 (n=2)</td>
</tr>
<tr>
<td>2</td>
<td>Schools</td>
<td>2</td>
<td>2003</td>
<td>15.6±0.7 (n=2)</td>
<td>0.50±0.02</td>
<td>1.6 ppm O₃: 0.027±0.004 (n=2)</td>
<td>0.005±0.001 (n=2)</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.2 ppm O₃: 0.039±0.008 (n=3)</td>
<td>0.008±0.002 (n=3)</td>
<td>7.4±0.1 (n=3)</td>
</tr>
<tr>
<td>3</td>
<td>Homes</td>
<td>3</td>
<td>2012</td>
<td>55±2 (n=2)</td>
<td>0.868±0.003</td>
<td>0.14±0.008 (n=4)</td>
<td>0.029±0.002 (n=2)</td>
<td>1.0±0.4 (n=2)</td>
</tr>
<tr>
<td>4</td>
<td>Offices</td>
<td>4</td>
<td>2000</td>
<td>78.8 (n=1)</td>
<td>0.49±0.03</td>
<td>0% RH: 0.027±0.008 (n=2)</td>
<td>0.005±0.001 (n=2)</td>
<td>1.4±0.3 (n=2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25% RH: 0.17±0.03 (n=2)</td>
<td>0.033±0.006 (n=2)</td>
<td>1.2±0.3 (n=2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50% RH: 0.059±0.008 (n=3)</td>
<td>0.012±0.002 (n=3)</td>
<td>1.4±0.4 (n=4)</td>
</tr>
</tbody>
</table>


Dust 2 and 3 can be seen as extremes in this small sample-set: Dust 2 had a significantly higher max d[O₃]/dt than the other dust samples (p<0.0022) and the lowest k_{Dust} at 50% RH, which indicates that the reactive compounds on the surface was removed fast and the replenishment was lower compared to the other dust samples; or it contained fewer catalytic active sites. The combination of the high maximum reaction rate and the low k_{Dust} indicates that Dust 2 contains the smallest amount of reactive organic compounds of the four dust samples. This is consistent with the low organic...
fraction (Table 5), though this fraction does not take the reactivity of the organic compounds into account.

Dust 3 had the lowest max $d[O_3]/dt$, though not statistically significant, and the highest $k_{Dust}$. The low max $d[O_3]/dt$ indicates that the reactive organic compounds on the surface were only removed slowly. The high $k_{Dust}$ indicates an effective replenishment of reactive compounds, or a high number of catalytic reactive sites, and thereby, as opposed to Dust 2, the highest amount of reactive organic compounds. This is consistent with the fact, that this dust is younger, and thus a smaller amount of reactive compounds may have been lost due to evaporation and reaction with oxygen during storage.

Though the high max $d[O_3]/dt$ and low $k_{Dust}$ for Dust 2 and the low max $d[O_3]/dt$ and high $k_{Dust}$ might indicate a correlation, this was not the case ($r^2=0.41$).

To compare the $k_{Dust}$-values with previous studies, we found that conversion to deposition velocities ($v_d$) (Tamas et al., 2006) was useful, since that took different volume-to-surface-areas in different experimental setups into account (see paper I for details). The comparison showed that $v_d$ for the indoor floor dust samples was comparable to the lower $v_d$-values found for carpets (see Table 2 in paper I), thus justifying the use of ozone concentrations much higher than realistic for indoor air conditions.

### 2.2.2.2 Correction for the organic fraction

As briefly described in paper I, the differences in the organic fraction in the four dust samples (see Table 5) was not enough to account for the differences in $k_{Dust}$. If the organic fraction was responsible, it would be expected that $k_{Dust}$ for the four dust samples would be more similar by division with the organic fraction. $K_{Dust}$ before and after normalization for the organic fraction are compared in Figure 16 and Figure 17 and the p-values for 2-sided t-tests are summarized in Table 6 and Table 7. After normalization, $k_{Dust}$ for Dust 2 are more similar to the three other dust samples, and it no longer differs significantly from Dust 3 ($p=0.0004$ vs. $p=0.14$). The differences between the three other dust samples have not changed substantially. From this it is concluded that though the low $k_{Dust}$ of Dust 2 can be explained by the low organic fraction, it cannot explain the differences between the other dust samples, and thus that $k_{Dust}$ is also substantially influenced by other factors, such as composition of the organic fraction and surface properties.

A similar normalization performed on max $d[O_3]/dt$ is summarized in Figure 18, Figure 19, Table 8 and Table 9. As for the normalization on $k_{Dust}$, the largest effect was found for Dust 2 due to the low organic content, but in this case the increase of max $d[O_3]/dt$ of Dust 2 resulted in a larger difference between Dust 2 and the 3 other samples. Thus it can be concluded that the organic fraction cannot explain the differences in max $d[O_3]/dt$. 

[39]
2.2.2.3 Rejuvenation of reaction sites in dust

Figure 20 shows the ozone absorption time profile for Dust 4 for exposure of previously unexposed dust (First exposure) and dust rejuvenated for one week and subsequently exposed to ozone (Second exposure). Steady state was achieved after ca. 85 hours (First exposure) whereas this was achieved already after about 5 hours for the rejuvenated dust. The ozone consumption until steady
state of the regenerated dust was 3% compared to the first exposure. In comparison the empty FLEC consumed only 0.4%.

The shorter time of the rejuvenated dust to reach steady state indicates that the major reason for the slow increase of \( C_{\text{outlet}} \) during the first exposure is mainly removal of ozone by chemical reactions with compounds readily available on the surface of the dust. During the rejuvenation period some compounds are transported to the surface, which results in a lower concentration of reactive compounds compared to the unexposed dust. \( C_{\text{Dust}} \) and thus \( k_{\text{Dust}} \) reached the same level during the first and second exposure as indicated by the extended x-axis in Figure 20.

![Figure 20: Ozone concentration at FLEC outlet for ozone exposure and ozone exposure of the same dust (Dust 4) after one week of rejuvenation with purified air. Compared to ozone exposure of an empty clean FLEC cell.](image)

### 2.2.2.4 Effect of humidity on \( k_{\text{Dust}} \) and \( \text{max } d[O_3]/dt \)

The humidity was shown to have a significant impact on \( k_{\text{Dust}} \) for Dust 4. (see Figure 21). At 25% RH, \( k_{\text{Dust}} \) was ca. 3 times higher than at 50% RH and ca. 6 times higher than at 0% RH. All three RH levels differed significantly (see Table 10).

No significant changes were found for \( \text{max } d[O_3]/dt \) as a function of RH (See Figure 22 and Table 11).

![Figure 21: Influence of humidity on \( k_{\text{Dust}} \) determined at 2.2 ppm ozone for Dust 4.](image)

### Table 10: P-values for 2-sided t-test \( k_{\text{Dust}} \) at different RH.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 vs. 50% RH</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>0 vs. 25% RH</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td>25 vs 50% RH</td>
<td>0.0072</td>
<td></td>
</tr>
</tbody>
</table>
Two previous studies has examined the effect of humidity on the deposition velocities of ozone on a number of building materials (Grontoft and Raychaudhuri, 2004; Grontoft et al., 2004). The $v_d$-values from these studies are visualized in Figure 23 together with the $v_d$-values obtained for Dust 4 in the present study. In this figure the material are separated into three different groups:

A: Have the lowest $v_d$ at 0% RH, which increases continuously as RH increase. This group includes wool carpet, wall paper, untreated woodwork and hard dense stonework.

B: Have the highest $v_d$ at 0% RH, which decreases continuously as RH increase. This group includes soft stone material and concrete.

C: Does not have a continuous relation between $v_d$ and RH. This group includes Vicenza calcareous stone, Maltese limestone, 3 types of concrete, and Dust 4 investigated in the present study. However, $v_d$ of these materials do not follow the same pattern. The stone materials have the highest $v_d$ at 0% RH, decreases until 50% RH and increase again until 90% RH, whereas the dust sample has the lowest $v_d$ at 0% RH and a maximum at 25% RH.

Table 11: P-values for 2-sided t-test of max d[O$_3$/dt at different RH.

<table>
<thead>
<tr>
<th></th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 vs 25 % RH</td>
<td>0.35</td>
</tr>
<tr>
<td>0 vs 50 % RH</td>
<td>0.67</td>
</tr>
<tr>
<td>25 vs. 50% RH</td>
<td>0.57</td>
</tr>
</tbody>
</table>
The RH/$v_d$ curves of the surfaces in group C (except for the dust sample) have been modeled to explain the mechanics (Grontoft, 2004). The decomposition of ozone is considered a combination of three different processes: 1: Reaction with the dry surface; 2: Reaction with adsorbed surface water up to the formation of one mono-layer coverage; 3: Reaction with additional surface water. The
minimum \( v_d \) at 50% RH for the stone materials was explained by the formation of one mono-layer of water according to BET-surface area. Below 50% RH \( v_d \) decreases as a function of RH, as the reaction sites in the material are blocked by water molecules. The reason for the increase above 50% RH is less understood, and is not relevant for the comparison with the dust sample investigated in the range 0-50% RH.

The major difference in \( v_d \) between the stone materials and the dust sample is the low value at 0% RH for the dust. A major difference between the samples is the presence of organic compounds on the surface of the dust, thus it is speculated that the reaction with the organic compounds requires some humidity to be efficient, possible because water might act as a plasticizer (Hansen, 1982) and aid the mass transport of organics to the surface of the dust. This is supported by the fact that max \( d[O_3]/dt \), which is a function of the compounds already present on the surface of the dust at the beginning of the exposure, is less affected than \( k_{Dust} \), which depends on the mass transport of organics at steady state.

### 2.2.2.5 SVOCs extracted from dust before and after ozone exposure

The details of the Pressurized Liquid Extraction (PLE) of organic compounds in the dust before and after ozone exposure are given in Paper I. A total of 71 compounds were identified in the PLE extracts from their EI-MS spectra and summarized in Table 12. The identification was performed as a combination of visual comparison of mass spectra of the unknown compound and of known compounds from the NIST database (NIST, 2011) and from the automated comparison determined by probability of a correct identification (Prob. ID).

Among the identified compounds were aldehydes (C\(_7\)-C\(_{10}\) and benzaldehyde), saturated carboxylic acids (C\(_8\)-C\(_{18}\) and benzoic acid) and their methyl esters, dimethyl esters (C\(_6\)-C\(_9\)), unsaturated carboxylic acid (C\(_{18}\)) and its ester and methyl ester, phthalates and traces of \( \alpha \)-pinene and limonene. Some of the identified compounds are known oxidation products (e.g. aldehydes) and reactive compounds (e.g. unsaturated carboxylic acids and esters thereof, \( \alpha \)-pinene and limonene). It is possible that some of the methyl esters originate from methylation of fatty acids during the PLE extraction with methanol at elevated pressure and temperature.
Table 12: Summary of tentatively identified compounds extracted from dust samples before ozone exposure. Most compounds were detected in all samples and the exceptions are given.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Prob ID</th>
<th>CAS</th>
<th>rt time [min]</th>
<th>Not detected in dust sample #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylpyrazine</td>
<td>60.7</td>
<td>109-08-0</td>
<td>4.611</td>
<td></td>
</tr>
<tr>
<td>2-furanmethanol</td>
<td>80.6</td>
<td>98-00-0</td>
<td>5.390</td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td>A</td>
<td>A</td>
<td>5.766</td>
<td>3</td>
</tr>
<tr>
<td>Styrene</td>
<td>42.9</td>
<td>100-42-5</td>
<td>6.452</td>
<td></td>
</tr>
<tr>
<td>Heptanal</td>
<td>89.9</td>
<td>111-71-7</td>
<td>6.820</td>
<td></td>
</tr>
<tr>
<td>α-pinene</td>
<td>19.9</td>
<td>80-56-8</td>
<td>7.827</td>
<td>1,3,4</td>
</tr>
<tr>
<td>1H,1H,2H,2H-Perfluorooc-tan-1-ol</td>
<td>96.9</td>
<td>647-42-7</td>
<td>7.860</td>
<td>2,3,4</td>
</tr>
<tr>
<td>N-methylmaleimide</td>
<td>94.1</td>
<td>930-88-1</td>
<td>8.114</td>
<td>3</td>
</tr>
<tr>
<td>Benzaldehyd</td>
<td>74.2</td>
<td>100-52-7</td>
<td>9.053</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>52.5</td>
<td>108-95-2</td>
<td>9.884</td>
<td></td>
</tr>
<tr>
<td>4-oxo-methylene pentanoic acid</td>
<td>97.8</td>
<td>624-45-3</td>
<td>10.062</td>
<td>3</td>
</tr>
<tr>
<td>2-pentylfuran</td>
<td>87.0</td>
<td>3777-69-3</td>
<td>10.088</td>
<td></td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>50.4</td>
<td>142-62-1</td>
<td>10.320</td>
<td></td>
</tr>
<tr>
<td>Octanal</td>
<td>84.8</td>
<td>124-13-0</td>
<td>10.680</td>
<td>3</td>
</tr>
<tr>
<td>Limonene</td>
<td>60.6</td>
<td>5989-54-8</td>
<td>11.629</td>
<td>3</td>
</tr>
<tr>
<td>2-ethyl-1-hexanol</td>
<td>61.6</td>
<td>104-76-7</td>
<td>11.730</td>
<td></td>
</tr>
<tr>
<td>Butanedioic acid dimethyl ester</td>
<td>95.8</td>
<td>106-65-0</td>
<td>11.883</td>
<td></td>
</tr>
<tr>
<td>2-hydroxybenzaldehyde</td>
<td>82.2</td>
<td>90-02-8</td>
<td>12.339</td>
<td>2,4</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>25.3</td>
<td>98-86-2</td>
<td>13.192</td>
<td>1</td>
</tr>
<tr>
<td>1-octanol</td>
<td>12.5</td>
<td>111-87-5</td>
<td>13.450</td>
<td></td>
</tr>
<tr>
<td>2-methoxyphenol</td>
<td>48.8</td>
<td>90-05-1</td>
<td>13.986</td>
<td></td>
</tr>
<tr>
<td>Benzoic acid methylester</td>
<td>56.2</td>
<td>93-58-3</td>
<td>14.340</td>
<td></td>
</tr>
<tr>
<td>Nonanal</td>
<td>69.5</td>
<td>124-19-6</td>
<td>14.765</td>
<td></td>
</tr>
<tr>
<td>Octanoic acid methylester</td>
<td>87.9</td>
<td>111-11-5</td>
<td>15.500</td>
<td></td>
</tr>
<tr>
<td>2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one</td>
<td>92.0</td>
<td>28564-83-2</td>
<td>16.312</td>
<td>2</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>50.1</td>
<td>65-85-0</td>
<td>17.765</td>
<td></td>
</tr>
<tr>
<td>Octanoic acid</td>
<td>95.5</td>
<td>124-07-2</td>
<td>17.942</td>
<td></td>
</tr>
<tr>
<td>Decanal</td>
<td>44.1</td>
<td>112-31-2</td>
<td>18.697</td>
<td></td>
</tr>
<tr>
<td>2-phenoxyethanol</td>
<td>90.7</td>
<td>122-99-6</td>
<td>19.199</td>
<td></td>
</tr>
<tr>
<td>Nonanoic acid methylester</td>
<td>66.2</td>
<td>1731-84-6</td>
<td>19.328</td>
<td></td>
</tr>
<tr>
<td>Benzothiazole</td>
<td>74.9</td>
<td>95-16-9</td>
<td>19.422</td>
<td></td>
</tr>
<tr>
<td>Hexanedioic acid dimethyl ester</td>
<td>94.5</td>
<td>627-93-0</td>
<td>20.085</td>
<td></td>
</tr>
<tr>
<td>Nonanal dimethyl acetal</td>
<td>75.7</td>
<td>18824-63-0</td>
<td>21.220</td>
<td>1,2</td>
</tr>
<tr>
<td>Nonanoic acid</td>
<td>89.7</td>
<td>112-05-0</td>
<td>21.464</td>
<td></td>
</tr>
<tr>
<td>P-tertbutylphenol</td>
<td>64.3</td>
<td>98-54-4</td>
<td>21.796</td>
<td>4</td>
</tr>
<tr>
<td>Monomethyletherhexanedioic acid</td>
<td>96.7</td>
<td>627-91-8</td>
<td>21.899</td>
<td>3</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>64.8</td>
<td>85-44-9</td>
<td>22.115</td>
<td></td>
</tr>
<tr>
<td>Decanoic acid methylester</td>
<td>59.8</td>
<td>110-42-9</td>
<td>22.259</td>
<td></td>
</tr>
<tr>
<td>2H-pyran-2,6(3H)-dione</td>
<td>56.7</td>
<td>5926-95-4</td>
<td>22.451</td>
<td>3</td>
</tr>
<tr>
<td>4,4,6-trimethylcyclohex-2-en-1-ol</td>
<td>15.5</td>
<td>NA</td>
<td>22.573</td>
<td></td>
</tr>
<tr>
<td>n-decanolic acid</td>
<td>86.8</td>
<td>334-48-5</td>
<td>22.856</td>
<td></td>
</tr>
<tr>
<td>5-oxo methylester L-proline</td>
<td>28.0</td>
<td>4931-66-2</td>
<td>22.975</td>
<td></td>
</tr>
<tr>
<td>Vanillin</td>
<td>57.5</td>
<td>121-33-5</td>
<td>23.089</td>
<td></td>
</tr>
</tbody>
</table>

[Continues]
The chromatograms of the dust extracted before ozone exposure revealed large similarities between the different dust samples and most of the 71 identified compounds were detected in all samples. The exceptions are indicated in Table 12. A comparison of the chromatograms of the extracts of the samples before ozone exposure is given in Figure 24 and Figure 25 (Retention time below and above 20 min). In general, peaks with retention times larger than 20 min were more intense than the earlier eluting peaks, which is consistent with a loss of the more volatile compounds during storage of the dust.
Figure 24: Comparison of the chromatograms for the four dust samples before ozone exposure for retention time 3-20 min (boiling point below ca. 220°C).

Figure 25: Comparison of the chromatograms for the four dust samples before ozone exposure for retention time above 20 min (boiling point above ca. 220°C).
2.2.5.1 Known terpene/ozone oxidation products
Only traces of monoterpenes (limonene and α-pinene) were detected in the extracts of dust before ozone exposure, yet the extracts of dust after exposure was analyzed with targeted Selected Ion Monitoring (SIM) for known terpene/ozone oxidation products previously identified (Atkinson and Arey, 2003; Calogirou et al., 1999) as summarized in Table 13. The targeted search for known terpenes and terpene/ozone oxidation compounds revealed only concentrations in trace levels and were not further analyzed and thus not included in Paper I.

Table 13: SIM parameters for known terpene/ozone oxidation products.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS</th>
<th>Rt</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-methyl-6-hepten-2-one (6-MHO)</td>
<td>10408-15-8</td>
<td>10.077</td>
<td>55</td>
</tr>
<tr>
<td>Dihydromycenol</td>
<td>18479-58-8</td>
<td>13.548</td>
<td>59</td>
</tr>
<tr>
<td>4-acetyl-1-methylcyclohexene (4-AMCH)</td>
<td>6090-09-1</td>
<td>15.853</td>
<td>95</td>
</tr>
<tr>
<td>3-Isopropyl-6-oxoheptanal (IPOH)</td>
<td>7086-79-5</td>
<td>21.761</td>
<td>67</td>
</tr>
<tr>
<td>4-oxopentanal (4-OPA)</td>
<td>626-96-0</td>
<td>5.481</td>
<td>72</td>
</tr>
<tr>
<td>Dihydrocarvone</td>
<td>7764-50-3</td>
<td>18.400</td>
<td>152</td>
</tr>
<tr>
<td>Linalool</td>
<td>78-70-6</td>
<td>14.654</td>
<td>71</td>
</tr>
<tr>
<td>Limonene</td>
<td>138-86-3</td>
<td>11.786</td>
<td>68</td>
</tr>
<tr>
<td>A: Oxidation products; B: Unreacted terpenes.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2.5.2 Formation of compounds during ozonolysis
The formation of gas phase compounds during exposure is not considered in this study due to the high ozone concentrations that would impair results obtained by sampling on Tenax TA by formation of Tenax degradation products and further reaction of adsorbed reaction products (Kleno et al., 2002).

An example of the chromatograms of Dust 3 before and after exposure is given in Figure 26 and Figure 27 (before and after 20 min respectively). In Figure 26 an increase for some peaks are observed, indicating that these are oxidation products. The compounds with a substantial increase after exposure are summarized in Table 14. Among these compounds are aldehydes, in particular C7-C10. Aldehydes are common ozonolysis products in several previous studies (Coleman et al., 2008; Weisel et al., 2013; Weschler et al., 2007; Wisthaler et al., 2005; Wang and Morrison, 2006; Rancière et al., 2011; Gall et al., 2013; Pandrangi and Morrison, 2008), and are a a common concern in the indoor air, since they may influence the perceived indoor air quality due to their generally low odor thresholds (Wolkoff, 2013).
Among the other identified products to increase after ozone exposure were 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one which has been reported as a degradation product of 1-deoxy-1-(L-Proline-D-fructose) (Shaw et al., 1971) and 2-ethyl-1-hexanol which is a known degradation product from the hydrolysis of DEHP (Norbäck et al. 2000).
Table 14: Percent of identified compounds in the exposed samples (2.2 ppm ozone) compared to the unexposed.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dust 1</th>
<th>Dust 2</th>
<th>Dust 3</th>
<th>Dust 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptanal</td>
<td>570</td>
<td>280</td>
<td>1000</td>
<td>480</td>
</tr>
<tr>
<td>Octanal</td>
<td>170</td>
<td>760</td>
<td>o.e.</td>
<td>650</td>
</tr>
<tr>
<td>2-ethyl-1-hexanol</td>
<td>56</td>
<td>90</td>
<td>210</td>
<td>1500</td>
</tr>
<tr>
<td>Butanediol acid dimethyl ester</td>
<td>41</td>
<td>1300</td>
<td>780</td>
<td>78</td>
</tr>
<tr>
<td>1-octanol</td>
<td>230</td>
<td>130</td>
<td>930</td>
<td>1000</td>
</tr>
<tr>
<td>Nonanal</td>
<td>1100</td>
<td>1100</td>
<td>2300</td>
<td>1400</td>
</tr>
<tr>
<td>2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2800</td>
<td>380</td>
</tr>
<tr>
<td>Decanal</td>
<td>310</td>
<td>470</td>
<td>930</td>
<td>270</td>
</tr>
<tr>
<td>2-phenoxyethanol</td>
<td>87</td>
<td>91</td>
<td>1500</td>
<td>71</td>
</tr>
<tr>
<td>Nonanoic acid methylester</td>
<td>97</td>
<td>150</td>
<td>390</td>
<td>43</td>
</tr>
<tr>
<td>Nonanal dimethyl acetal</td>
<td>o.e.</td>
<td>o.e.</td>
<td>620</td>
<td>250</td>
</tr>
<tr>
<td>Octanedioic acid dimethyl ester</td>
<td>69</td>
<td>770</td>
<td>3100</td>
<td>22</td>
</tr>
</tbody>
</table>

The compounds are listed in the order of increasing retention time. Results are rounded to two significant figures for clarity. Abbreviations: o.e.: Only detected in exposed sample; n.d.: Not detected in neither samples.

2.2.2.5.3 Removal of compounds during the ozonolysis

One monounsaturated fatty acid and ester thereof (octadecenoic acid and octadecenoic methyl ester) were identified in the dust extracts as described in paper I. Both are expected to react with ozone. The results are summarized in Figure 28. These results further support the hypothesis that reactive compounds have not been exhausted at steady state. The increase of octadecenoic acid methyl ester in three of the dust samples could be explained by hydrolysis of lipids to form the free fatty acid during PLE extraction and simultaneous esterification of the acid with methanol (Kocsisová et al., 2005). This indicates that the PLE method with methanol, high pressure and temperature creates artifacts, which might be prevented by use of a non-alcohol solvent or a lower temperature.

![Figure 28: Octadecenoic acid and octadecenoic acid methylester in dust samples before and after ozone exposure. Total exposure time is indicated for each of the dust samples. Error bars indicate standard deviation of two samples.](image-url)
In this thesis, no further investigation of the ratio between chemical reaction and heterogeneously breakdown of ozone has been conducted. A previous study by Coleman et al. found that 0.07-024 mole of products volatilized per mole of ozone consumed in the reaction between ozone (120 ppb) and aircraft building materials and clothing fabrics (Coleman et al., 2008), which further supports that the amount of ozone available for chemical reactions is so negligible, that it cannot exhaust reactive compounds before steady state.

Other compounds such as squalene (410 g/mol, BP 252°C at 25 mm/Hg) and cholesterol (387 g/mol, BP 360°C, decomposes) have been reported in dust (Weschler et al., 2011) and act as effective ozone scavengers, especially squalene, due to the 6 double bounds (Petrick and Dubowski, 2009). These compounds are difficult to analyzed with GC-MS due to the high boiling points.

### 2.3 Conclusions

Steady state reaction rates ($k_{Dust}$) and maximum reaction rates ($\max d[O_3]/dt$) of the interaction between ozone and floor dust were determined based on ozone consumption versus time curves for four different samples. $k_{Dust}$ was in the range 0.039-0.14 s$^{-1}$ pr. g dust at 50% RH. It was shown that the steady state reaction rate was independent of $C_{inlet}$ (1.6 and 2.2 ppm). Ozone $v_a$-values converted from $k_{Dust}$ for the dust samples were in the range 0.008-0.029 cm/s and comparable to carpet and indoor environment studies measured at lower ozone concentrations. Relative humidity was found to influence $k_{Dust}$ with a maximum value at 25% RH relative to 0 and 50% RH.

From the amount of added ozone and initial amount of SVOCs it was concluded that not all unsaturated volatiles were likely to have completely reacted when the system reached steady state, and thus that the removal of ozone at this point was caused both by heterogeneous breakdown on surfaces and chemical reactions limited by mass transport of reactant molecules from within the dust particles. The major reaction products from the dust/ozone reaction included aldehydes, such as heptanal, octanal, nonanal and decanal, that may impact the indoor air quality.

### 2.4 Perspectives

The chemical analysis of the dust extracted before and after ozone exposure has the major limitation that some volatiles are most likely lost either through the effluent air during the exposure or during the PLE extraction. It is expected that the ozonolysis of organic compounds in the dust will result in a range of lower boiling reaction products. To analyze these VOCs, sampling on Tenax followed by TD-GC-MS would be more suitable than the PLE extraction. It was considered to sample the effluent air on Tenax even with the high (2.2 ppm) ozone exposure experiments, but the high residue ozone concentration was expected to cause too much interference from ozone/Tenax degradation products (Kleno et al., 2002) and also increase the risk of ozonolysis of compounds already adsorbed on the Tenax (Calogirou et al., 1996). These compounds could either be evaporated from the dust itself or primary reaction products from the ozonolysis on the dust (Wolkoff and Wilkins, 1994). It was therefore decided that only low ozone concentration experiments were suited for analysis of the effluent air. Another way of avoiding the high efficient ozone concentrations could be to turn the ozone generator off during sampling of VOCs on Tenax, but with this method there is a risk of
underestimating the most volatile compounds such as e.g. formaldehyde, which might mainly be present in the effluent air during ozonolysis.

All the ozone exposure experiments in this thesis have been carried out at extremely high ozone concentrations, which will never occur in any realistic exposure scenario. The experiments are planned to be extended to a more realistic ozone concentration (50-100 ppb). These experiments will focus on collection and analysis of VOCs in the FLEC effluent air formed during the ozonolysis of chemicals in the dust. From the experiences with high ozone concentrations, we have learned that though the ozone reacts readily with dust, the dynamics of the dust/ozone system is slow. Depending on the dust sample it took 1-4 days for the system to reach equilibrium at 2.2 ppm ozone, and with a realistic ozone concentration of 50 ppb it would require 6-25 weeks before the same amount of ozone had been added to the system. The aim of these analyses will be to follow the VOC release at least until steady state. Since the experiments in this thesis also concluded that not all C-C double bond had reacted at steady state, it is possible that the VOC release should be followed even further than to the point of steady state.
3 Section IIa: Field study

3.1 Introduction

3.1.1 Pilot Study – Field study (CISBO Work Package 1.1)

The background behind the pilot study in 5 selected Danish homes was to follow a number of selected indoor air parameters over a period of one year to be able to monitor seasonal and habitual variations. A number of different methods should also be compared and evaluated prior to another larger study in the CISBO project (WP 1.2), involving 60 homes, but with simpler, cheaper and less time consuming methods.

A number of different criteria were considered for selection of the homes, such as age of the house, presence of pets, smoking inhabitants, known mold problems, buildings with or without a basement, with or without a woodstove, different means of heating etc. However, for practical reasons and limitations in time and especially in equipment, only 5 homes were selected for the pilot study. With this amount of homes, the investigation of such a number of parameters could not be validated with any statistical significance. The only criteria in the selection process were no smoking inhabitants and willingness to participate in all 4 sampling campaigns over a year.

The field study was performed in collaboration with DTU, SBI and NRCWE. Seasonal changes in air exchange rates were investigated by DTU and SBI, and the temporal and spatial behavior of selected chemical, biological and particulate pollutants was evaluated by NRCWE (Frankel et al., 2012a; Frankel et al., 2012b). The air exchange rates measured and calculated by DTUbyg and SBI are presented in this thesis, since the hypothesis is that seasonal variation of chemicals in the homes might be controlled by variation of air exchange rates as a consequence of users’ response to changes in outdoor conditions such as temperature.

3.1.2 Residential measurements

Though many environmental measurements are performed with focus on occupational settings, it is also important to evaluate residential settings, since people in average spend 15-16 h per day in their homes of other domestic environments (Leech et al., 2002; Brasche and Bischof, 2005).

When entering people’s homes it was necessary to take the bulkiness and noise levels of the sampling equipment into account. Since this study required several sampling campaigns in each home, it was important that the inhabitants could live a relatively normal life during sampling, both to ensure their willingness to participate in the whole study and to obtain data that was representative for normal behavior. Especially sampling in the bedroom during nighttime could cause considerations due to noise even from sound insulated pumps.
3.2 Theory

3.2.1 Passive gas samplers
The radial diffusive sampler consists of two parts. The outer membrane allows gaseous molecules to cross and they are then adsorbed to the inner adsorbing surface. The outer body used for aldehydes, NO₂, and ozone is the same and acts both as a diffusive surface and as UV-protection of the samples.

The adsorption of gaseous molecules to the adsorbing surface is controlled by Fick’s diffusion law (Eq. 21):

\[
\frac{dm}{dt} = D \cdot S \cdot \frac{dC}{dl} \Rightarrow \frac{m}{t} = D \cdot \frac{S(C_d - C_a)}{l}
\]

Where:
- \(\frac{dm}{dt}\): Adsorbed mass \(m\) during the time \(t\)
- \(D\): Diffusion coefficient
- \(S\): Surface area of the diffusive surface
- \(\frac{dC}{dl}\): Concentration gradient between concentration at the diffusive and adsorbing surface.
- \(C_d\): Concentration at the diffusive surface
- \(C_a\): Concentration at the adsorbing surface

For a negligible analyte concentration at the adsorbing surface \((C_a \approx 0)\), Eq. 21 can be approximated to:

\[
\frac{m}{t \cdot C} = \frac{D \cdot S}{l} = Q \Rightarrow C = \frac{m}{t \cdot Q}
\]

Where:
- \(Q\): Sampling rate [l/min ]
- \(m\): Adsorbed mass [µg]
- \(t\): Exposure time [min]
- \(C\): Average analyte concentration [µg/l]

The sampling rate \(Q\) depends on the surface area of the diffusive surface \((S)\) and the diffusive distance \((l)\). For an optimal analytical sensitivity the \(S/l\) ratio is improved in the Radiello® radial diffusive sampler (Figure 29) without increase of the adsorbing surface. A larger adsorbing surface would require a larger extraction solvent volume which would cancel out the improvement of \(Q\) with regard to the analytical sensitivity.

[54]
The sampling rate $Q$ is a function of the geometrical constant and the diffusive coefficient $D$, which is a thermodynamic property of each analyte and varies with both temperature and pressure:

$$Q = D \cdot \frac{2\pi hr}{\ln \frac{r_d}{r_a}}$$

Where:

- $Q$: Sampling rate [l/min]
- $D$: Diffusion coefficient [cm$^2$/min]
- $h$: Height of the sampler
- $r$: Radius of the outer body
- $r_d$: Diffusive radius
- $r_a$: Adsorbing cylinder radius

The geometrical factor is determined by the dimensions of the sampler and the length of the diffusive path through the micro porous structure of the outer body ($r_d$). The dimensions of the sampler ($h$, $r$, and $r_a$) are easy to measure, but $r_d$ can only be determined experimentally.

The correction of $Q$ as a function of atmospheric pressure is usually negligible since it is linear and the pressure seldom varies much. Usually the correction is within ±1.5% (Radiello, 2006). The temperature on the other hand, has a much larger effect on the sampling rate with an exponential correlation. It is thus important to measure the average temperature at each sampling to be able to
obtain the relevant corrections. The relation between Q and temperature differs for different analytes.

The major advantage of the passive samplers is their simplicity in the field. No pumps or power supply is required and the handling in the field can be performed by inhabitants. The non-existing noise is also a advantage.

The major drawback of passive sampling is the lack of time resolved data, since it is only possible to obtain average concentration over the whole exposure time.

3.2.1.1 Ozone

In Radiello® cartridges for ozone sampling, ozone reacts with 4,4’-dipyridylethylene coated on a silica gel matrix to form ozonure, which is hydrolyzed to 4-pyridylaldehyde by H₂O present in the silica gel (Figure 30). The production of 4-pyridyl aldehyde from 4,4’-dipyridylethylene is a specific reaction of ozone. Neither nitrogen oxides nor other organic compounds cause interference.

![Figure 30: Reaction of ozone and 4,4’-dipyridyl ethylene for absorption of ozone during sampling](image)

When the cartridge is analyzed for ozone, 4-pyridyl aldehyde is reacted with 3-methyl-2-benzothiazolinone hydrazine (MTBH) to yield the corresponding azide (Figure 31). The formed MBTH azide is yellow and the concentration can be determined by the absorbance at 430 nm.

![Figure 31: Formation of MBTH-azide yellow for analysis of ozone](image)

The sampling rate at 298 K is 24.6 ml/min and is linear in the exposure range from 10.000 to 4.000.000 µg·m⁻³·min⁻¹ and is not influenced by humidity or wind speed. For temperatures different from 298 K the sampling rate can be calculated from the following equation:

\[
Q_T = Q_{298} \left( \frac{T}{298} \right)^{1.5}
\]
Where:

\[ Q_T \]: Sampling rate at any temperature T in Kelvin

\[ Q_{298} \]: Sampling rate at the reference temperature 298 K

\[ T \]: Temperature in Kelvin

Calculation of the sample rate from Eq. 24 is valid in the temperature range 263-313 K (-10 to 40 °C)

The drawback of the passive samplers for ozone is that the diurnal variation cannot be observed (Sabersky et al., 1973; Jakobi and Fabian, 1997).

### 3.2.1.2 NO\textsubscript{2}

The cartridges in the Radiello\textsuperscript{®} passive samplers for NO\textsubscript{2} are made of microporous polyethylene coated with triethanolamine which chemochromically adsorbs NO\textsubscript{2} as nitrite (NO\textsubscript{2}\textsupscript{-}). The nitrite ion is determined by the colorimetric reaction with sulphanilamide and N-(1-naphthyl)ethylendiamine dihydrochloride (NEDA) by the modified Griess reaction (Griess, 1879) shown in Figure 32 and Figure 33. This method has been approved as an European standard for determining nitrite in water (European standard, 1993).

![Reaction of sulphanilamide and nitrite to form the corresponding diazonium cation.](image1)

![Reaction of the diazonium cation with NEDA to form the azo dye.](image2)
The azo dye formed in the reaction with NEDA (Figure 33) is quantified by the absorption at 537 nm with aqueous calibration solutions of sodium nitrite.

The sampling rate for NO$_2$ at 298 K ($Q_{298}$) is 78 ml/min and for temperatures different from 298 K the sampling rate can be calculated from the following equation, with the same definitions as in Eq. 24:

$$Q_T = Q_{298} \left( \frac{T}{298} \right)^{7.0}$$

This equation is valid in the temperature range 263-313 K (-10 to 40 °C). The sampling rate is unaffected by humidity in the range 15-90%.

### 3.2.1.3 Aldehydes

The cartridges for sampling of aldehydes were made of magnesia-silica gel (Florisil®) coated with 2,4-dinitrophenylhydrazine (2,4-DNPH). During sampling the carbonyl group in aldehydes (and ketones) react with 2,4-DNPH in a condensation reaction to form hydrazones and water (Brady and Elsmie, 1926).

![Reaction of 2,4-DNPH and aldehyde](image)

The sampling rates for a range of aldehydes are reported by Radiello® and given in Table 17 (at 298 K). The sampling rates vary with temperature as given in Eq. 26 with the same definitions as Eq. 24.

$$Q_k = Q_{298} \left( \frac{T}{298} \right)^{0.35}$$

### 3.2.2 Measurements of particles

#### 3.2.2.1 Grimm

The measuring principle of the Grimm Portable Dust Monitor used in the pilot field campaign, is based on scattering of laser light from a particle (solid, liquid or gas) (Grimm, 2013). Air is sampled through a measuring cell exposed to a laser of a well-defined wavelength ($\lambda_0$, 655 nm for Grimm version 1.109). When a particle passes the laser beam, some light is scattered and a light-pulse is measured at a scattering angle of 90° (Figure 35).
A factor \( \alpha \) is defined by the particle diameter of a spherical particle divided by \( \lambda_0 \) \( \alpha = d_p/\lambda_0 \). The effect of scattering depends strongly on the particle size compared to \( \lambda_0 \):

- For particles much smaller than \( \lambda_0 \) \( \alpha \ll 1 \), the intensity of the scattered light is proportional to the sixth power of the particle diameter \( I \approx d_p^6 \).
- For particles with diameters similar to \( \lambda_0 \) \( \alpha \approx 1 \) there is no simple relation between the scattered intensity and the particle diameter. The scattering depend in the refractive index of the particles, which requires complex calculations (MIE-scattering) (Bohren and Huffman, 2004).
- For particles particle sizes larger than \( \lambda_0 \) \( \alpha \gg 1 \) the scattered intensity is proportional to the particle cross sectional area \( I \approx d_p^2 \) and not strongly dependent on shape or particle composition.

The Grimm 1.109 dust monitor measures particles in the size range 0.25-32 µm. With a \( \lambda_0 \) of 655 nm the lower particle size range is within the MIE scattering range, but this should be compensated by the size of the opening angle of the detector (Grimm, 2013), thus the method assumes proportionality between scattered intensity and cross sectional area.

A number of assumptions are made in the calculation of particle size distribution as effect of light scattering in the Grimm dust monitor:

- Only one particle is in the measuring volume for each measurement. This is achieved by focusing the laser to achieve a small measuring volume, and by aerodynamically focusing of the sample air to focus the particles in the sampling area. For environmental measurements the particle number concentration is usually low enough for this assumption to be valid (Grimm, 2013).
- A spherical geometry is assumed, though the cross sectional area does not depend strongly on particle shape. The spherical geometry is often seen for aerosols but not necessarily for other particle types such as e.g. fibers as in this thesis. Determination of shape factors and correction for these are beyond the scope of this thesis.
- The scattering also depend on the refractive index of the particles. The manufacturer-supplied calibration curve between scattering and particle size is based on monodisperse polystyrene latex (PSL) aerosols with a refractive index of \( m=1.59 \) (Heim et al., 2008). Other
types of particles might have different refractive indexes. For the measurements performed in this thesis refractive index has not been taken into account.

### 3.2.2.2 P-TRAK
The P-TRAK particle counter measures ultrafine particles between 0.02-1 µm in real time. The method is based on condensation particle counting (CPC) using isopropyl alcohol. Small particles pass through a saturator tube, where they mix with alcohol vapor. The particle/alcohol mixture passes through a cooling condenser tube where the supersaturated alcohol condenses onto the particles, causing them to grow into larger droplets; large enough for optical detection (Figure 36).

![Figure 36: Working principle of P-TRAK™ Ultrafine Particle Counter (TSI, 2013a).](image)

This method yields no information on the original size of the particles.

### 3.3 Material and methods

#### 3.3.1 The homes
Key parameters of the 5 selected homes are summarized in Table 15. None of the homes were equipped with air condition and none of the inhabitants were smokers. All homes were located in the Great Copenhagen area, and their locations are indicated on the map in Figure 37.

<table>
<thead>
<tr>
<th>City</th>
<th>Home A</th>
<th>Home B</th>
<th>Home C</th>
<th>Home D</th>
<th>Home E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Construction year</td>
<td>1964</td>
<td>1921</td>
<td>2007</td>
<td>1947</td>
<td>2004</td>
</tr>
<tr>
<td>Floor area</td>
<td>130</td>
<td>143</td>
<td>104</td>
<td>190</td>
<td>90</td>
</tr>
<tr>
<td>Basement</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Number of adults/children</td>
<td>2/1</td>
<td>2/2</td>
<td>2/0</td>
<td>2/0</td>
<td>1/0</td>
</tr>
<tr>
<td>Pets</td>
<td>1 dog</td>
<td>2 cats</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Type of cooking</td>
<td>Electrical</td>
<td>Electrical</td>
<td>Electrical</td>
<td>Electrical</td>
<td>Electrical</td>
</tr>
<tr>
<td>Wood stove</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Dist. to heavy traffic [m]</td>
<td>200</td>
<td>200</td>
<td>5400</td>
<td>1200</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 15: Key parameters of the five homes selected for the sampling campaign
3.3.1.1 **Home A**
Home A was a one family house located in a residential neighborhood about 200 m south of closest road with heavy traffic, 1.3 km west of the nearest highway (Hillerødsmotorvejen) and 20 km north-west of Central Copenhagen.

3.3.1.2 **Home B**
Home B was a two floor house with a basement and a woodstove, which were used extensively during the winter season. The house was located in a residential neighborhood about 200 m north of the closest road with heavy traffic, about 600 m east of the closest highway and 13 km north of Central Copenhagen.

During the period of the sampling year, a number of renovation projects, including painting and sanding, were performed, but none of these were done during any of the 4 sampling campaigns.

3.3.1.3 **Home C**
Home C was a town house located in a residential neighborhood about 450 m north and west of the sea, 5.4 km south of the closest highway (Øresundsmotorvejen), 2.5 km south of the start and landing lanes of Copenhagen Airport and 11 km south of Central Copenhagen.

3.3.1.4 **Home D**
Home D was a one family house with a basement and it was selected because of known fungal problems in one of the bedrooms. The problems were addressed via rodalon treatment, painting and repair of a problematic outer wall prior to the sampling campaign. The house was located in a
residential neighborhood about 400 m east of the closest road with heavy traffic, 1.2 km west of the closest highway (Helsingør motorvej) and 7 km north of Central Copenhagen.

### 3.3.1.5 Home E
Home E was the only apartment in the study. It was located in the city Helsingør about 200 m west of the sea, about 100 m south of the closest road with heavy traffic and 40 km north of Central Copenhagen. The apartment was on 2nd floor.

### 3.3.2 Diaries
For each of the sampling periods the inhabitants were asked to fill out a small questionnaire regarding their behavior with regard to a number of parameters. The parameters included bedtimes, presence in the home, opening of windows and doors, cooking and drying of clothes indoor. A diary page is given in App. C. In the ideal world, it would be nice to have as throughout account of all inhabitants' behavior during the sampling week – and also some behaviors such as cleaning in between. But in the design of the questionnaire, it was more important that the inhabitants filled out all required information, so the number of questions was minimized. During the sampling campaigns the inhabitants were asked to comment on the workload of filling out the questionnaire. Though it seemed a simple task to fill out, a general comment was that in real everyday life, it was somewhat a challenge, and a couple of questionnaires were even filled out through an interview with the inhabitants at the end of the sampling campaign.

### 3.3.3 Air Exchange Rates (AER)
Measurement and calculation of AERs were performed by DTUbyg and SBI. The measurements were performed using constant concentration methods with a target level of 4 ppm of Freon. The concentration of tracer gas was monitored by an Innova Multi-Gas Monitor Type 1302 and an Innova Multipoint Sampler and Doser 1303 (Lumasense Technologies, Santa Clara, CA.) The concentration of tracer gas was separately controlled in different rooms of each home. Whenever possible, the instruments were located behind closed doors in a room that was not directly investigated in the experiment. This was done in order to minimize potential leakage of tracer gas from the measurement setup. However, prior to the experiments, the instruments were tested for leakage, which was negligible. The average overall AER for an entire home was calculated as the total airflow entering the home, as measured by the instrument (the sum of airflows into all measured rooms), divided by the total volume of the home.

### 3.3.4 Temperature and relative humidity
Measurement of temperature and humidity was performed by DTUbyg, and were logged by HOBO loggers (U12-012 data logger, Onset Computer Corp., USA) placed in the living room and bedroom. The measuring interval was 5 min. Outdoor temperatures were measured by HOBO loggers placed in a shady position protected from rain.

### 3.3.5 Particle counters
The concentration of airborne particles was measured numerically. The Grimm Portable Dust Monitor (model 1.109; Grimm Technologies, Inc. Douglasville, GA) was used to measure airborne
particles (0.75-15 μm; one measurement per minute) in the living rooms of the homes during the sampling time.

The ultrafine particles (0.02-1 μm) were measured by DTUbyg with a P-TRAK ultrafine particle counter 8525 for two hours Saturday from 7-11 AM during the measurement campaigns. Continuous measurements throughout the whole sampling campaigns were not performed, since the instrument was not suitable for unsupervised measurements over longer time, due to the need of refilling with isopropanol.

3.3.6 Radiello passive samplers
One of each passive sampler (ozone, NO₂ and aldehydes) was placed in the living room and bedroom 1.5 m above the floor. Each sampler was exposed during a whole measuring week equal to four days. The temperature during each measurement period was logged, and the average was used for temperature correction of the sampling rate according to Eq. 24 (ozone), Eq. 25 (NO₂) or Eq. 26 (aldehydes).

3.3.6.1 Ozone
Ozone concentrations in the 5-home field study were determined as 4-day averages. For the sampling in the intervention study performed by SBI, ozone concentrations were determined as 14-day averages; most of the samples were taken during the winter-season and some during the spring season. The ideal sampling time in outdoor environments according to the manufacturer is 3-7 days, but up to 14 days are suggested. With indoor sampling the concentration are typically lower than outdoor, thus saturation of the samplers should not be a problem with the sampling times used in this thesis. However the stability of the samplers have not been investigated.

The O₃ sampling cartridges were reacted and extracted with 5 ml MBTH in water (5 g/L). The solution was left for 1 h to ensure complete reaction between 4-pyridylaldehyde and MBTH in order to obtain quantitative formation of MBTH-azide yellow, which was measured in a plate reader spectrometer at 450 nm (ELx808, Bio-Tek instruments, Inc, VT.). A six-point calibration curve with 4-pyridylaldehyde in MTBH solution was obtained.

3.3.6.2 NO₂
The NO₂ sampling cartridges were extracted with 5 ml milliQ water (Millipore, Mass.) by stirring vigorously in a vortex mixer for 1 min. 5 ml sulphanilamide solution (10 g in 1 L 1.2M HCl) was added to 0.5 ml of the extract. The solution was stirred and left to react for 5 min. After 5 min 1 ml NEDA (250 mg in 250 ml water) was added, the solution was stirred and left to react for 10 min. A six point calibration curve with NaNO₂ in water treated as the extracts was obtained. The absorbance of the formed azo-dye (Figure 33) was measured in a plate reader spectrometer at 490 nm (ELx808, Bio-Tek instruments, Inc, VT.)

3.3.6.3 Aldehydes
The aldehyde sampling cartridges were extracted with 3 ml acetonitrile for 30 min. The extracts were analyzed by HPLC (Waters 1525) using a diode array detector at 360 nm (Waters 2489). Water
(solvent A; milliQ, Millipore, Mass.) and acetonitrile (Solvent B; Fluka LC-MS-Chromasol) was used as eluents at 1 ml/min with a gradient (Table 16).

Table 16: HPLC gradient for aldehyde analysis.

<table>
<thead>
<tr>
<th>Time</th>
<th>% A</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>11</td>
<td>40</td>
</tr>
</tbody>
</table>

A standard mixture of carbonyl-DNPH (Supelco, Bellefonte, PA, Carbonyl-DNPH Mix 1) was used for six-point calibration ($r^2 > 0.999$). For methacrolein and p-tolulaldehyde the sampling rate was not supplied, and the sampling rate of similar aldehyde was used; acrolein for methacrolein and benzaldehyde for p-tolulaldehyde. These could be calculated from the diffusive coefficients and the geometrical constant of the sampler (Eq. 23).

It should be noted that the chromatographic method is not able to separate acrolein-DNPH and acetone-DNPH.

Table 17: Summary of aldehydes analysed in this thesis.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Molar mass [g/mol]</th>
<th>b.p. [°C]</th>
<th>Sampling rate [ml/min]$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>CH₂O</td>
<td>30.03</td>
<td>-19</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>C₂H₄O</td>
<td>44.05</td>
<td>20</td>
</tr>
<tr>
<td>Acrolein</td>
<td>C₃H₆O</td>
<td>56.06</td>
<td>53</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>C₅H₁₀O</td>
<td>58.08</td>
<td>50</td>
</tr>
<tr>
<td>Methacrolein</td>
<td>C₄H₆O</td>
<td>70.09</td>
<td>69</td>
</tr>
<tr>
<td>Valeraldehyde</td>
<td>C₆H₁₂O</td>
<td>86.13</td>
<td>102</td>
</tr>
<tr>
<td>Hexanal</td>
<td>C₆H₁₂O</td>
<td>100.16</td>
<td>130</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>C₇H₆O</td>
<td>106.12</td>
<td>178</td>
</tr>
<tr>
<td>p-Tolualdehyde</td>
<td>C₆H₁₀O</td>
<td>120.15</td>
<td>204</td>
</tr>
</tbody>
</table>

$^a$: Sampling rates for aldehydes on 2,4-DNPH coated Florisil® (at 298 K). (Radiello, 2007a). $^b$: No information on sampling rate supplied, see text.

### 3.3.7 Sampling of VOCs on Tenax

Air sampling in the homes was performed 1.5 m above the floor on Perkin Elmer stainless steel tubes (i.d. ¾”) packed with 0.2 g Tenax TA adsorbent material for TD-GC-MS. Pre-cleaning of the tubes and adsorbent was performed by heating to 275 °C with a nitrogen flow for 2 hours. Sampling was performed with an BG1400 pump (BGI, Inc., Waltham, MA, USA) at an air flow of 190±7 ml/min.

A Perkin-Elmer ATD 400 was coupled to a Varian GC-MS (GC: CP-3800/MS: 1200L) system with El ionization. The GC-MS was equipped with a CP Sil19CB 30 m x 0.32 μm i.d (0.25 μm film thickness) column. Desorption was carried out at 275 °C for 20 min followed by flash desorption of the cold trap into the GC; the GC oven program was: 35 °C hold 4 min, ramp 1: 4 °C min⁻¹ to 120 °C, ramp 2: 8 °C min⁻¹ to 250 °C, ramp 3: 20 °C min⁻¹ to 280 hold 2 min. Helium was used as a carrier gas with a controlled flow rate of 1.6 mL min⁻¹.

The GC-MS data was exported to DataAnalysis (Version 4.0, Bruker Daltronik, GmbH, Bremen, Germany). An automated function (dissect) was used to create deconvoluted spectra of the chromatographic peaks. For each mass spectrum, a search was performed in the NIST database (NIST, 2011), and a Rfit value was reported as a measure of the fit of the unknown compound to the
database mass spectra (max Rfit = 1000). The identification was based on a combination of Rfit, manual inspection and boiling point compared to retention time.

3.4 Results and discussion
With only five homes in the sampling campaign, it was not expected that we would find results that could be generalized to other buildings with the same characteristics since the statistical material was too small. The results in this section should be considered as a test of different sampling methods and measurements in inhabited homes and mainly considered as single cases. In spite of the small statistical material, seasonal changes across the five homes are considered.

3.4.1 Temperatures and humidity
Temperature and relative humidity indoor and outdoor during the sampling period was considered a fundamental characteristic of each home and sampling period. It was used as background for interpretation of other measurement data from the field campaign. The temperature was also used for calculation of sampling rate of the passive samplers.

The average indoor temperatures are summarized in Figure 38 A and B. The indoor temperature is relative constant both with regard to the different homes and season. Only the summer season stands out with a higher average temperature than the three other seasons. This is also consistent with the higher outdoor temperature (Figure 39) and the fact that none of the homes were equipped with air condition to provide cooling of incoming outdoor air.

![Figure 38: Average indoor temperature during the measurement weeks. A: Average of all five homes during each season. B: Average of all four season for each home. The error bars indicate the standard deviation within each season and home respectively, and does not include the variation within each measurement.](image)

The average outdoor temperatures from loggers placed in a shady place are summarized in Figure 39. The seasonal distribution follows, what would be expected for Danish conditions with comparable spring and fall temperatures (ca. 10°C) and higher, but still moderate summer temperatures (ca. 22°C), and winter temperature close to 0°C.

The standard deviations are about 4°C within each season which indicates that each of the sample campaigns was performed in similar conditions for all 5 homes, even though the total sampling period for each campaign was 5 weeks.
Figure 39: Average outdoor temperatures for each season, averaged for all 5 homes. The error bars indicate the standard deviation within each season, and does not include the variation within each measurement.

The relative indoor humidity (% RH) is summarized in Figure 40 A and B. When the seasons are compared (Figure 40A), there is not much variation in % RH and the variation within each season is higher than the difference between the seasons. Due to the difference in outdoor and indoor temperature it is not reasonable to compare indoor and outdoor % RH.

The total range of % RH for the five homes during the year was from 22% RH in home C during the fall sampling to 60% RH in home D during the fall sampling. The average % RH during the four seasons is remarkably lower for home C than the four other homes. This difference is mainly caused by a low % RH in fall and summer (22% vs. an average of 49% in fall and 25% vs. 44% in summer) whereas the values for spring and winter are closer to the average (45% vs. 48% in spring and 50% vs. 46% in winter). This difference indicates that the indoor % RH is influenced by user behavior and not only by building characteristics and outdoor conditions.

Figure 40: Average indoor relative humidity during the measurement weeks. A: Average of all five homes during each season. B: Average of all four season for each home. The error bars indicate the standard deviation within each season and home respectively, and does not include the variation within each measurement.

The average outdoor % RH is summarized in Figure 41. The total range over the year was from 52% during a spring sampling to 92% during a winter sampling. In general the % RH was lowest in the summer with relative little variation (±2.6%) and highest in the winter time with a higher variation (±10.2%). The low variation during the summer periods reflects five sampling weeks with stable warm weather, whereas the three other seasons had somewhat more mixed weather conditions.
The high outdoor % RH during winter time cannot be expected to be reflected in the indoor % RH since the low outdoor temperature actually results in a low absolute humidity.

The RH can be converted to absolute humidity (\(\text{g water vapour/m}^3\ \text{air}\)) when the temperature is known (Vaisala, 2013). The absolute humidity is directly comparable for measurements at different temperatures. Figure 42 shows that the indoor and outdoor absolute humidity correlates \((r^2=0.56)\).

Indoor temperature and H\(_2\)O mixing ratios in temperate zone Australian homes have been reported for winter/spring and summer/autumn (Molloy et al., 2012). The indoor temperatures were similar to those obtained in this thesis, with an average of 20.3±1.4 °C in spring/winter and 22.1±2.1 °C in summer/autumn. Average outdoor temperatures for summer/autumn at 18.1±3.0 °C were also similar to the temperatures measured in this thesis, whereas winter/spring average at 15.6±2.0 °C was slightly higher. The H\(_2\)O mixing ratios \([\text{g H}_2\text{O/kg air}]\) were also similar in the two studies, with slightly higher values for summer/fall than winter/spring. A field study in five European cities (Milan, Copenhagen, Dublin, Athens and Nicosia) reported indoor temperatures and % RH in winter and summer (Dafni et al., 2010). The temperature in houses were in the range 11-25 °C in winter and 17-30 °C in summer; a broader range than found in the present thesis, which is to expect with the more diverse climates. Relative humidity were in the range 23-60% RH during winter and 32-70% RH during summer, which again is a broader range than in this thesis.

### 3.4.2 Diaries - Opening of windows

The inhabitant diaries revealed that windows and doors were open much longer during the summer measurement (Figure 43). The numbers of hours with open doors or windows in the living room or bedroom was significantly higher in summer than any of the three other seasons (spring \(p=0.0026\); fall \(p=0.0016\) and winter \(p=0.00011\)), which is also consistent with the higher outdoor temperature and no air-condition in any of the homes. During the winter, the opening of windows and doors was significantly lower than during spring \((p=0.026)\) but not lower than during fall \((p=0.31)\). In the comparisons between the different homes no statistical differences were found \((p=0.22-0.86)\) due to the high variation within each home caused by the seasonal variation. It should be noted that the diary was not sufficiently completed for home D in summer, thus the low average. In home E windows were generally more open, but the differences to the other homes were not significant.
3.4.3 Air exchange rate (AER)

When the total AER is compared across the seasons (Figure 44A) the values for the summer campaign are significantly higher than fall (p=0.060) and winter (p=0.033) and close to significantly higher than spring (p=0.12). From Figure 45 it is evident that home E has a higher total AER than the other four homes, especially during summer and spring. For the four other homes (A-D) the summer total AER is significantly higher than spring total AER (p=0.015). None of the other seasons are significantly different from each other.

When the total AER for the five homes are compared across the seasons (Figure 44B), there are no significant differences (p=0.13-0.91) which is a consequence of the high seasonal variation indicated by the high standard deviation on the average across the seasons. However in Figure 45 it can be seen that home E in general have a higher total AER than the other four homes, home D has a relatively low total AER in all four seasons compared to the other homes and home D has a low total AER in all other seasons than summer.

The recommended AER for a home is app 0.5 h$^{-1}$ according to the Danish building regulations (SBI, 2011). This requirement is not met in 9 out of the 20 measurements as indicated in Figure 45. Home C and D only meet this criterion during the summer measurement; home D is the only home to meet it during winter and home C also fails during fall.
A field study in five European cities (Milan, Copenhagen, Dublin, Athens and Nicosia) reported AER in winter and summer (Dafni et al., 2010). AER were 0.16–1.1 h⁻¹ in winter and 0.2–0.97 h⁻¹ during summer. The winter values are comparable to those found in this thesis, but the values for summer are substantially lower, which is likely to be caused by air conditioning in the homes in the southern cities. Six of the 10 investigated homes were cooled by a combination of natural ventilation and air-conditioning (4 homes) or HVAC (Heating, Ventilation, and Air Conditioning; 2 homes), which are a good reason for the inhabitant to keep windows closed; a factor which this thesis has shown to correlate with AER.

### 3.4.4 Particles - Grimm

Particle number concentrations in the size range 0.75–15 µm were monitored in the living room of each home during the each sampling period. Some examples of different situations are given in Figure 47-49.

Figure 47 shows the changes in particle number concentration over a period of 4 days (Thursday-Monday). The number concentration varies greatly throughout the day with some fast particle production events followed by a relative slow decay during several hours. The diary from this family is not detailed enough to explain the causes for each of these spikes. Particles from cooking are expected to be smaller than the ones measured in this case (Abt et al., 2000). This is confirmed since the diary states that cooking occurred around 18–19 PM and no major peaks in particle concentration occurs at this time.

The family in home C (Figure 47) consists of two persons who both work away from home, whereas the family in home D (Figure 48) consists of two retired people. The comparison of the particle number concentration in these two homes shows different patterns. In home C only relatively few well-defined particle events occur, whereas in home D there are more but less well-defined events. This indicates that the particle number concentration in the size range is mainly controlled by the activities of the inhabitants. This is further confirmed by a sampling period in home C in the fall, where the inhabitants where not at home during the weekend (Figure 49) and during this period the particle concentration was at a constant low level.
Figure 47: Grimm particle number concentration over a sample period in spring in home C. Fewer relatively well defined peaks are observed for people working away from the home.

Figure 48: Grimm particle number concentration over a sample period in spring in home D.

Figure 49: Grimm particle number concentration over a sample period in fall in home C. The low constant period is recorded during inhabitants’ absence.
A simple way to describe the particle number concentration throughout a measurement week is by the average and standard deviation. Due to the large variations during the days the standard deviations were as high as 177% as summarized in Figure 50. The average particle number concentration was in the range 70-2600 counts/L (0.07-2.6 counts/cm³). For comparison with other studies, it is essential that the same size range has been measured, and often indoor air particle number concentrations are reported as mass concentrations or in other size ranges.

If the number concentrations are recalculated to mass concentrations, the comparison between different studies requires less about the similarity of the studies, since the small particles contributes less to the mass concentration, and the difference between different methods are often the lower size cut-off. Mass concentrations will be discussed at the end of this section.

Though the average number concentration is not sufficient to describe the full particle exposure, it can be used to compare the particle number across seasons and homes to explore more general tendencies. In Figure 53 the average particle number concentration over the five homes are compared for the different seasons. The particle number concentration was significantly lower during the summer season than during spring (p=0.027) and during winter (p=0.093). The p-value for the difference between summer and fall was 0.13 and thereby close to significance on the 10% level. None of the other seasons differed significantly from each other (p=0.24-0.61). The lower particle number concentrations during summer could be explained by the higher AER between indoor and outdoor air, and thereby also indicate that the primary source for particles in this size range might be indoor sources.

The high AER and low Grimm particle number concentrations during summer indicate a correlation, but as shown in Figure 52 there is a poor correlation between those factors (r²=0.15).
Figure 51: Average particle number concentration (Grimm) over the 5 investigated homes during each season. The error bars indicate the standard deviation within each season, and does not include the variation within each measurement.

Figure 52: Correlation between the AER rate and average Grimm particle number concentration for all measurements in the five homes.

Figure 53 shows the average particle number concentration across all four season for each of the five homes. The concentration in home D is significantly lower than both home C \( (p=0.022) \) and home E \( (p=0.013) \) and there is no significant difference between any of the other homes \( (p=0.22-0.99) \).

Figure 53: Comparison of Grimm particle data from the 5 homes (A-D). Average particle size (0.75-15 µm) over all seasons for each of the 5 homes. The error bars indicate the standard deviation within each home, and does not include the variation within each measurement.

If it is assumed that the particles are spherical with a density of 1 g/cm³, the mass distribution can be estimated as summarized in Figure 54 A & B. The median of each size bin has been used for the calculations. The individual relation between both seasons and homes are similar to those found for the number distribution, but the mass distribution is more convenient for comparison with previous studies.
Abt et al. (2000) reported particle mass concentration in the size range 0.7-10 µm in homes in Boston (Table 18), which is similar to the results obtained in the present thesis. Outdoor particles were found to contribute significantly to indoor particle mass concentration in this size range.

Numerous studies reports PM_{10} particle mass concentrations in homes; a few are summarized in Table 18. When mass distribution is used, PM_{10} could be expected to be comparable to the data obtained in this thesis, i.e. the particles below 0.75 µm contribute less to the total mass, but as seen in the table, the PM_{10} mass concentrations are about a factor of 10 higher than those obtained both in this thesis and the study by Abt et al. (2000), indicating that the particles <0.75 µm contributes substantially to the mass concentration.

Table 18: Reported particle mass concentrations.

<table>
<thead>
<tr>
<th>Location</th>
<th>Size</th>
<th>Method</th>
<th>Particle mass concentration [µg/m^3]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copenhagen</td>
<td>0.75-15 µm</td>
<td>Grimm</td>
<td>5.2±2.5</td>
<td>This thesis</td>
</tr>
<tr>
<td>Homes, Boston, US</td>
<td>0.7-10 µm (7 size bins)</td>
<td>APS</td>
<td>4.6</td>
<td>Abt et al., 2000</td>
</tr>
<tr>
<td>Homes in Hong Kong; Fall &amp; winter</td>
<td>PM_{10}</td>
<td>Gravimetric, sampling on filter with cyclone</td>
<td>45.0-69.5</td>
<td>Chao and Wong, 2002</td>
</tr>
<tr>
<td>Homes at roadsides, Birmingham</td>
<td>PM_{10}</td>
<td>Realtime TEOM</td>
<td>16-48</td>
<td>Jones et al., 2000</td>
</tr>
<tr>
<td>Urban flats, Birmingham</td>
<td>PM_{10}</td>
<td></td>
<td>15-88</td>
<td></td>
</tr>
<tr>
<td>Rural homes, Birmingham</td>
<td>PM_{10}</td>
<td></td>
<td>27-45</td>
<td></td>
</tr>
<tr>
<td>Homes, Helsinki</td>
<td></td>
<td></td>
<td>=15</td>
<td></td>
</tr>
<tr>
<td>Homes, Athens</td>
<td>PM_{10}</td>
<td>Gravimetric, sampling on filter with cyclone</td>
<td>=40</td>
<td>Hoek et al., 2008</td>
</tr>
<tr>
<td>Homes, Amsterdam</td>
<td>PM_{10}</td>
<td></td>
<td>=25</td>
<td></td>
</tr>
<tr>
<td>Homes, Birmingham</td>
<td></td>
<td></td>
<td>=15</td>
<td></td>
</tr>
</tbody>
</table>

APS: Aerodynamic Particle Size; TEOM: Tapered Element Oscillating Microbalance.
3.4.5 Ultrafine particles

The particle number concentrations (count/cm$^3$) for the ultrafine particles (<1 µm) for the Saturday morning measurements are given in Figure 55. As for the larger particles, the particle number concentrations are not constant over the measurement period; some periods contain substantial peaks. The diaries were not detailed enough to assign these peaks to inhabitants behavior or other incidents. The measurement periods were relatively short (2 h) and represent only a snapshot of the indoor conditions. Thus an average concentration over the measurement period might not be representative, which should be kept in mind in the comparison between the different homes and seasons.

![Graphs showing ultrafine particle concentrations for Spring, Summer, Fall, and Winter]

Figure 55: Ultrafine particles (<1 µm) for a 2 hour sampling Saturday morning. X-axis: counts/cm$^3$; same scale for all but home C spring for easier comparison; Y-axis: Time of day [hh:mm]. No data were recorded for Home C and E during winter.

The average ultrafine particle number concentration compared across seasons and homes shows some seasonal variation but similar values for the homes (Figure 56 A & B). The high average for home C is mainly caused by the high value for spring. Though some seasonal variation is indicated, the differences between seasons are not significant (p=0.09 for summer vs. fall to p=0.41 for summer vs. winter).
Some correlation between AER and ultrafine particle number concentration was found ($r^2=0.29$); this indicates an outdoor source such as traffic which could be expected. Two extremes for particle number concentration and AER were excluded from the linear regression as indicated (Figure 57 A). No correlation was found between the ultrafine and particles and the 0.75-15 µm particles ($r^2=0.07$) (Figure 57 B). The times for the measurements of ultrafine particles and the times where lightning of candles or cooking was indicated in the diaries did not coincide, thus the correlation between these two parameters was not investigated, though it is a known source of indoor ultrafine particles (Glytsos et al., 2010).

Average ultrafine particles in rural Swedish homes were measured from midnight to 8 PM and particle number concentration in the range 2000-6000 counts/cm$^3$ were found (Matson, 2005), which is comparable to the number concentrations found in this thesis, though the concentration range was larger in this thesis.

### 3.4.6 Ozone

The indoor ozone concentrations (bedroom and living room) measured in the five homes during spring, summer and winter are summarized in Figure 58. The ozone concentration was in the range 0.82-41 ppb with the highest values during summer. The following section will discuss these results with regard to seasonal variation, outdoor to indoor concentration, AER and room to room variation.
3.4.6.1 Seasonal variation

Figure 58 indicates a seasonal variation with high indoor ozone concentrations during summer and lower during the other seasons. This can be seen more clearly in Figure 59 A, where the average ozone concentrations for the five homes for each of the seasons are given. For bedrooms the ozone concentration during summer was significantly higher than during the other seasons (p=0.02-0.04), but none of the other seasons differed significantly (p=0.43-0.53). For living rooms the summer season was significantly higher than the winter and the second spring season (p=0.05). None of the other seasons differed significantly (p=0.09-0.86).

Figure 59: A: Indoor average ozone for all five homes during each season. B: I/O ratio of ozone for all five homes during each season. The error bars indicate the standard deviation between each season and home, respectively.

Figure 60: Outdoor ozone concentration by season. The error bars indicate the standard deviation between each season.
The primary source for indoor ozone is expected to be transport of ozone from the outdoor air. The outdoor ozone concentrations at the five different homes during each of the sampling campaigns are summarized in Figure 60. As opposed to the indoor ozone concentration, the first spring and summer where not significantly different (p=0.59), whereas all other seasons differed significantly (p=0.00003-0.010). This difference is also shown in the ratio of indoor to outdoor ozone concentration (I/O) (Figure 59 B). The highest I/O-values were surprisingly found during the winter, where windows generally was kept more closed and the AER were low (section 3.4.3) and thus a low infiltration of outdoor ozone was expected. The explanation for this is not clear, but could in part be the low outdoor concentrations.

A summary of some I/O ozone ratios cited in the literature is given in Table 19. The ratios are in the range <0.1-1.0, which are comparable to the values found in this thesis. Two of these studies report I/O ratios during both summer and winter (Liu et al., 1995; Bernard et al., 1999) whereas the all other studies have either only analyzed during summer or have not reported the time of year. For both studies, where summer and winter could be compared, higher I/O ozone ratios were found during the summer, where AER tends to be higher.

Table 19: Summary of I/O ozone ratios from homes with negligible indoor sources of ozone. Adapted from Weschler (2000)

<table>
<thead>
<tr>
<th>Location</th>
<th>I/O</th>
<th>Notes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copenhagen, (n=5)</td>
<td>0.08±0.08</td>
<td>Spring</td>
<td>This thesis</td>
</tr>
<tr>
<td></td>
<td>(0.02-0.02)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.24±0.16</td>
<td>Summer</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.03-0.6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.2±0.7</td>
<td>Winter</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.5-2.3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>So. California (n=1)</td>
<td>0.70</td>
<td>Summer, natural ventilation. I/O value</td>
<td>Sabersky et al., 1973</td>
</tr>
<tr>
<td></td>
<td></td>
<td>determined at the maximum ozone</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>concentration at midday.</td>
<td></td>
</tr>
<tr>
<td>Washington (n=5)</td>
<td>0.5-0.7</td>
<td></td>
<td>Moschandreas et al., 1978</td>
</tr>
<tr>
<td>Baltimore (n=6)</td>
<td>0.5-0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boston, MA (n=10)</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tucson, AZ (n=41)</td>
<td>0.3</td>
<td>72 hour average, two year period.</td>
<td>Lebowitz et al., 1984</td>
</tr>
<tr>
<td>Houston, TX (n=12)</td>
<td>&lt;0.1</td>
<td>Conventional air conditioning, average over app 100 days.</td>
<td>Stock et al., 1985</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>Summer, average of 6 days, air-condition on, windows closed</td>
<td></td>
</tr>
<tr>
<td>New Jersey (n=6)</td>
<td>0.62</td>
<td>Summer, average of 6 days, air-condition off, windows open</td>
<td>Zhang and Lioy, 1994</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>Summer, average of 6 days, air-condition off, windows closed</td>
<td></td>
</tr>
<tr>
<td>Toronto (n=40)</td>
<td>0.07</td>
<td>Winter, weekly averages.</td>
<td>Liu et al., 1995</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Summer, daily averages</td>
<td></td>
</tr>
<tr>
<td>Munich</td>
<td>0.5-1.0</td>
<td>Natural ventilation, summer, 2 day average</td>
<td>Jakobi and Fabian, 1997</td>
</tr>
<tr>
<td>So. California (n=126)</td>
<td>0.37</td>
<td>Feb-Dec, 24 hour average</td>
<td>Avol et al., 1998</td>
</tr>
<tr>
<td>Mexico City (n=145)</td>
<td>0.20</td>
<td>November-June 14 day average, no air-condition</td>
<td>Romieu et al., 1998</td>
</tr>
<tr>
<td>Montpellier (n=40)</td>
<td>0.38</td>
<td>Winter, 5 day average</td>
<td>Bernard et al., 1999</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>Summer, 5 day average</td>
<td></td>
</tr>
</tbody>
</table>
Though AER may explain some of the variation of ozone outdoor to indoor ratio, plots of AER per home and AER per room vs. I/O for ozone (Figure 61 A & B) showed no correlation neither in general nor for any of the individual homes.

![Figure 61: Correlation with indoor to outdoor ozone ratio A: AER. B: AER by room.](image)

This shows that though the indoor ozone concentration is influenced by both the outdoor ozone concentration and AER, these two factors are not the only ones to influence indoor ozone. Another factor could be the interaction with different surfaces in different homes. If this was a major parameter, it would be expected that I/O for ozone would correlate with AERs within each home, but this was not the case. Another explanation could be that other parameters such as reactive VOCs with a possible seasonal parameter influence the seasonal variation of ozone.

### 3.4.6.2 Spatial variation

The concentrations in the bedrooms and living rooms were found to correlate \( (r^2=0.93, \text{slope } 0.73) \), (Figure 62). One data point (Home C summer) had a high bedroom concentration compared to the living room and was excluded from the linear regression. The slope of 0.73 of the linear regression of bedroom vs. living room ozone concentration indicates that the ozone concentration in general were lower in the living room, but bedroom and living room were not statistically different (paired t-test: \( p=0.68 \)).

![Figure 62: Correlation between ozone concentration in bedroom and living room. * Excluded from the linear regression.](image)
3.4.6.3 Intervention study

As a part of CISBO WP 2, residential ozone measurements, sampled over 14 days, for 60 homes have been tested for correlations with the lung function of elderly people. The work in this thesis has only contributed with the analysis of the passive ozone samplers and has not been involved in the work on biological markers and interpretation of the correlations. For the intervention study, two samples for each home have been averaged to obtain a 28-day average, but in the following description of the data, each 14-day sample is treated as one and no averaging of different samples have been performed.

Figure 63 shows the average ozone concentration and standard deviation for the winter (November to February) and spring (March to May) season. A significant difference between the two seasons were found (p=0.042). No significant difference was found between bedroom and living room (p=0.087). A direct comparison of the average ozone concentrations in the 5-home and the 60 home study would require that the selection of homes in both studies were representative, which is not expected with the low number of homes. Though both seasons were statistically different in the comparison of the two studies (winter p=4×10^{-12}; spring p=8×10^{-5}) with generally lower values for the 60-homes study, a plot of all data points shows that they might as well represent the same population (Figure 64).

The correlation between ozone concentrations in the living room and bedroom is shown in Figure 65. Compared to the 5-home study a poorer correlation was found (r^2=0.32 vs. 0.93 and paired t-test p=0.020 vs. 0.68). The major difference between the two studies is the number of homes, how many times each home was visited, and the sampling time. It is likely that different homes will have a different spatial distribution of ozone (and other chemicals) caused by e.g. construction and user behavior. In the 5-home study each home was visited five times, and the repetition of each home might increase the total correlation.
3.4.7 Aldehydes

3.4.7.1 Composition

The concentrations of the 9 analyzed aldehydes in the 5 homes are summarized in Figure 66 A-C (living room, bedroom and outdoor). The relative abundance of the different aldehydes are similar for the indoor measurements (living room and bedroom), where formaldehyde, acrolein/acetone and hexanal were the three most abundant aldehydes, whereas the composition of the aldehydes in the outdoor air was substantially different, and dominated by hexanal. Since the indoor composition does not change substantially during the different seasons or in the different homes, the comparisons in the following sections will be based on the total aldehyde concentration, i.e. the sum of the 9 aldehydes, thus not including less volatile aldehydes, such as decanal, which are not analyzed with this method.
Formaldehyde is the aldehyde which has attained the most attention in the literature, due to its known health effects. The concentration range of formaldehyde was 6.7-69 µg/m³ with an average of 24.3 µg/m³, thus not exceeding the WHO guideline value (100 µg/m³ for a 30 minute average exposure (WHO, 2010), though the daily variations and possible peak concentrations are not known, since no online monitoring was used. Diurnal variations for formaldehyde in Mexican homes are reported, and no substantial variation was found (Baez et al., 2003), thus indicating that the average over the whole sampling period may represent the exposure. Reported concentration ranges of formaldehyde, acetaldehyde and hexanal are summarized in Table 20. The findings in this thesis are consistent with the reported values for formaldehyde and acetaldehyde, but higher for hexanal.

### Table 20: Reported indoor residential concentrations of formaldehyde.

<table>
<thead>
<tr>
<th>Location</th>
<th>Formaldehyde [µg/m³]</th>
<th>Acetaldehyde [µg/m³]</th>
<th>Hexanal [µg/m³]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copenhagen, suburban (n=5)</td>
<td>6.7-69</td>
<td>4.4-46.7</td>
<td>7.8-171</td>
<td>This thesis</td>
</tr>
<tr>
<td>European cities †(n=10; 9 suburban, 1 urban; 4 close to heavy traffic)</td>
<td>5.8-62.6</td>
<td>0.7-41.6</td>
<td>113.3</td>
<td>Dafni et al., 2010</td>
</tr>
<tr>
<td>Paris, urban and suburban (n=30)</td>
<td>34.4±1.9</td>
<td>10±1.8</td>
<td></td>
<td>Clarisse et al., 2003</td>
</tr>
<tr>
<td>Strasbourg (n=22; 17 urban and suburban, 5 countryside)</td>
<td>13.3-123.4</td>
<td>3.1-80.3</td>
<td>0-47.2</td>
<td>Marchand et al., 2006</td>
</tr>
<tr>
<td>Strasbourg (n=162)</td>
<td>32.2±14.6</td>
<td>14.3±9.7</td>
<td>8.6±8.1</td>
<td>Marchand et al., 2008</td>
</tr>
<tr>
<td>Strasbourg (n=40)</td>
<td>15.0±5.8</td>
<td></td>
<td></td>
<td>Molloy et al., 2012</td>
</tr>
<tr>
<td>New Jersey, suburban (n=6)</td>
<td>33.1-125.1</td>
<td>0.80-15.6</td>
<td>7.9-54.1</td>
<td>Zhang et al., 1994</td>
</tr>
<tr>
<td>Mexico, heavy traffic (n=2)</td>
<td>37-47</td>
<td></td>
<td></td>
<td>Baez et al., 2003</td>
</tr>
</tbody>
</table>

†: Milan, Copenhagen, Dublin, Athens and Nicosia

#### 3.4.7.2 Spatial variation

A good correlation between the total aldehyde concentration in the bedroom and in the living room was found ($r^2=0.97$; slope=0.97, Figure 67 A), and a paired t-test showed that the two measurement positions did not differ significantly (p=0.61). Thus in the correlation between indoor and outdoor total aldehyde concentration, the indoor concentration is the average of living room and bedroom (Figure 67 B). If the two high outdoor values caused by a high acrolein/acetone and a high hexanal concentration (marked with *) are excluded, a correlation was found between indoor and outdoor total aldehyde concentration ($r^2=0.27$; slope 0.05, Figure 67 B), with a significant higher indoor concentration (p=0.00004).

![Figure 67: Total aldehyde concentrations. A: Correlation between living room and bedroom. B: Correlation between indoor and outdoor. * Excluded from linear regression.](image-url)
Reported I/O ratios for formaldehyde are summarized in Table 21. The values in this thesis are substantially higher than the reported values. This can be explained by high outdoor concentrations caused by heavier traffic in the previous studies (Salthammer, 2013).

<table>
<thead>
<tr>
<th>Location</th>
<th>I/O formaldehyde</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copenhagen, suburban (n=5)</td>
<td>20 (6.4-48.6)</td>
<td>This thesis</td>
</tr>
<tr>
<td>Strasbourg (n=22; 17 urban and suburban, 5 countryside)</td>
<td>9</td>
<td>Marchand et al., 2006</td>
</tr>
<tr>
<td>New Jersey, suburban (n=6)</td>
<td>7.2±5.9</td>
<td>Zhang et al., 1994</td>
</tr>
<tr>
<td>Mexico, heavy traffic (n=2)</td>
<td>4.4</td>
<td>Baez et al., 2003</td>
</tr>
</tbody>
</table>

### 3.4.7.3 Seasonal variation

Seasonal variation was found for three seasons. The values for summer were significantly lower than for both spring and fall (p=0.0032, p=0.0066), whereas spring and fall did not differ significantly (p=0.36) (Figure 68).

![Figure 68: Seasonal variation of the total indoor aldehyde concentrations. No data was obtained for winter.](image)

A direct comparison of I/O ratios is not relevant, since it was shown that the composition of indoor and outdoor total aldehydes were substantially different (Figure 66).

### 3.4.7.4 Correlations with other parameters

The total aldehyde concentration in the bedroom and living room was found to correlate well with a slope close to 1 (Figure 67 A), thus the average of the two measurement positions are used for the comparison with other parameters, except for indoor ozone, since these have only been measured at one position for each home.

The seasonal variation (Figure 68), with low total aldehyde concentrations during summer, indicates a relation with the AER, which was high in the summer. A negative correlation between AER and total aldehyde concentration ($r^2=0.53$, slope -105, Figure 69 A) indicates that the major source of aldehydes is indoor, and that ventilation can remove substantial amounts. The negative, correlation between AER and hexanal ($r^2=0.35$, slope -34, Figure 69 B), indicates that though hexanal was also found in the outdoor air, it must have an indoor source.
One data-point (Home E, summer) had a high AER compared to the other measurements, and is excluded from the correlations (Figure 70 A-C). Though it is only one data-point, and not enough to make a firm conclusion, it seems that with regard to removal of indoor aldehydes, an AER of 5 h\(^{-1}\) is not substantially more efficient than at 2 h\(^{-1}\). The same tendency was observed for hexanal and formaldehyde.

As described in Paper I, aldehydes are formed as a product from the reaction between C-C double bonds and ozone, thus a correlation between the ozone and the aldehyde concentration is expected. For indoor ozone, a negative correlation was found for ozone concentrations below 40 ppb (\(r^2=0.65\), slope -5.5, Figure 70); thus, showing that aldehydes are found in lower concentrations at high ozone concentrations. At a first glance this is conflicting with the hypothesis that a major source for aldehydes is ozonolysis, since a high ozone concentration should cause formation of more aldehydes. This counter-intuitive relation may be caused by the short half-life of indoor ozone of about 7 min (Weschler, 2000). As described in Paper I, ozone is removed by a number of processes, and the measured indoor ozone concentration might not be representative for the amount available for chemical reactions, but may represent the residual amount after chemical reactions. Thus, in this case, a high aldehyde concentration means that a large amount of ozone has been removed through chemical reactions. High indoor concentration of ozone may thus indicate a low abundance of reactive compounds. The correlation between total aldehyde concentration and outdoor ozone below 200 ppb was positive, though with a poorer correlation than with indoor ozone (\(r^2=0.27\), slope 1.5, Figure 70 B). This indicates that more aldehydes are formed when more
ozone is available from the outdoor air, though the higher ozone concentration is not reflected in the indoor ozone due to the short half-life of ozone. This also explains the poor correlation between I/O for ozone and AER (Figure 61A), and shows that the mechanisms of indoor ozone are complex and controlled both by both transport and both gas- and surface chemical reactions.

![Figure 70: Correlation between total indoor aldehyde concentration and A: Indoor ozone concentration, B: Outdoor ozone concentration.](image)

No correlation was found between total aldehyde concentration and Grimm particle number concentration \(r^2=0.03\) or indoor temperature \(r^2=0.05\) and only a poor correlation with RH \(r^2=0.15\).

### 3.4.8 NO\(_2\)

As opposed to ozone and aldehydes, no correlation between the sampling positions (bedroom and living room) was found \(r^2=0.12\), slope 0.28). According to the equations for temperature correction, the sampling rate of NO\(_2\) was most influenced by changes in temperature (Eq. 25 for NO\(_2\) vs. Eq. 24 for ozone).

Though the temperature was logged in the same room as each of the passive samplers, and at an outdoor position, even small differences e.g. due to placement of logger and sampler might influence the calculated NO\(_2\) concentration. Swaans et al. (2007) have investigated the sampling rate of the Radiello passive NO\(_2\) samplers and substantial variations were found.

Similar, no concentration was found between indoor and outdoor NO\(_2\) concentrations \(r^2=0.005\), slope -0.078).

Though the passive samplers are convenient for field sampling, especially for a study involving more homes, the uncertainty of the uptake rate of NO\(_2\) introduces too large uncertainties in the determination of NO\(_2\) concentration, thus the following comparisons must be considered with caution due to the sampling uncertainties.

Some differences were found for the different seasons, but the seasonal variation was not as clear as for some of the other parameters (Figure 71 A). No significant difference was found between the 5 homes \(p=0.07\) for home B & E to \(p=0.66\) for home A & D, Figure 71 B).
Figure 71: Average NO$_2$ concentration. A: Average of all five homes during each season. B: Average of all four seasons for each home. The error bars indicate the standard deviation between each season and home, respectively, and does not include the standard deviation within each measurement.

None of the homes had gas stoves and none of the inhabitants were smoking. One home (Home B) was equipped with a woodstove. It was not the primary heating source, and was only burning during winter. This may be reflected both in the slightly higher concentration during winter (Figure 71 A) and the slightly higher total average of home B (Figure 71 B).

None of the buildings are located close to heavy traffic, and thus the NO$_2$ concentration is expected to be in the lower range for suburban locations. Reported values for indoor NO$_2$ are summarized in Table 22.

Table 22: Reported indoor concentration and I/O ratios of NO$_2$ in homes similar to the homes in this thesis.

<table>
<thead>
<tr>
<th>Type of home</th>
<th>NO$_2$ [µg/m$^3$]</th>
<th>I/O</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copenhagen, suburban (n=5)</td>
<td>3-22</td>
<td>1.5±1.0</td>
<td>This thesis</td>
</tr>
<tr>
<td>England, rural house, electric cooker</td>
<td>10.2</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>England, main road suburban flats, gas stove (n=40)</td>
<td>20.7</td>
<td>0.88</td>
<td>Tan et al., 2013</td>
</tr>
<tr>
<td>Australia</td>
<td>15.8±7.3</td>
<td>0.9±0.4</td>
<td>Molloy et al., 2012</td>
</tr>
<tr>
<td>England, suburban</td>
<td>21.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>England, no fossil fuel cooking (n=354)</td>
<td>7.9</td>
<td></td>
<td>Raw et al., 2004</td>
</tr>
</tbody>
</table>

A study of 876 homes in England reported NO$_2$ indoor concentrations from both rural, suburban, urban and central urban homes as well as homes with natural gas oven, natural gas cooking but no gas oven, and no fossil fuel cooking (Raw et al., 2004). Both the location of the homes and the type of heating and cooking influenced NO$_2$ substantially. Increasing mean concentrations were found when moving closer to the central urban locations (16.1 µg/m$^3$ for rural to 33.1 16.1 µg/m$^3$ for central urban). Similar, increasing concentrations were found in homes with more indoor combustion (11.5 µg/m$^3$ with no fossil cooking to 42.8 µg/m$^3$ with a gas stove). The homes in this thesis can be categorized as suburban with no fossil cooking, thus the concentrations (3-22 µg/m$^3$, total average 8 µg/m$^3$) is consistent with the data obtained by Raw et al. (2004)

No correlations were found between indoor NO$_2$ and any other parameters (AER: $r^2$=0.019; total aldehyde $r^2$=0.006; candles and woodstove $r^2$=0.01; indoor ozone $r^2$=0.033), but this could be caused by the uncertainty in uptake rate.
3.4.9 Sampling of VOCs on Tenax

Due to breakdown of the TD-GC-MS instrument during analysis, a large fraction of the VOC sampled on Tenax was lost, and it was therefore not possible to investigate the seasonal variation. Organic compounds have been identified for the five homes during the fall season, but no quantifications were carried out. A total 85 compounds were identified (Table 23). They are divided into four categories according to the area counts in the chromatograms: Major compounds (Ma), with an area count more than 10% of the largest identified peak in the chromatogram; Minor compounds (Mi) with an area count of 2-10% of the largest peak; compounds in trace amount (T) with an area count of less than 2% of the largest peak; and not detected (n.d.) which are compounds that are identified in at least one home, but where no peak could be found with matching mass spectrum and retention time in the given home.

Aromatics may be overrepresented among the identified compounds, since these often have characteristic peaks, whereas alkanes, acids, and esters often have a high degree of EI fragmentation, resulting only in lower mass fragments, which is not sufficient for identification. A large fraction of the peaks, including major peaks, in the chromatograms could not be identified, thus, besides the identified compounds the samples also contained alkanes, acids and esters of unidentified chain lengths.

The retention time depends both on the interaction with the column material and the boiling point, thus a completely linear correlation between retention time and boiling point cannot be expected, but a large deviation from the trend, indicate a wrong identification. Different isomers, such as the 3C and 4C substituted benzenes were assigned on basis of both mass spectra and boiling points.

A number of the identified compounds are found in essential oils, and thus often used in flavors and fragrances in common household products. These include:

- Limonene and three not further identified monoterpenes; common in a number of household products (Rastogi et al., 2001). Aside from the lemon scent in many household products, limonene is the main compound in the headspace of earl grey tea (Wolkoff, 1990).
- 2-Pentylfuran; a major flavor compound in poppy seed (Hui and Yiu, 2005).
- p-Cymene; related to monoterpenes and found mainly in cumin (Li and Jiang, 2004) and thyme (Grigore et al., 2010).
- Benzaldehyde; the fragrance of almond (Scoot and Scott, 1922) and a product of the oxidation of polystyrene products.
- Benzyl alcohol; found in jasmine, hyacinth and ylang-ylang among others and used as a solvent for paints, lacquers and epoxy resin coatings (Merck, 1989).
- (+)-Menthone; mainly found in peppermint; (Schmidt et al., 2009).
- Benzyl acetate; found in jasmine and ylang-ylang and used widely in cosmetics (The Good Scents Company, 2012).
- Menthofuran; found in pennyroyal (Anderson et al., 1996).
- Anethole; found in anise, fennel, licorice and basil among others; (Ashurst, 1999)
- Vanillin; found in vanilla and used as synthetic vanilla (Gobley, 1858) and common as a fragrance in a number of personal care products (Rastogi et al., 2001).
- Phenylethyl alcohol; widely occurring in nature in essential oils of rose, hyacinth, orange blossom, ylang ylang among others.
- E-2-Hexenyl benzoate; e.g. found in aroma extracts from tea (Kawakami et al., 1995)

Other compounds which have known indoor sources include:

- Styrene and xylenes; used in the production of various types of plastic used as food containers and carpet backing. Styrene may be a source for benzaldehyde.
- p-Cresol; a component of human sweat (Fiege, 2000) and in coal tar (Fardyanti et al., 2013).
- Benzothiazole; a degradation product from rubber accelerants.
- 2-Phenoxyethanol; often used in dermatological products such as skin creams and sunscreen (De Paepe et al., 2000).
- o-Hydroxybiphenyl; an insecticide used for waxing of citrus fruits (Farrow et al., 1977).
- N-methyl-2-pyrrolidone; a common solvent in paints (BASF, 2007).

Some of the aromatic identified compounds are combustion products and are thus commonly found in urban air. These compounds include the C_3 and C_4 substituted benzenes, naphthalene, methylnaphthalene and benzo[b]thiophene; found in tar.

Phenylmaleic anhydride is a known degradation products of Tenax TA in the presence of ozone (Klenø et al., 2002); thus, probably an analytical artifact.

The compounds containing at least one non-aromatic C-C double bond, which are thus expected to be reactive to ozone, are marked (*) in Table 23.
Table 23: Tentatively Identified VOCs from Tenax air samples in the five homes during fall.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M</th>
<th>b.p. (litt) [°C]</th>
<th>CAS</th>
<th>Rt  [min]</th>
<th>Rfit</th>
<th>Home</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/p-Xylene</td>
<td>106</td>
<td>138 H</td>
<td>a</td>
<td>4.3</td>
<td>963</td>
<td>Ma</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>106</td>
<td>144 95-47-6</td>
<td>4.9</td>
<td>962</td>
<td>n.d.</td>
<td>Mi</td>
</tr>
<tr>
<td>Styrene*</td>
<td>104</td>
<td>145 100-42-5</td>
<td>5.1</td>
<td>968</td>
<td>Mi</td>
<td>T</td>
</tr>
<tr>
<td>Furfural</td>
<td>96</td>
<td>162 98-01-1</td>
<td>5.5</td>
<td>721</td>
<td>Ma</td>
<td>Ma</td>
</tr>
<tr>
<td>Cumene</td>
<td>120</td>
<td>152 98-82-8</td>
<td>5.6</td>
<td>989</td>
<td>T</td>
<td>n.d.</td>
</tr>
<tr>
<td>Heptanal</td>
<td>114</td>
<td>153 111-71-7</td>
<td>6</td>
<td>752</td>
<td>Ma</td>
<td>Ma</td>
</tr>
<tr>
<td>Propylbenzene</td>
<td>120</td>
<td>159 103-65-1</td>
<td>6.3</td>
<td>998</td>
<td>Mi</td>
<td>T</td>
</tr>
<tr>
<td>1-Ethyl-4-methylbenzene</td>
<td>120</td>
<td>162 622-96-8</td>
<td>6.7</td>
<td>984</td>
<td>Mi</td>
<td>T</td>
</tr>
<tr>
<td>Monoterpane*</td>
<td>136</td>
<td>a</td>
<td>a</td>
<td>7.1</td>
<td>741</td>
<td>Ma</td>
</tr>
<tr>
<td>1-Ethyl-2-methylbenzene</td>
<td>120</td>
<td>164 611-14-3</td>
<td>7.2</td>
<td>991</td>
<td>Ma</td>
<td>n.d.</td>
</tr>
<tr>
<td>2-Pentyl furan</td>
<td>138</td>
<td>155 3777-69-3</td>
<td>7.3</td>
<td>962</td>
<td>Ma</td>
<td>Ma</td>
</tr>
<tr>
<td>Butylcyclohexane</td>
<td>140</td>
<td>179 1678-93-9</td>
<td>7.3</td>
<td>947</td>
<td>Mi</td>
<td>T</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>120</td>
<td>164 108-67-8</td>
<td>7.5</td>
<td>995</td>
<td>Ma</td>
<td>n.d.</td>
</tr>
<tr>
<td>(1-Methylpropyl)-benzene</td>
<td>134</td>
<td>173 135-98-8</td>
<td>7.7</td>
<td>860</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Limonene*</td>
<td>136</td>
<td>176 138-86-3</td>
<td>7.9</td>
<td>686</td>
<td>Mi</td>
<td></td>
</tr>
<tr>
<td>m-Menth-6-ene*</td>
<td>138</td>
<td>NA 13837-70-2</td>
<td>8</td>
<td>736</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>m-Cymene</td>
<td>134</td>
<td>175 535-77-3</td>
<td>8.3</td>
<td>993</td>
<td>Ma</td>
<td></td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>106</td>
<td>178 100-52-7</td>
<td>8.5</td>
<td>930</td>
<td>Ma</td>
<td></td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene</td>
<td>120</td>
<td>176 526-73-8</td>
<td>8.5</td>
<td>837</td>
<td>Ma</td>
<td></td>
</tr>
<tr>
<td>Monoterpane*</td>
<td>136</td>
<td>a</td>
<td>a</td>
<td>8.7</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>1-Methyl-3-prop benzene</td>
<td>134</td>
<td>181 1074-55-1</td>
<td>9.1</td>
<td>972</td>
<td>Ma</td>
<td></td>
</tr>
<tr>
<td>Monoterpane*</td>
<td>136</td>
<td>a</td>
<td>a</td>
<td>9.6</td>
<td>880</td>
<td>T</td>
</tr>
<tr>
<td>Methylpropiophenol</td>
<td>134</td>
<td>184 a</td>
<td>9.7</td>
<td>947</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>C4-substituted benzene</td>
<td>134</td>
<td>a</td>
<td>a</td>
<td>10</td>
<td>997</td>
<td>Mi</td>
</tr>
<tr>
<td>C4-substituted benzene</td>
<td>134</td>
<td>a</td>
<td>a</td>
<td>10.2</td>
<td>984</td>
<td>T</td>
</tr>
<tr>
<td>Ethynylidimethyl benzene*</td>
<td>132</td>
<td>a</td>
<td>a</td>
<td>10.6</td>
<td>797</td>
<td>T</td>
</tr>
<tr>
<td>1,3-Benzodioxole</td>
<td>122</td>
<td>172 274-09-9</td>
<td>10.9</td>
<td>908</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>3-Chloro-2,4-pentanedione</td>
<td>134</td>
<td>173 1694-29-7</td>
<td>10.9</td>
<td>841</td>
<td>Mi</td>
<td></td>
</tr>
<tr>
<td>Ethyldimethylbenzene</td>
<td>134</td>
<td>a</td>
<td>a</td>
<td>10.9</td>
<td>945</td>
<td>Mi</td>
</tr>
<tr>
<td>p-Isopropenylphenol</td>
<td>134</td>
<td>218 4286-23-1</td>
<td>11.3</td>
<td>642</td>
<td>Mi</td>
<td></td>
</tr>
<tr>
<td>Tetramethylbenzene</td>
<td>134</td>
<td>a</td>
<td>a</td>
<td>11.3</td>
<td>954</td>
<td>T</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>120</td>
<td>202 98-86-2</td>
<td>12</td>
<td>951</td>
<td>Mi</td>
<td></td>
</tr>
<tr>
<td>Ethynylidimethyl benzene*</td>
<td>132</td>
<td>a</td>
<td>a</td>
<td>12.2</td>
<td>970</td>
<td>T</td>
</tr>
<tr>
<td>1,2,3,4-Tetramethylbenzene</td>
<td>134</td>
<td>204 488-23-3</td>
<td>12.2</td>
<td>Mi</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Benzylalcohol</td>
<td>108</td>
<td>205 100-51-6</td>
<td>12.5</td>
<td>786</td>
<td>Mi</td>
<td></td>
</tr>
<tr>
<td>1-Indanone</td>
<td>132</td>
<td>244 83-33-0</td>
<td>12.6</td>
<td>914</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>Methylbutylbenzene</td>
<td>148</td>
<td>a</td>
<td>a</td>
<td>12.6</td>
<td>932</td>
<td>Mi</td>
</tr>
<tr>
<td>4-Methylpyridazine</td>
<td>94</td>
<td>227 1120-88-3</td>
<td>12.8</td>
<td>737</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>1,1'-methylenebispyrrolidine</td>
<td>154</td>
<td>204 7309-47-9</td>
<td>13</td>
<td>937</td>
<td>Ma</td>
<td></td>
</tr>
<tr>
<td>(+)-Menthone</td>
<td>154</td>
<td>209 3391-87-5</td>
<td>13.5</td>
<td>726</td>
<td>Ma</td>
<td></td>
</tr>
<tr>
<td>p-Cresol</td>
<td>194</td>
<td>220 93-51-6</td>
<td>13.6</td>
<td>696</td>
<td>n.d.</td>
<td></td>
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<tr>
<td>Valeric anhydride</td>
<td>186</td>
<td>229 2082-59-9</td>
<td>13.7</td>
<td>892</td>
<td>Mi</td>
<td></td>
</tr>
<tr>
<td>5,6-Dimethyl-3(2H)-benzofuranone</td>
<td>162</td>
<td>162 20895-43-6</td>
<td>13.7</td>
<td>800</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>N-Methyl-2-pyrrolidinone</td>
<td>99</td>
<td>203 872-50-4</td>
<td>13.8</td>
<td>879</td>
<td>Ma</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>128</td>
<td>218 91-20-3</td>
<td>14.1</td>
<td>992</td>
<td>Mi</td>
<td></td>
</tr>
<tr>
<td>1-Methylenep-1H-indene*</td>
<td>128</td>
<td>216 2471-84-3</td>
<td>14.3</td>
<td>783</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>Benzyl acetate</td>
<td>150</td>
<td>212 140-11-4</td>
<td>14.4</td>
<td>866</td>
<td>Mi</td>
<td></td>
</tr>
<tr>
<td>Menthofuran</td>
<td>150</td>
<td>196 494-90-6</td>
<td>14.4</td>
<td>820</td>
<td>Mi</td>
<td></td>
</tr>
<tr>
<td>Henetyl alcohol</td>
<td>122</td>
<td>220 60-12-8</td>
<td>14.6</td>
<td>932</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>Benzo[b]thiophene*</td>
<td>134</td>
<td>220 95-15-8</td>
<td>14.6</td>
<td>992</td>
<td>Mi</td>
<td></td>
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<tr>
<td>2-Ethyl-2,3-dihydro-1-H-indene</td>
<td>146</td>
<td>NA 56147-63-8</td>
<td>14.7</td>
<td>851</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>4-[1-Methylpropyl]-2,3-dihydrofuran*</td>
<td>126</td>
<td>NA 34379-54-9</td>
<td>14.8</td>
<td>972</td>
<td>n.d.</td>
<td>Ma</td>
</tr>
<tr>
<td>Methylphenylethanone</td>
<td>134</td>
<td>226 a</td>
<td>15.4</td>
<td>964</td>
<td>T</td>
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</tbody>
</table>

Continues...
The primary source was indoor and that the air quality with regard to aldehydes could be improved by sampling for assessment of the indoor air quality. Seasonal variations were found for several parameters (temperature, air exchange rates, particles conditions. Thus indicating that each 5 week measurement campaign fell well into periods of similar climate substantial. The standard deviation of the outdoor temperature for the five homes within each season was 4 °C, indicating that each 5 week measurement campaign fell well into periods of similar climate conditions.

Phthalate (possible butyl decyl phthlate) a a 32 929 Ma Ma Ma Ma
Phthalate a a 33.4 Ma T T T T
E-2-Hexenyl benzoate* 204 298 76841-70-8 33.7 921 n.d. T Mi n.d. T
3-Isopropylbenzophenone 224 NA 32388-73-1 35.1 832 n.d. T n.d. n.d. Mi
2-(Benzoyloxy)-1-phenyl-ethanone 240 NA 33868-50-7 35.5 989 n.d. n.d. n.d. T Mi

Continued

<table>
<thead>
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<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzothiazole</td>
<td>135</td>
<td>227</td>
<td>95-16-9</td>
<td>16.1</td>
<td>916</td>
</tr>
<tr>
<td>2,6-Heptanedione</td>
<td>128</td>
<td>213</td>
<td>13505-34-5</td>
<td>16.7</td>
<td>948</td>
</tr>
<tr>
<td>2-Methyl-2-cyclohexen-1-one*</td>
<td>110</td>
<td>181</td>
<td>1121-18-2</td>
<td>16.9</td>
<td>783</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>142</td>
<td>241</td>
<td>91-57-6</td>
<td>17.2</td>
<td>982</td>
</tr>
<tr>
<td>1-Methylnaphthalene</td>
<td>142</td>
<td>242</td>
<td>90-12-0</td>
<td>17.4</td>
<td>973</td>
</tr>
<tr>
<td>Anethole*</td>
<td>148</td>
<td>234</td>
<td>104-46-1</td>
<td>17.4</td>
<td>927</td>
</tr>
<tr>
<td>2-Phenoxyethanol</td>
<td>138</td>
<td>247</td>
<td>122-99-6</td>
<td>17.8</td>
<td>778</td>
</tr>
<tr>
<td>2-Hydroxy-4-methylbenzaldehyde</td>
<td>136</td>
<td>220</td>
<td>698-27-1</td>
<td>18.1</td>
<td>971</td>
</tr>
<tr>
<td>2-Methylnifuran</td>
<td>132</td>
<td>197</td>
<td>4265-25-2</td>
<td>18.5</td>
<td>932</td>
</tr>
<tr>
<td>1-Vinylphthalene</td>
<td>154</td>
<td>137</td>
<td>827-54-3</td>
<td>19.4</td>
<td>934</td>
</tr>
<tr>
<td>Hexyl-2-methylpropanoate</td>
<td>172</td>
<td>199</td>
<td>2349-07-7</td>
<td>20.5</td>
<td>938</td>
</tr>
<tr>
<td>Tertbutylphenol</td>
<td>150</td>
<td>a</td>
<td>a</td>
<td>21.4</td>
<td>779</td>
</tr>
<tr>
<td>3-Oxo-4-phenylbutyronitrile</td>
<td>159</td>
<td>NA</td>
<td>19212-27-2</td>
<td>21.5</td>
<td>830</td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td>168</td>
<td>285</td>
<td>132-64-9</td>
<td>23.3</td>
<td>911</td>
</tr>
<tr>
<td>Vanillin</td>
<td>152</td>
<td>285</td>
<td>121-33-5</td>
<td>23.4</td>
<td>908</td>
</tr>
<tr>
<td>Dimethyl phthalate</td>
<td>194</td>
<td>283</td>
<td>131-11-3</td>
<td>23.6</td>
<td>944</td>
</tr>
<tr>
<td>1,2-Dibutoxy-1-ethoxyethane</td>
<td>246</td>
<td>NA</td>
<td>13264-32-9</td>
<td>24.8</td>
<td>983</td>
</tr>
<tr>
<td>Dodecanoic acid, 1-methylethyl ester</td>
<td>242</td>
<td>281</td>
<td>10233-13-3</td>
<td>24.9</td>
<td>786</td>
</tr>
<tr>
<td>o-Hydroxybiphenyl</td>
<td>170</td>
<td>282</td>
<td>90-43-7</td>
<td>25.1</td>
<td>796</td>
</tr>
<tr>
<td>Diethyl phthalate</td>
<td>222</td>
<td>295</td>
<td>84-66-2</td>
<td>26.8</td>
<td>992</td>
</tr>
<tr>
<td>n-Hexyl salicylate</td>
<td>222</td>
<td>290</td>
<td>6259-76-3</td>
<td>26.8</td>
<td>938</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>182</td>
<td>305</td>
<td>119-61-9</td>
<td>27.9</td>
<td>957</td>
</tr>
<tr>
<td>Phenylmaleic anhydride</td>
<td>174</td>
<td>NA</td>
<td>36122-35-7</td>
<td>27.2</td>
<td>934</td>
</tr>
<tr>
<td>Diisobutyl hexanedioate</td>
<td>258</td>
<td>281</td>
<td>141-04-8</td>
<td>27.7</td>
<td>605</td>
</tr>
<tr>
<td>(1-Hydroxy cyclohexyl)phenyl methane</td>
<td>204</td>
<td>NA</td>
<td>947-19-3</td>
<td>28.8</td>
<td>943</td>
</tr>
<tr>
<td>2-Sec-butyl-1-phenyl-1,3-butanedione</td>
<td>218</td>
<td>NA</td>
<td>10225-40-8</td>
<td>30.1</td>
<td>879</td>
</tr>
<tr>
<td>N-butyl benzenesulfonamide</td>
<td>213</td>
<td>314</td>
<td>3622-84-2</td>
<td>33.3</td>
<td>958</td>
</tr>
<tr>
<td>E-2-Hexenyl benzoate*</td>
<td>204</td>
<td>298</td>
<td>76841-70-8</td>
<td>33.7</td>
<td>921</td>
</tr>
<tr>
<td>3-Isopropylbenzophenone</td>
<td>224</td>
<td>NA</td>
<td>32388-73-1</td>
<td>35.1</td>
<td>832</td>
</tr>
<tr>
<td>2-(Benzoyloxy)-1-phenyl-ethanone</td>
<td>240</td>
<td>NA</td>
<td>33868-50-7</td>
<td>35.5</td>
<td>989</td>
</tr>
</tbody>
</table>

a: More than one possible isomer, which cannot be distinguished by MS or the boiling point, thus neither boiling point or CAS is given. * Marks compounds containing at least one C-C double bond that is expected to be reactive to ozone. Abbreviations: Ma: Major compound; Mi: Minor compound, T: Compound in trace amount; n.d.: Not detected. See text for definitions.

The wide range of compounds found in the different homes shows how complex our indoor chemical climate is, and that the difference between what is present in different homes is substantial.

### 3.5 Conclusions

The standard deviation of the outdoor temperature for the five homes within each season was 4 °C, thus indicating that each 5 week measurement campaign fell well into periods of similar climate conditions.

Seasonal variations were found for several parameters (temperature, air exchange rates, particles 0.75-15 μm, ozone, and aldehydes), and it is thus important to take the season into account in sampling for assessment of the indoor air quality.

AER was found to correlate with the indoor concentration of aldehydes, thus indicating that the primary source was indoor and that the air quality with regard to aldehydes could be improved by
adequate ventilation. It seemed that removal of aldehydes was not improved substantially by raising AER to more than 2 h\(^{-1}\).

For ozone, where the major source is infiltration of outdoor air, a correlation with AER was expected, but not found. The seasonal patterns for AER and ozone were similar, but the factors influencing the indoor concentration of ozone are more complex and involves removal through both heterogeneously breakdown on surfaces and reaction with chemicals. Especially the correlation with reactive VOCs, which have not been investigated, could be interesting. The aldehydes, which are known reaction products from ozonolysis, had a negative correlation with indoor ozone, but a positive correlation with outdoor ozone, indicating that the measured indoor ozone is more representative for what is left after chemical reactions, rather than for what is available.

A good correlation was found between sampling positions within each home (bedroom and living room) for ozone and aldehydes, thus indicating both a good mixing of these compounds within the home and an acceptable reproducibility of the passive samplers. This appeared not to be the case for NO\(_2\), and thus passive samples can only be recommended for ozone and aldehydes, while for use of passive NO\(_2\) samplers, great caution should be taken. However NO\(_2\) levels were found to be in accordance with the expected levels for this type and location of homes, thus passive samplers might still be useful for evaluation of high vs. low concentrations, e.g. in rural vs. urban homes.

Home B had renovations and painting performed between the sampling periods and was equipped with a woodstove, which was used during winter, still the only parameter where this could be observed was on the NO\(_2\) levels, and here the concentrations were not substantially higher than in the homes without in indoor combustion source.

Some correlations as well as seasonal variation were found for several parameters. Though these correlations could be used to understand some of the dynamics within the homes, the correlations were not strong enough, and the statistical material was not large enough, to predict the analytical more difficult parameters from the easier obtainable.

A total of 85 VOCs, including a wide range of fragrance compounds were identified in the five homes during the fall season.

### 3.6 Perspectives

If correlation with user behavior is a priority, the diaries must contain more detailed information about events such as cooking, combustion, cleaning etc., but evaluation with the inhabitants revealed that they found it difficult enough to fill out the diaries in the present form and to remember all details. Request for more information would thus probably just result in poorer quality of the reported data. A solution, though tedious, could be to utilize some kind of automated monitoring of inhabitants, such as video or motion sensors.

Two major concerns in planning the field sampling campaign were not to scare the participants away, and to find equipment that was available through the whole year. Both considerations put a limit on the number of samples that could be obtained, since each extra air sample required one more pump and bulky isolation for noise reduction. When I look back at the results the single
determination of each sample is a major weakness and at least one sampling campaign with double or triple sampling to investigate the variability of the samples would have strengthened the data. Especially for the VOC sampling on Tenax it proved to be a major weakness with only one sample, since the tubes could only be thermally desorbed once, and when the analysis was lost.
4 Section IIb: Low Temperature Plasma ionization-MS on filter samples

4.1 Introduction

Teflon air sampling filters (PM$_{2.5}$) from the CISBO sampling campaign (Section IIa) was analyzed by Low Temperature Plasma Ionization q-TOF Mass Spectrometry (LTP-MS), which led to a general investigation of the quantitative properties, advantages and challenges for this non-chromatographic ambient mass spectrometric technique.

Some of this work is presented in Paper II (draft), which are summarized in the following along with additional results not included in the paper.

This section is an exploratory investigation of the concept of LTP-MS quantification, and should not be considered as a finished analytical method. Several assumptions had to be made, and the validity of these as well as ways to improve the method are discussed.

4.1.1 Phthalates in Mass Spectrometry

The challenges of interference between different ions of phthalates are briefly discussed in paper II, and discussed further in this section.

A mixture of dimethylphthalate (DMP), diethyl phthalate (DEP), dibutylphthalate (DBP), butylbenzyl phthalate (BBP) and diethylhexylphthalate (DEHP) was used to evaluate the quantitative properties of LTP-MS. The challenge with this approach without prior separation was that the resulting mass spectra consist of a mixture of protonated molecular ions and their fragments ions for all 5 compounds.

GC-MS with electron ionization (EI) is commonly used for analysis of phthalates. With EI a high degree of fragmentation occurs and the molecular ions ([M]+) are only minor peaks in the mass spectrum. For most phthalates the phthalic anhydride ion (C$_8$H$_5$O$_3$) at m/z 149 is the base peak.

The relative intensities of the most dominant ions from DEHP in EI-MS and LTP-MS are given in Table 24, with [M]+ (m/z 390) given for EI and [M+H]+ (m/z 391) for LTP. From this it is clear, that LTP is a softer ionization technique with less fragmentation than EI.

<table>
<thead>
<tr>
<th>m/z</th>
<th>113</th>
<th>149</th>
<th>167</th>
<th>239</th>
<th>279</th>
<th>390</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative intensity in EI-MS</td>
<td>16</td>
<td>100</td>
<td>50</td>
<td>0</td>
<td>32</td>
<td>1</td>
</tr>
<tr>
<td>Relative intensity in LTP-MS</td>
<td>40</td>
<td>100</td>
<td>78</td>
<td>18</td>
<td>27</td>
<td>14a</td>
</tr>
</tbody>
</table>

a: For LTP-MS the value for [M+H]+ at m/z 391 is reported.

The relative intensities of [M]+ in EI-MS according to the NIST database (NIST, 2011) are given in Table 25 along with the relative intensity of [M+H]+ found in the 5-phthalate mixture used for quantification on the filters. From this is can be seen that the protonated molecular ions in LTP-MS are more dominant than the molecular ions in EI-MS.
Table 25: Relative intensities of [M]$^+$ in EI-MS according to the NIST database (NIST, 2011) and of [M+H]$^+$ in LTP of the mixture of phthalates.

<table>
<thead>
<tr>
<th></th>
<th>DMP</th>
<th>DEP</th>
<th>DBP</th>
<th>BBP</th>
<th>DEHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular mass (M)</td>
<td>194</td>
<td>222</td>
<td>278</td>
<td>312</td>
<td>390</td>
</tr>
<tr>
<td>Relative intensity of [M]$^+$ (EI)</td>
<td>6.3</td>
<td>1.5</td>
<td>0.4</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Relative intensity of [M+H]$^+$ (LTP)</td>
<td>8</td>
<td>9</td>
<td>28</td>
<td>11</td>
<td>9</td>
</tr>
</tbody>
</table>

The [M+H]$^+$ ion in LTP-MS could be suitable for quantification, but several of the fragment ions are more intense. To find the best quantifier ion for each phthalate in the mixture, it is important to evaluate the fragmentation pattern of the individual compounds to avoid interference between different compounds with the same fragment ions.

A proposed fragmentation mechanism for DEHP in MALDI-MS is given in Figure 72 (Keki et al., 2003). Though it is not the same ionization technique, LTP and MALDI both are considered soft ionization techniques, and the fragments in Figure 72 are consistent with the fragments seen in LTP-MS. Assuming that the four other phthalates follows the same fragmentation patterns, proposed fragmentation schemes are shown in Figure 73, which is consistent with the observed fragments.

---

**Figure 72:** Proposed fragmentation pattern of DEHP determined from LTP-MS of m/z 391 and m/z 279. Relative intensities are given for the analysis of a solution containing only DEHP (single) and a mixture containing 5 phthalates including DEHP.
A summary of the expected ions in LTP-MS of the five phthalates are given in Table 26. From this table, characteristic ions for each phthalate was selected as quantifier ions. The following ions were selected: m/z 391 for DEHP, 313 for BBP; 177 for DEP, and 163 for DMP. No characteristic ion was found for DBP.
Table 26: Summary of relative intensities and contributions of fragment and protonated molecular ions [M+H]+ in LTP-MS of 5 compound phthalate mixture (DMP, DEP, DBP, BBP and DEHP in equal amounts). Marking in bold indicate [M+H]+.

<table>
<thead>
<tr>
<th>m/z</th>
<th>391</th>
<th>313</th>
<th>279</th>
<th>239</th>
<th>223</th>
<th>205</th>
<th>195</th>
<th>177</th>
<th>163</th>
<th>149</th>
<th>91</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative intensity in LTP-MS of phthalate mixture [%]</td>
<td>9</td>
<td>11</td>
<td>28</td>
<td>14</td>
<td>9</td>
<td>100</td>
<td>8</td>
<td>36</td>
<td>20</td>
<td>89</td>
<td>8</td>
</tr>
<tr>
<td>DMP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>DEP</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>DBP</td>
<td></td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BBP</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEHP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: Theoretical possible fragment, but only found in very low abundance.

4.2 Summary of paper II - Direct quantitative analysis of PAHs, phthalates and fatty acids on Teflon filters using Low Temperature Plasma ionization MS

The following section will summarize as well as elaborate on the interpretation of the data presented in Paper II.

Low Temperature Plasma ionization (LTP) is a relatively new ionization technique, which has been used in a range of different applications such as rapid screening of pharmaceuticals (Liu et al., 2009), real-time monitoring of on-going chemical reactions in solution (Ma et al., 2009), on a surface (Nørgaard et al., 2013b), direct analysis of free fatty acids and phenolics in olive oil (Garcia-Reyes et al., 2009), drugs of abuse in biofluids (Jackson et al., 2010), explosives (Garcia-Reyes et al., 2010; Chen et al., 2013; Yang et al., 2012; Dalgleish et al., 2012), formations of coatings (Nørgaard et al., 2011; Xu et al., 2013), crude oil (Benassi et al., 2013), degradation of lithium ion batteries (Vortmann et al., 2013), on-line detection of indoor volatile organic compounds (VOCs) (Gong et al., 2011), structural elucidation of unsaturated fatty acids and esters (Zhang et al., 2011) and for imaging (Wu et al., 2013). Most of these studies focus mainly on the qualitative detection or on-line monitoring of selected compounds, and the quantitative properties and challenges of the method is not yet fully investigated.

Paper II presents the investigation of the quantitative properties of LTP-MS utilized on PM$_{2.5}$ filters sampled in Danish homes. Fatty acids and phthalates dominated the LTP-MS spectra of the samples. Standard solutions of these compounds were used for the quantitative evaluation. A mixture of polycyclic aromatic hydrocarbons (PAHs) was also evaluated for future use of this method to outdoor air samples, were these compounds are prominent. The experimental details are described in Paper II.

The advantage of the LTP-MS is the direct non-destructive analysis of a surface without prior sample preparation. However, one of the major drawbacks with this direct method is the lack of separation that results in interference, especially for the phthalates as described in section 4.1.
The PAHs were analyzed simultaneously as a mixture of 16 different PAHs, whereas the five phthalates and the five free fatty acids were analyzed both as a mixture and one compound as an individual compound for each type (DEHP and palmitic acid). The analysis of mixtures and individual compounds were performed to evaluate the matrix effect of the method. Structures and boiling points of the investigated compounds are given in App. D.

The results from the investigation of the quantitative properties are summarized in Table 27. From these it was concluded that LTP-MS can be used for semi-quantitative analysis, but the linearity was limited with a dynamic range of about 1-2 decades for the mixtures and up to 3 decades for the individual compounds. The major limitation of the dynamic range was saturation of the detector, especially for the mixtures with several compounds. The method could be more suited for fast screenings of high vs. low concentration. Linear dynamic ranges of 3-4 orders of magnitude for LTP-MS on an ion trap for explosives in favourable cases has been reported (Harper et al., 2008), this is comparable to the ranges obtained for individual compounds, but more than for the investigated mixtures.

Free fatty acids have been quantified directly from olive oil via spiked samples (Garcia-Reyes et al., 2009). Neither linear dynamic range nor LOQ were reported, but the calibration curve is given from 0.5-2% free fatty acid in the olive oil, which is a smaller range than the quantification ranges reported in Paper II. No problems with saturation was reported, but this could be explained by the relative narrow concentration range, and the fact that only one compound was spiked at the time, thus the spiked samples could be expected to behave like the palmitic acid in Paper II, though other free fatty acids were also present in smaller amounts. A similar study for analysis of melamine in milk reported linear ranges of about 2 decades (Huang et al., 2009).

Both LOQ and the maximum concentration before saturation were better for palmitic acid and DEHP analyzed as individual compounds compared to in the mixtures. A comparison of the calibration curves indicated saturation of the MS detector for both individual compound and mixture (see Figure 75).

![Figure 74: Comparison of LTP-MS calibration curve for palmitic acid analyzed as an individual compound and as a part of the 5-compound free fatty acid mixture.](image-url)
LTP-MS has been reported as a convenient method for preparation-free analysis of complex biological samples, such as drug tablets, nicotine in smokeless tobacco, insecticide in deceased canine stomach and caffeine in human urine (Harper et al., 2008). In most of these cases the only compounds to ionize efficiently were the analyte ions, thus the usually problematic salts and matrix interferences were not active in LTP or were suppressed by the analyte ions. This situation is different from the one described in this thesis, where several compounds have similar ionization efficiency, and are thus competing.

4.2.1 Dependence of boiling point on response factor

For the PAHs an interesting dependence between the molecular mass and the response factor was observed. The response factor was at a maximum for fluoranthene and pyrene at m/z 203 (b.p. 375°C and 404°C) as shown in Figure 76. A further investigation into the ion traces of the different ions during the sampling period (response versus time; Figure 77), showed that the ion trace for the PAHs with molecular mass below 203 peaked within short time of the introduction of the sample filter to the LTP, whereas the ion traces of the PAHs with molecular mass above 203 only increased slowly throughout the analysis time. This effect can be explained by the boiling points and vapor pressure of the different PAHs. For the lower molecular masses, the elevated temperature (ca. 80°C)
in the LTP sampling region, caused the PAHs to evaporate and thus become exhausted from the surface of the filter, whereas PAHs with higher molecular mass evaporate much slower at that temperature. A similar dependence was observed for the fatty acids, whereas the comparison was not applicable for the phthalates, since both fragment and protonated molecular ions with different stabilities were analyzed.

![Figure 75: Dependence between molecular mass of PAH and response factor.](image)

It was thus concluded that efficient ionization requires the analyte to be in the gas phase. It is thus likely that the ionization process mainly occurs in the gas phase for the compounds investigated in this thesis. Efficient LTP ionization of non-volatile compounds has previously been reported for organo-functionalized silanes (Nørgaard et al., 2011).

### 4.2.2 LTP-MS of residential Teflon filters

The LTP-MS method was applied to Teflon filters from the sampling campaign (section IIa). The spectra of unexposed filters used for background subtraction are given in Figure 78 (negative ion mode) and Figure 79 (positive ion mode). Ions from both free fatty acids ($m/z$ 199 and 255) and phthalates ($m/z$ 149) were prominent in the background. But as shown in Figure 80 a substantial
increase in signal was observed for these ions when the blank filter was replaced with a sample filter (at 0.5 min).

Figure 77: Background LTP-MS of unexposed Teflon filter in negative mode

Figure 78: Background LTP-MS of unexposed Teflon filter in positive mode

Figure 79: Comparison of background and sample signal. A: negative ion mode, TIC and EIC at \( m/z \) 255; B: Positive ion mode, TIC and EIC at \( m/z \) 149.
Typical background corrected mass spectra of residential Teflon filters are given in Figure 81 (negative ion mode) and Figure 82 (positive ion mode). In negative mode, the dominating ions can be assigned to [M-H]- ions of free fatty acids (m/z 255 from palmitic acid; 283 from stearic acid; 297 from nonadecanoic acid). Since the most naturally occurring free fatty acids contain an even number of carbon atoms (Haslam and Kunst, 2013), it is surprising to find nonadecanoic acid in substantial amounts. Other studies have however reported natural sources such as human breath (Baranska et al., 2013), cooked ham (Barba et al., 2013), honey (Bianchi et al, 2011), and red wine (Lee et al., 2011).

In positive mode the, the dominating ions can be assigned to phthalates and free fatty acids (m/z 113 from [M+H]+ of BBP; 149 from phthalate fragment; 167 from fragment of DEP; 227 from [M+H]+ of myristic acid; 257 from [M+H]+ of palmitic acid; 279 from [M+H]+ of DBP or fragment of DEHP; and 391 from [M+H]+ of DEHP).

The LTP-MS quantifications of free fatty acids and phthalates on 40 Teflon filter samples are summarized in Table 28. A compound is considered detected if the ratio of the quantifier ion on the sample filter and on the blank filter is above 3 (S/N>3), and can be quantified if the concentration is within the dynamic linear range (Table 27). The concentration range is rounded to the nearest 100 for clarity. To evaluate the homogeneity of the distribution of sampled compounds on the filters, the average standard deviation between the sample spots on the same filter was determined for m/z
149 in positive mode (16%) and for m/z 255 in negative mode (18%). This indicates that the point of sampling causes some variation of the signal, but that the signals measured at different points are comparable.

Table 28: Summary of results for 40 air samples of free fatty acids and phthalates determined with LTP-MS on Teflon filters.

<table>
<thead>
<tr>
<th></th>
<th>n detected (S/N&gt;3) [%]</th>
<th>n (C&gt;LOQ) [%]</th>
<th>n quantified (max C&gt;C&gt;LOQ) [%]</th>
<th>Concentration [ng/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric acid</td>
<td>60</td>
<td>25</td>
<td>25</td>
<td>330-2000</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>80</td>
<td>45</td>
<td>45</td>
<td>320-9500</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>93</td>
<td>88</td>
<td>70</td>
<td>970-7500</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>75</td>
<td>58</td>
<td>53</td>
<td>550-12000</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>85</td>
<td>83</td>
<td>83</td>
<td>536-34000</td>
</tr>
<tr>
<td>DMP</td>
<td>75</td>
<td>15</td>
<td>15</td>
<td>37-140</td>
</tr>
<tr>
<td>DEP</td>
<td>88</td>
<td>43</td>
<td>43</td>
<td>33-589</td>
</tr>
<tr>
<td>BBP</td>
<td>95</td>
<td>48</td>
<td>48</td>
<td>8-550</td>
</tr>
<tr>
<td>DEHP</td>
<td>95</td>
<td>28</td>
<td>28</td>
<td>32-780</td>
</tr>
</tbody>
</table>

The phthalate concentrations within the dynamic linear range are summarized in Figure 83. None of the filters were above the linear range for any of the phthalates. DEHP, which is the phthalate with the highest boiling point, was almost exclusively found in the samples collected during summer, which could be explained by higher release due to higher air and surface temperatures. BBP was most prominent during winter, were the air exchange rates were generally lower as described in section 3.4.3. The statistical material and certainty of the quantification is not sufficient to determine the source of the phthalates further.

Figure 82: Phthalates above LOQ determined by LTP-MS on residential Teflon filters. Season, home and room is indicated for each sample.
Indoor air concentration of phthalates collected on aminopropyl silica adsorbent in Swedish apartments (Bergh et al., 2011), on XAD-2 in homes in Cape Cod, US (Rudel et al., 2003), on XAD-2 (gas) and glass fiber filter (particles) in newly decorated Chinese apartments (Pei et al., 2013) have been reported, Table 29. The phthalate concentrations determined on residential Teflon filters in the present study are comparable to those found in the Swedish apartments, but lower than those found in American homes. Sampling on Teflon filters will only collect compounds adsorbed to particles in the air, thus the concentrations determined by this method is expected to be lower than those obtained by sampling on an adsorbent, which collects both gas phase and particle-bound compounds. This effect can be seen in the gas vs. particle data from the Chinese apartments, in which the phthalate concentrations were higher; probably caused by off-gassing from new products (Pei et al., 2013). Though sampling on Teflon filter and quantification with LTP-MS is not the most accurate method, this shows that comparable results can be obtained.

Table 29: Reported indoor air phthalate concentrations.

<table>
<thead>
<tr>
<th>Reported indoor air concentrations [ng/m³]</th>
<th>Bergh et al., 2011</th>
<th>Pei et al., 2013</th>
<th>Rudel et al., 2003</th>
<th>This thesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMP</td>
<td>n.d.-380</td>
<td>n.d.-6578</td>
<td>n.d.-1322</td>
<td>NA</td>
</tr>
<tr>
<td>DEP</td>
<td>38-2200</td>
<td>484-4779</td>
<td>n.d.-857</td>
<td>590-4300</td>
</tr>
<tr>
<td>BBP</td>
<td>&lt;1.0-300</td>
<td>n.d.-3733</td>
<td>n.d.-3497</td>
<td>n.d.-480</td>
</tr>
<tr>
<td>DEHP</td>
<td>42-890</td>
<td>29-2143</td>
<td>275-8954</td>
<td>77-1000</td>
</tr>
</tbody>
</table>

n.d.: Not detected.

The free fatty acid concentrations above LOQ are summarized in Figure 84. For the samples with a concentration above the dynamic linear range, the maximum concentration is indicated (*). The free fatty acid concentrations are more constant throughout the year, with the exception of the high concentration of the winter season, which may be caused by the lower air exchange rate during winter, thus indicating an indoor source of the free fatty acids, such as human debris or emissions from cooking.

Though the mass spectra from LTP-MS of the residential Teflon filters were dominated by phthalates and fatty acids in positive mode and fatty acids in negative mode, a number of other minor peaks were also observed. The throughout identification of other compounds was complicated and not feasible since the absence of a chromatographic separation made it impossible to distinguish between molecular ions and fragment ions from different compounds. None of the peaks were intense enough to obtain MS/MS analysis.
4.3 Low ozone conditions

Previous studies utilizing the LTP-source have shown that ozone is generated in the plasma from ambient oxygen in sufficient amounts to cause ozonolysis of terpenes placed on a filter under similar conditions to those in this thesis (Nørgaard et al., 2013b). As described in paper I, indoor floor dust contains compounds reactive to ozone, e.g. unsaturated fatty acids, which was also found on the residential Teflon filters (oleic acid at $m/z=281$). The unsaturated sapienic acid (cis-6-hexadecenoic acid) is a major component of human sebum and thus expected to be found in the samples (Drake et al., 2008). Since sapienic acid was not found on the filter samples, it was speculated that it might have reacted with ozone during the ionization; thus, an experiment was designed to test if the ozone generated from the LTP source was sufficient to react with an unsaturated free fatty acid under the conditions used for quantification. Oleic acid was used as a standard, since sapienic acid was not available in satisfactory purity. To minimize the ozone formation the sample table, LTP-probe, and MS-inlet were encapsulated in a Rilsan bag, thus shielding the plasma and ionization area from ambient air. The bag was open in one end to allow for sample handling and the dry gas from the MS-inlet served as a purging gas ($N_2$>99% purity with regard to oxygen). Without shielding, an average concentration of about 850 ppb ozone was measured in the sampling area; with shielding and a $N_2$ flow of 4 L/min about 50 ppb, and thus comparable to indoor conditions, though in the higher range. A droplet of oleic acid in methanol was placed on a Teflon filter as described for the quantification performed in Paper II. No reduction of $[M-H^-]$ or formation of product ions was observed, thus showing that the exposure time and/or ozone concentration was not sufficient to cause detectable ozonolysis of double bonds in free fatty acids. This indicates that if sapienic acid were present in the
air, degradation occurred before the LTP-MS analysis and was not caused by the ozone during the ionization.

4.4 Direct TD-GC-MS of Teflon filters

Another direct, but destructive method, was investigated for the analysis of the residential Teflon filters. A filter was placed in an empty sample tube for Thermal Desorption (TD) GC-MS. This method also required minimal sample preparation but yielded chromatographic separation.

4.4.1 Material and methods

Each filter was cut into quarters with a scissor and spiked with 10 µl known standard in the concentration range 1.5-90 ng/µl (phthalates) and 0.5-230 ng/µl (free fatty acids), respectively. Each piece of filter was placed in a pre-cleaned empty Perkin Elmer stainless steel tube (i.d. ¼”) for TD-GC-MS analysis. Pre-cleaning of the tubes was performed by heating to 275 °C with a nitrogen flow for 2 hours.

A Perkin-Elmer ATD 400 was coupled to a Varian GC-MS (GC: CP-3800/MS: 1200L) system with EI ionization. The GC-MS was equipped with a CP Sil19CB 30 m x 0.32 µm i.d (0.25 µm film thickness) column. Desorption was carried out at 275 °C for 20 min followed by flash desorption of the cold trap into the GC. The GC oven program was: 35 °C hold for 4 min, ramp 1: 4 °C min⁻¹ to 120 °C, ramp 2: 8 °C min⁻¹ to 250 °C, ramp 3: 20 °C min⁻¹ to 280 hold for 2 min. Helium was used as a carrier gas with a controlled flow rate of 1.6 mL min⁻¹.

Mass spectral data was acquired over a mass range of m/z 46-500. Concentrations were determined by a 6 point calibration curve in duplicate. For the phthalate mixture m/z 149 was used as quantifier ion for DEP, DBP, BBP and DEHP; m/z 163 was used as quantifier ion for DMP. For the fatty acid mixture the [M]+ was used as quantifier ion for the saturated fatty acids; [M-H₂O]+ was used for oleic acid (Table 30). A third analysis of each concentration was used for determination of recovery as described for LTP-MS in Paper II.
**4.4.2 Results**

The quantitative properties of the TD-GC-MS method for phthalates and free fatty acids are summarized in Table 30. A satisfactory calibration ($r^2>0.93$) was found for all compounds except DEHP ($r^2=0.77$). No sign of saturation was observed for any of the compounds for the concentrations used, and thus no maximum value is reported.

**Table 30: Summary of quantitative properties of TD-GC-MS for phthalates and free fatty acids;**

<table>
<thead>
<tr>
<th>Quantifier ion</th>
<th>Calibration</th>
<th>Recovery [%] [n=6]</th>
<th>Recoverya [%] [n=3]</th>
<th>LOQb [ng/m^3]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r^2$</td>
<td>Response factor [area count/(ng/µl)]</td>
<td>Intercept [ng/µl]</td>
<td></td>
</tr>
<tr>
<td>Phthalate mixture</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMP 163 (fragment)</td>
<td>0.997</td>
<td>$6.6\cdot10^7$</td>
<td>$-8.6\cdot10^7$</td>
<td>100±50</td>
</tr>
<tr>
<td>DEP 149 (fragment)</td>
<td>0.997</td>
<td>$7.9\cdot10^7$</td>
<td>$4.8\cdot10^7$</td>
<td>87±15</td>
</tr>
<tr>
<td>DBP 149 (fragment)</td>
<td>0.987</td>
<td>$1.2\cdot10^8$</td>
<td>$9.7\cdot10^8$</td>
<td>91±26</td>
</tr>
<tr>
<td>BBP 149 (fragment)</td>
<td>0.998</td>
<td>$9.0\cdot10^7$</td>
<td>$4.2\cdot10^7$</td>
<td>95±11</td>
</tr>
<tr>
<td>DEHP 149 (fragment)</td>
<td>0.765</td>
<td>$9.4\cdot10^7$</td>
<td>$4.9\cdot10^7$</td>
<td>48±19</td>
</tr>
<tr>
<td>Free fatty acids mixture</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lauric acid 200 (M^+)</td>
<td>0.976</td>
<td>$4.8\cdot10^6$</td>
<td>$-1.5\cdot10^7$</td>
<td>127±42</td>
</tr>
<tr>
<td>Myristic acid 228 (M^+)</td>
<td>0.982</td>
<td>$9.9\cdot10^6$</td>
<td>$-2.0\cdot10^7$</td>
<td>122±33</td>
</tr>
<tr>
<td>Palmitic acid 256 (M^+)</td>
<td>0.982</td>
<td>$1.4\cdot10^7$</td>
<td>$6.1\cdot10^8$</td>
<td>118±24</td>
</tr>
<tr>
<td>Oleic acid 264 ([M-H2O]+)</td>
<td>0.934</td>
<td>$4.2\cdot10^8$</td>
<td>$-2.3\cdot10^7$</td>
<td>124±38</td>
</tr>
<tr>
<td>Stearic acid 284 (M^+)</td>
<td>0.984</td>
<td>$1.8\cdot10^8$</td>
<td>$4.9\cdot10^9$</td>
<td>112±18</td>
</tr>
</tbody>
</table>

$^a$: Recovery calculated only for the three highest standards. $^b$: LOQ calculated for ¼ filter; $^c$: n=2; $^d$: n=1.

**4.4.2.1 Free fatty acids**

The calibration was satisfactory for all fatty acids, though with a lower $r^2$ for oleic acid, which was quantified with the [M-H2O]^+ ion. The recoveries were generally too high in the low concentration range, but better for the three highest standards (Table 30), indicating some uncertainty in the determination of lower concentrations even above LOQ. The calibration curves for palmitic and oleic acid is given in Figure 85 as examples.

Compared to LTP-MS, LOQ was a factor of about 88-2700 lower with TD-GC-MS. The largest improvement is seen for the only unsaturated free fatty acid; oleic acid, thus indicating that the double bond might have a negative impact on the efficiency of the LTP ionization compared to the
EI-ionization. This is further supported by the fact that oleic acid had the lowest response factor of the free fatty acids in LTP-MS and comparable to the unsaturated free fatty acids in TD-GC-MS (Table 27 and Table 30).

4.4.2.2 Phthalates

DEHP had the poorest quantitative properties of the phthalates ($r^2=0.77$; recovery 48%). The difference is also clear in the calibration curves, as shown in Figure 86. The calibration curve of DEP is similar to that of the three remaining phthalates. DEHP was the latest eluding phthalate and may to some degree be retained in the cold trap, thus causing both reduction of the signal and increase of the background. This can probably explain the lower $r^2$ in the calibration. The higher background is also reflected in the high intercept in the calibration compared to the response factor. Compared to LTP-MS, LOQ was a factor of about 30-250 lower with TD-GC-MS.

![Figure 85: Calibration curves for DEHP and DEP with TD-GC-MS.](image)

4.4.2.3 Comparison of LTP-MS and TD-GC-MS

Direct TD-GC-MS of the filters had several advantages over LTP-MS:

- LOQs were substantially lower with TD-GC-MS. This is most likely caused by the fact that TD-GC-MS analyses the whole filter, whereas LTP-MS only analyses a spot. Thus LOQ for TD-GC-MS can be increased/decreased by change of the percentage of the filter to be analyzed.
- Chromatographic separation eliminated the interference between compounds with similar ions, such as the phthalates. In this case it was possible to analyze DBP with TD-GC-MS, which was not possible with LTP-MS due to the lack of adequate quantifier ions.
- Chromatographic separation decreased the risk of saturation of the MS detector and would thus allow compounds in lower abundance to be analyzed simultaneous with compounds in higher abundance.
- The automated sample handling and well controlled conditions in TD-GC-MS compared to the manual sample handling and ambient conditions in LTP-MS, gives a lower standard deviation for TD-GC-MS.
- For LTP-MS the quantitative properties seemed to depend on the complexity of the sample, which could pose a major problem for real samples. This was also eliminated by the chromatographic separation.

Since most of these advantages are typical for methods utilizing chromatographic separation, it is difficult to evaluate the efficiency of the LTP-ionization in itself. To do that, a chromatographic system, such as a GC, should be coupled to the LTP-ion sources as described by Nørgaard et al. (2013a). The only drawback of TD-GC-MS is that it is destructive and requires desorption of a major portion of the filter, whereas LTP-MS is practically non-destructive and only requires a small sampling spot.

Poor correlations were found between the filter samples analyzed with LTP-MS and TD-GC-MS for both phthalates and free fatty acids. Only the samples within the dynamic linear range for the LTP-MS analysis are included. For all samples TD-GC-MS grossly underestimates the concentration with a factor of about 100 for the free fatty acids, 30 for DEP and 3 for DEHP compared to LTP-MS. The best correlation was found for stearic acid and DEP ($r^2=0.65$ and 0.48).

Figure 86: Correlation between concentrations of free fatty acids and phthalates on residential Teflon filters determined by LTP-MS and TD-GC-MS. All axes are concentration [ng/m$^3$].
The substantial difference between the concentrations determined with the two methods indicates that some of the assumptions are not valid; thus, the concentrations cannot be used without a better understanding of the cause of the difference. In the following, these assumptions will be discussed along with suggestions for improvements and additional experiments.

Quantification with LTP-MS is built on three major assumptions:

A: The standards applied via droplets are released from the filter in the same manner as the compounds sampled via air sampling. When applying the droplet of analytes to the filters, it was clear that the solvent did not penetrate the filter. Thus it can be expected that the analytes were mainly present at the surface of the filter. The analytes sampled from air, are on the other hand expected to penetrate into the filter, and thus not only be present at the surface. This difference would, probably underestimate the concentrations of SVOCs on the filter samples, since compounds within the filter material is expected to be more difficult to release. This difference could be investigated if the standards were applied onto the filters via gas phase sampling, e.g. with different sampling times of the same known gas phase concentration. However, for this method to be valid, an investigation of the breakthrough volume for the Teflon filter should also be performed.

B: The distribution of sampled SVOCs on the filters are homogenously distributed over the surface. If the concentration at the center of the filter is higher than at the edge, LTP ionization in the center of the filter will overestimate the total air concentration. To investigate this assumption, the signal intensity as a function of the center of the filter could be measured. Since the experiments were carried out, an improved version of the LTP has been developed, with a more automated sampling table, which would enable such an investigation.

C: The ionization area on the filter is smaller than the area of the droplet of standards. If this assumption is not true it would underestimate calibrated response factor and therefore overestimate the concentration of sample compounds. This assumption could be tested in the same manner as for assumption B, but with the signal intensity as a function of the distance to the center of the droplet of standards as the parameter to measure.

Though the LTP-MS method is based on several assumptions, it is interesting to note that the concentrations of phthalates determined with this method are in the same order as reported in previous studies, opposed to the concentrations determined with TD-GC-MS (Table 29).

The major difference between the desorption and ionization in LTP-MS and TD-GC-MS, is that the former only desorb and ionize a small section of the filter whereas the latter theoretically desorb and ionize everything on the filter. Thus, the only assumption for LTP-MS, that is also relevant for TD-GC-MS, is assumption A; this could be tested in the same manner as for LTP-MS.
4.5 PCA of residential Teflon filters

A way to characterize the total composition of the filters is to consider the total mass spectrum as a fingerprint of the sample, thus also including the signal from non-quantified and non-identified SVOCs. The fingerprints can be compared by principal component analysis (PCA) by grouping according to season or home. It is assumed that the LTP-MS method yields a representative mass spectrum of the sampled VOCs and SVOCs.

4.5.1 Method

The mass list of background subtracted MS-spectra for each filter sample obtained as described in Paper II was exported to Mass Frontier 7.0 (2011, Thermo Fischer Scientific Inc., San Jose, CA) for PCA analysis. The mass list were given as ratios in relation to the highest peak, which means that the PCA would not find any differences caused by different amount of a given compound only differences in the relative compound ratios.

4.5.2 Results and discussion

Great care should be taken with respect to interpretation of the PCA. With respect to interpretation of the seasonal grouping it should be noted that differences between seasons may be influenced by storage time or differences in LTP conditions during analysis.

The PCA plots (PC1, PC2) of both negative and positive mode data sorted by home and season are shown in Figure 88. None of the PCA-plots show any distinct grouping.

Figure 88 shows positive (A) and negative (B) MS data sorted by home, with no distinct grouping for any home. This study only included five relatively similar homes, which is not a large statistical material. It cannot be ruled out that with a larger group of different homes, it would be possible to distinguish different types of houses or pinpoint homes with some kind of problems such as high SVOC concentrations due to degassing of new furniture or building materials.

Figure 88 shows positive (C) and negative (D) MS data sorted by season. In negative mode, fall shows the most distinct grouping whereas spring and winter have more overlays and summer is spread over a larger part of the plot. In positive mode summer stands out from the three other seasons which seems to be in groups, but with large overlaps.

Since each measured season spans over 5 weeks in a changing climate, some overlays of the seasons would be expected, since the conditions in the four seasons not necessarily differs substantially.
4.5.3 Conclusions

A linear concentration/response correlation was found for LTP-MS within a limited dynamic range. The detector reached saturation within only a factor of 10-100 of the quantification limit (LOQ). For free fatty acids, which were analyzed in negative mode, the maximum concentration before saturation was reached was higher than for the compounds analyzed in positive mode, which is most likely because more compounds ionize efficiently in positive mode, thus causing more matrix interference.

For compounds with little fragmentation, e.g. free fatty acids and PAHs, the chromatographic separation can be substituted with the high resolution mass spectral separation, but this poses a major problem for simultaneous analysis of compounds with a higher degree of fragmentation, e.g. phthalates. The maximum concentration within the linear range is substantially decreased for compounds analyzed in a mixture, and this would most likely also be the case for compounds in a complex matrix. The method is more suited for a fast screening of high vs. low concentration prior to a more conventional quantification or for applications where only a fast qualitative method is required.

The correlation between boiling point/vapor pressure and response factor for PAHs and fatty acids shows that the LTP ionization efficiency of the compounds may depend on their volatility and the
time subjected to heat; thus indicating that the ionization takes place in the gas phase after evaporation rather than the plasma itself causes ionization on the surface.

Concentrations of free fatty acids and phthalates on residential Teflon filters were determined. All compounds were detected in most samples, but they were below LOQ for about half of the filters for the phthalates and about one third of the filters for the free fatty acids. Only palmitic acid and oleic acid exceeded the linear dynamic range. No PAHs were detected on any of the samples.

The LTP-MS method was compared to a direct TD-GC-MS method and the quantitative properties of TD-GC-MS was superior to those of LTP-MS both with regard to LOQ and linear dynamic range. The correlations between concentrations determined with the two methods were however poor with about 100 times lower determined concentration determined with TD-GC-MS than for LTP-MS.

The PCA analysis showed some tendencies toward grouping, but not enough to be conclusive.

4.5.4 Perspectives

Along with the additional experiments suggested in Section 4.4.2 to establish a further understanding of the quantitative properties, the method could be improved in several other ways:

- As opposed to TD-GC-MS much of the sample handling in LTP-MS is manual. The uncertainties from the deposition of standards onto the filter could be improved if an auto sampler system was developed for the LTP, or even better if standards were applied with a well-controlled gas phase deposition to better mimic the real sample conditions. An automated sampling table, which could scan automatically over a larger area of the filter, could improve the variation of the analysis of the sample filters.

- The limitation of the maximum concentration is believed to be caused mainly by detector saturation, and could thus be improved by using SIM-mode (Selected Ion Monitoring) for the detection of the compounds of interest. Several compounds could be detected in alternating SIM traces, which would decrease measurement time for each ion, and thus risk of increasing LOQ. With SIM, information of all other masses than the selected is lost.

- LOQ could be improved by an optimization of the LTP settings; a more powerful plasma could ionize more efficiently. This has not been performed in this study, since it would also cause a higher ion count in the higher concentration range, thus result in saturation at lower concentrations if SIM is not used. More power to the LTP probe also poses a greater risk of burning it. After LTP-MS analysis of filters in this thesis have been performed, the LTP-probe in the lab has been improved as part of other on-going studies. The experiments should be repeated with the new probe, which is believed to increase the sensitivity.

Many of the drawbacks of LTP-MS compared to TD-GC-MS are coupled to the lack of chromatographic separation, some could be overcome by used of SIM-mode, but for the isobaric isomers of PAHs and the different fragments of phthalates, the use of SIM mode would not be sufficient.
Some of these suggested improvements needs to be tested before Paper II can be submitted for publication.
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8 Appendixes

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Appendix A (Paper I)

Ozone reaction characteristics of indoor floor dust examined in the emission cell “FLEC”

Authors: Anni Vibenholt, Per Axel Clausen and Peder Wolkoff
Ozone reaction characteristics of indoor floor dust examined in the emission cell “FLEC”

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HIGHLIGHTS

• Catalytic and chemical processes contributed to the ozone consumption at steady state.
• Ozone scavenging effect of dust was comparable to that of carpets.
• Aldehydes were major reaction products from the ozonolysis of SVOCs in dust.
• A bell shaped curve described the dependency of relative humidity on the reaction rate.

ABSTRACT

Ozone reacts with C-C double bonds in common indoor VOCs and SVOCs contained in indoor dust and may be catalytically degraded on dust surfaces. The reaction between floor dust and ozone was investigated in the FLEC emission cell at different ozone concentrations and relative humidities (0%, 25%, and 50% RH). One gram of dust was spread on a clean stainless steel plate which was placed in the FLEC. Steady state reaction rate (K_{Dust}) at 2.2 ppm ozone was determined for four different floor dust samples collected in Danish homes and offices. This high concentration was necessary in order to measure and determine the consumption in the outlet air from the FLEC. Measurements were corrected for FLEC wall effects by subtraction of the steady state reaction rate between ozone and a FLEC on a stainless steel plate without dust (K_{FLEC}). The composition of organic compounds in the dust was analyzed by pressurized liquid extraction and thermal desorption GC–MS before and after ozone exposure.

K_{FLEC} was independent of the ozone concentration and the reaction was treated as first order. The same was indicated for K_{Dust} since it remained unchanged at 2.2 and 1.6 ppm ozone for one dust sample. However, the measured K_{Dust} in the FLEC should be considered an average rate constant due to the FLEC geometry. K_{Dust} was in the range 0.039–0.14 1/s pr. g dust at 50% RH. K_{Dust} was 3 times higher at 25% RH than at 50% RH and 6 times higher than at 0% RH.

The inhomogeneity of the dust was assessed by experiments in triplicate with a new portion of dust each time. The relative standard deviation of K_{Dust} at 50% RH was 5.9–20%.

The major identified compounds before and after ozone exposure included aldehydes, saturated and unsaturated linear alkanic acids, benzoic acid and their methyl esters, dimethyl esters, phthlates and traces of α-pinene and limonene. Substantial increase of C_7–C_9 aldehydes was observed after ozone exposure.

© 2014 Published by Elsevier Ltd.

Keywords:
Floor dust
FLEC
Ozone
Aldehydes
Reaction rate
VOC/SVOC
Indoor air

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Published by Elsevier Ltd. 2014. Published online xxxx.
1. Introduction

1.1. Background

1.1.1. Composition of house dust

Floor dust consists of a number of different compounds such as sand, human and animal debris containing fatty acids, wax esters, squalene and cholesterol (Lampe et al., 1983; Nicolaides et al., 1972; Weschler et al., 2011), textile fibers (Clausen et al., 2003), and SVOCs accumulated from air and indoor surfaces (Clausen et al., 2004). The organic content of floor dust varies greatly. A previous study found 26–57% organic fraction in dust from homes in New Zealand (Ferguson et al., 1986) and a mean organic fraction of 33% in dust was found in seven Danish offices (Mølhave et al., 2000). Household dust contains a wide range of both VOCs and SVOCs such as alkanes, aldehydes, carboxylic acids and their esters and phthalates (e.g. Hirvonen et al., 1994; Wolkoff and Wilkins, 1994) and squalene and cholesterol (Weschler et al., 2011).

1.1.2. Presence of dust in homes and offices

The amount of surface dust is highly variable. For instance in Canadian homes (n = 1022) dust loadings were in the range 2.0–4081 mg m\(^{-2}\) based on whole-house floor vacuum samples (Rasmussen et al., 2013); in 12 Danish office buildings 40–890 mg m\(^{-2}\) (Gyntelberg et al., 1994).

1.1.3. Presence of ozone in homes and offices

Sources of ozone in the indoor environment include infiltration of ozone from outdoor air, office equipment such as printers and photocopieters and ozone based air cleaners (Weschler, 2000). The major source of indoor ozone in homes is infiltration of ozone from the outdoor air (20–70%). Indoor ozone reacts fast with other chemicals in the air and surfaces. Thus measured indoor ozone concentrations are lower than what have been available for reactions. Outdoor air ozone peak concentrations up to 140 ppb have been reported (Weschler, 2000).

1.1.4. Possible reaction between surfaces and ozone

Under normal indoor conditions, removal of ozone occurs primarily through surface deposition and air exchange and the typical reported half-life is 7–10 min (Weschler, 2000). Only a small fraction of the VOCs found in indoor air react fast enough with ozone to compete with typical air exchange rates. The common feature of the fast reacting compounds is the C–C double bond in e.g. monoterpenes such as limonene and \(\alpha\)-pinene (Destaillets et al., 2006), and unsaturated fatty acids (Zeng et al., 2013). The deposition rates for material surfaces are considered combinations of catalytic decomposition of ozone and ozonolysis of VOCs and SVOCs adsorbed on the surfaces and dust.

1.1.5. Aims

Previous studies have investigated the interaction between ozone and materials in a simulated and real aircraft cabin (Tamas et al., 2006; Weisel et al., 2013; Wisthaler et al., 2005), between ozone and building materials (Granotof and Raychaudhuri, 2004; Klén et al., 2001; Knudsen et al., 2003; Lambie et al., 2011; Nicolas et al., 2007; Sabersky et al., 1973) and carpets (Morrison and Nazaroff, 2000, 2002; Weschler et al., 1992), but to our knowledge no studies on the interaction between indoor dust and ozone have been reported. The aim was to develop and explore a new method for characterization of dust. This was carried out by measurement of the ozone consumption of four different house and office floor dust samples over time; study of the effect of relative humidity on the reaction; and, study of the effect of the ozone exposure on the composition of organic compounds in the dust.

2. Material and methods

2.1. Chemicals

Decane (99.8%, Fluka), methanol (LC-MS grade, Fluka), DEHP (Pestanal\textsuperscript{\textregistered} grade, Fluka), squalene (\(\geq 98\%\) pure), and cholesterol (\(\geq 99\%\) pure) were purchased from Sigma Aldrich. Ottawa sand (General purpose grade, particle size 20–30 mesh) was purchased from Fisher Chemical.

2.2. Dust samples

Four different samples of floor dust collected by vacuuming were investigated, as summarized in Table 1. Dust 1 was collected in office buildings and institutions in the Aarhus area in Denmark. None of the buildings had any known indoor climate problems (Mølhave et al., 2000). Dust 2 was collected in schools, without any known indoor climate problems, in Aarhus and Copenhagen (Mølhave et al., 2006). Dust 3 was obtained from vacuum cleaner bags collected from private homes with no known moisture or mold problems, no fur-bearing pets and no smoking inhabitants (unpublished). All dust samples consist of several pooled individual samples; Dusts 1–3 were homogenized according to a standard procedure (Mølhave et al., 2000). The procedure included removal of large items (clips, insects, etc.) and treatment in a food processor (Robot 2 Coupe 700 W) to cut down larger textile fibers. The remaining dust was sieved through a 1.0 mm sieve. Dust 4 was collected in an office building with a standard industrial vacuum cleaner and the particle fraction was separated by sieving (500 \(\mu\)m) (Clausen et al., 2003). All dust samples were stored at room temperature in closed glass jars.

2.3. Organic fraction

The organic fraction of the dust samples were determined with thermogravimetric analysis (TGA) performed on a Mettler Toledo TGA/SDTA 851e in air to ensure complete decomposition. The heating rate for all samples was 10 \(^\circ\)C min\(^{-1}\) in the range from 25 \(\circ\)C to 1000 \(\circ\)C.

2.4. Specific surface area

The specific surface area of the dust was determined by multi-point Kr-BET at 77.4 K, according to DIN-ISO 9277 by a Quantachrome Autosorb-3 (Quantachrome, Germany). The dust was degassed for about 40–60 h under vacuum at room temperature prior to analysis in order to minimize evaporation of SVOC on the surface.

2.5. Settled bulk density

The settled bulk density of Dusts 1–4 was determined by weighing about 5 g of dust in a 100 cm\(^3\) graduated cylinder. The cylinder was tapped gently to achieve the settled density and the volume was read off.

2.6. Test design

The intention was to simulate the heterogeneous interaction of dust sedimented on a surface and ozone in the air. An amount of the dust was placed in a FLEC\textsuperscript{\textregistered} (Field and Laboratory Emission Cell, Chematec, Roskilde, DK; Wolkoff et al., 1995; Wolkoff, 1996). Ozone was added to the supply air and measured at the FLEC outlet as a function of time. (see Fig. S3). Before each experiment the ozone consumption of the empty FLEC cell was determined and...
used to calculate \( k_{\text{FLEC}} \). The experiment was terminated when a steady state or quasi steady state outlet ozone concentration was reached. Steady state reaction rate \( k_{\text{Dust}} \) was determined from inlet and outlet ozone concentrations and corrected for the contribution of the FLEC stainless steel (SS) surfaces to the degradation of ozone by use of \( k_{\text{FLEC}} \). Additional experiments were carried out to study the influence of the relative humidity (RH) on \( k_{\text{Dust}} \) and the possible rejuvenation of reaction sites during ozone-free condition. All experiments were performed in duplicate or triplicate, with a new portion of dust for each experiment (Table 1). Finally, the changes in composition of the extractable organic compounds in the dust were analyzed.

### 2.7. Experimental setup

The test system consisted of a SS bottom plate, a SS FLEC (volume = 3.5 \( \times \) 10 \(^{-3} \) m\(^3\); test area = 0.0177 m\(^2\)) with a FLEC air supply, an ozone generator and an ozone monitor (Figs. S1 and S3). Compressed medical grade air was used for both ozone generation and the FLEC air supply. Ozone was generated photochemically by a mercury lamp in a thermostated lamp housing controlled by a high-performance variable power supply (Clausen et al., 2001). The air flow through the ozone generator was 50 mL min\(^{-1}\) and the ozone enriched air was mixed with humidified air with a flow of 450 mL min\(^{-1}\) in a T-union before the FLEC inlet to a total flow through the FLEC of 500 mL min\(^{-1}\). During the ozone/dust experiments the measured ozone concentration in the FLEC inlet air flow was 2.17 ± 0.05 ppm (\( n = 16 \)) (O\(_3\) inlet). The RH was supplied by the FLEC air supply unit (Wolkoff et al., 1995) and monitored by a Testo 650 (TestoTerm GmbH & Co., Germany). If not stated otherwise, all experiments were carried out at 50% RH. Experiments were performed to determine possible loss of dust due to resuspension in the air flow of the FLEC during the experiments. This was done by triplicate sampling on Teflon filters (Millipore, 37 mm, 1.0 \( \mu \text{m} \) pore size) at the FLEC outlet (sampling volume 3 m\(^3\), 4 d). The weighed amount of dust on the filters was not significantly different from zero \((0.08 \pm 0.11 \text{ mg})\), 95% confidence interval).

### 2.8. Ozone measurements

The ozone was measured by a UV based monitor (API model 400); detection limit 1 ppb (API, San Diego, CA). Ozone concentration was measured at the outlet with a sample flow of 630 mL min\(^{-1}\). The additional air flow above 500 mL min\(^{-1}\) required by the monitor was delivered from ambient laboratory air with an ozone concentration below 15 ppb. The ozone concentration was corrected for the dilution factors.

The ozone concentrations from the ozone generator (O\(_3\) inlet [ppb]) was measured before each experiment; the outlet of the empty and dust loaded FLEC (O\(_3\) outlet [ppb]) were measured online for each experiment. A relation between these measurements was used to determine \( k_{\text{Dust}} \), which minimized the effect from changes in the ambient ozone concentration.

#### 2.9. Determination of the reaction rate of ozone with dust in the FLEC

The steady state first order reaction rate of ozone with dust in the FLEC \( k_{\text{Dust}} \) was calculated from O\(_3\) inlet, the outlet ozone concentration of the empty FLEC cell at steady state (O\(_3\) in FLEC [ppb]), the FLEC outlet ozone concentration at steady state from a dust sample (O\(_3\) out dust [ppb]), and the air exchange in the FLEC (Ex [1/s]) as given in Eq. (1); \( k_{\text{FLEC}} \) is calculated according to Eq. (2) (Kleno et al., 2001).

\[
\frac{d[O_3]}{dt} = \frac{O_{3 \text{ in}} - O_{3 \text{ out}}}{O_{3 \text{ out}} F_{\text{FLEC}}} - Ex + k_{\text{FLEC}} \quad (1)
\]

\[
k_{\text{FLEC}} = \frac{O_{3 \text{ out}} F_{\text{FLEC}}}{O_{3 \text{ out dust}} - 1} \times Ex \quad (2)
\]

It is necessary that the dust or sample material removes less than O\(_3\) inlet in order to be able to measure O\(_3\) outlet. Thus O\(_3\) outlet was undetectable at 50 ppb O\(_3\) inlet showing that determination of \( k_{\text{Dust}} \) is not possible at realistic indoor ozone levels within a reasonable timeframe.

All results are given as mean ± standard deviation of independent experiments. Two-sided t-test was used for determination of statistical differences \((p < 0.05)\).

### 2.10. Determination of maximum reaction rate

The maximum reaction rate was calculated from the maximum of the numerical first derivative of O\(_3\) out vs. exposure time \( [dO_3]/[dt] \) (see Fig. 2). A running average over 30 min yielded a satisfactory characterization of the experimental data; thus maximum \( [dO_3]/[dt] \) was determined from the running average of the first derivative of \( [dO_3]/[dt] \) over 30 min.
2.11. Degradation of ozone in an empty FLEC

An empty FLEC was exposed to ozone in varying O_3 inlet (145–2200 ppb). O_3 inlet was measured immediately before each experiment. The exposure continued until O_3 outlet was constant (app. 40 min). The reaction rate (\( k_{\text{FLEC}} \)) was obtained from Eq. (2).

2.12. Reaction of ozone with dust in the FLEC

Immediately before each dust experiment the FLEC cell was wiped with tissue paper wetted with 2-propanol and allowed to dry before assembly. The empty cell was purged with ozone at the same concentration as the following dust sample until a steady state was reached (ca. 40 min). The purging of ozone also served to clean the stainless steel surface. O_3/FLEC was used for calculation of \( k_{\text{Dust}} \) according to Eq. (1).

Nominally 1 g of dust was weighed, spread and, distributed on the clean SS bottom plate in a circle with exactly the same size as the FLEC (i.d.:15 cm; see Fig. S1). This was performed by gently tapping it underneath a piece of weighing paper as evenly as possible. All results are normalized to the amount of dust and given per g of dust.

The ozone exposure continued until O_3 outlet was constant \( (O_3_{\text{Dust}}), \) i.e. the system had reached steady state or quasi steady state. The time until steady state was 1–5 d and the exposure continued for one more day to ensure that O_3 outlet was constant \( (\pm 10 \text{ ppb}) \).

Dust 2 was also tested at a lower O_3 inlet (1.6 ppm) and Dust 4 was tested at 0%, 25%, 50% RH.

2.13. Rejuvenation of reaction sites in dust

Dust 4 was exposed to ozone until steady state was achieved after 7 d and allowed rejuvenation for another 7 d with medical grade air and no ozone. Medical grade air was supplied by the FLEC air supply with the same setup as for the ozone exposure experiments (450 mL min^(-1) 50% RH). After rejuvenation the dust was reexposed to ozone under the same conditions as during the first ozone exposure.

2.14. Extraction and analysis of organic compounds in the dust

After ozone exposure the dust was collected from the SS bottom plate of the FLEC and extracted by pressurised liquid extraction (PLE) (ASE 200, Dionex, CA) in methanol within the same day. Unexposed dust was also extracted for comparison. The extraction method was: Heating for 9 min to 200 °C, static conditions for 10 min at 200 °C and 2000 psi and purging with nitrogen for 60 s.

For the PLE extraction an empty PLE cell was packed with inert Ottawa sand. The cell and sand was pre-cleaned by a similar extraction cycle. After pre-cleaning an appropriate amount of the sand was replaced with 1 g of dust and extracted. The extracts were kept at 4 °C until analysis. Then the extracts were injected on Tenax TA tubes (5 μL). The tubes were purged in a flow of He to remove the solvent. This was done to avoid interference from less volatile compounds using the Tenax as a solid phase extraction media (Kroefoed-Sørensen and Clausen, 2004) (see Figs. S4 and S5).

The Tenax TA tubes were analyzed by thermal desorption gas chromatography and mass spectrometry (TD-GC–MS) using a Perkin Elmer Turbo Matrix 350 thermal desorber coupled to a Bruker SCION TQ GC–MS system (Bruker Daltonics, Bremen, DE). Desorption was carried out in a He flow in the reverse direction to the injection flow at 275 °C for 20 min followed by flash desorption of the cold trap into the GC. The column was a 30 m × 0.25 mm with 0.25 μm film thickness (VF-SMS, Agilent Technologies, Santa Clara, US). The GC oven program was: 50 °C for 4 min, ramp 1:4 °C min^(-1) to 120 °C, ramp 2:50 °C min^(-1) to 250 °C hold for 2 min. Helium was used as carrier gas at an inlet pressure of 0.97 bar (ca. 1.5 mL min^(-1)). The mass spectrometer was operated in the mass range m/z 50–500 scan mode using electron ionization. Transfer line and ion source were kept at 275 °C. No compounds eluted later than DEHP at 28.4 min (b.p. 385 °C), which can be considered an upper limit for this method.

Unknown compounds in the QC–MS chromatograms were screened and identified using the AMDIS software and NIST database (Stein, 1999, 2011) (see Table S1).

Decane in methanol injected onto Tenax tubes was used as an external calibrant for semi-quantification of selected VOCs and SVOCs in decane-equivalents. A 6 point calibration curve in the concentration range 0.0007–0.6 μg/injection was obtained (\( r^2 = 0.98 \)).

3. Results and discussion

3.1. Degradation of ozone in an empty FLEC

The time until steady state for the FLEC/dust system was substantial compared to the blank empty FLEC alone (ca. 60 h vs. ca. 40 min). For O_3 inlet in the range 145–2200 ppb \( k_{\text{FLEC}} \) was constant \((0.11 \pm 0.01) \text{ l/s} \), see Fig. S2). The reaction is therefore considered a first order reaction that only depends on the number of active sites on the stainless steel and not on the ozone concentration. This indicates that available catalytic reaction sites is large compared to the number of molecules of ozone.

The reaction rate \( (k_{\text{FLEC}}) \) was determined for two different FLECs. The two \( k_{\text{FLEC}} \)-values did not differ significantly \( (p = 0.73) \).

The heterogeneity of the dust samples was assessed via tripli- cate experiments with a new portion of dust for each experiment. The relative standard deviation of \( k_{\text{Dust}} \) within each sample (Dusts 1–4) was 5.7–20% for the experiments at 50% RH.

For a completely homogenous layer of the dust on the 177 cm^2 sampling area the average layer thickness can be determined from the settled bulk density (Table 1) as 0.04–0.08 mm for Dusts 1–4. The dust was not completely homogenously dispersed, and the coverage was estimated to about 50% of the sampling area, thus the average layer thickness is estimated to 0.08–0.16 mm.

It was considered to sieve the dust to obtain a better dispersion on the sample area, but was avoided due to the risk of loss of material during sieving. To assess the impact of the distribution of dust on \( k_{\text{Dust}} \) one experiment was conducted with the dust centered in a small pile. No markedly difference was found for \( k_{\text{Dust}} \) for the dust sample spread evenly across the whole surface and the centered sample.

3.2. Reaction of ozone with dust in the FLEC

Our hypothesis is that the degradation of ozone in the FLEC is caused both by chemical reactions with unsaturated organic compounds on the dust surface and by catalytic degradation by the dust and SS surfaces. Both factors might change during the exposure time. The chemical reaction consumes readily available reactive organic compounds on the surface of the dust, and these are continuously replenished via mass transport from the core of the dust to its surface. At steady state the consumption and mass transport is expected to be in equilibrium. The catalytic degradation is more constant, but the decomposition of reactive compounds on the surface of the dust might generate new catalytic active sites.

Thus, the maximum reaction rate reflects the amount of readily available reactive compounds on the surface of the dust at the beginning of the exposure. A high maximum reaction rate indicates a fast consumption of the available reactive compounds. The stea...
dy state reaction rate characterizes the amount of catalytic reactive sites on the surface as well as mass transport of reactive chemical compounds from within the dust to the surface. A high steady state reaction rate indicates either a high number of catalytic sites or a high total concentration of reactive organic compounds.

The ozone absorption time profiles (O$_3$ outlet [ppb]) in the gradient at steady state was 1.0–1.6 ppm for Dusts determined at 2.2 ppm ozone (Table 1). This is expected. This is due to the fast reaction rate (k$_{Dust}$) is independent of O$_3$ inlet. That O$_3$ inlet was measured 1.6 ppm on Dust 2 showed a slightly, but not statistically, lower reaction rate. The experiments with an empty FLEC cell were required. The experiments with an empty FLEC cell was independent of Dust 1 and 4. Dust 2’s initial reaction rate was much higher and steady state was reached faster, whereas the reaction rate of Dust 3 was lower but its ozone consumption was higher.

3.2.1. Influence of ozone concentration on k$_{Dust}$

The differences between the reaction profiles are reflected in k$_{Dust}$ determined at 2.2 ppm ozone (Table 1). k$_{Dust}$ was in the range 0.039–0.14 1/s. k$_{Dust}$ for Dust 1 and 4 was not significantly different (p = 0.18), whereas Dust 2 and 3 differed significantly from the other dust samples (p = 0.0001–0.041). A correction for organic matter yielded a slightly larger difference in k$_{Dust}$ and could thus not explain the difference. Dust 3 had a significantly larger surface area (Table 1), but this difference was not sufficient to account for the differences in k$_{Dust}$.

A concentration gradient of ozone from the inlet slit of the FLEC (O$_3$ inlet [ppb]) to the outlet (O$_3$ outlet [ppb]) is expected. This is due to the fast reaction of ozone with the dust which close to the inlet slit consumes a large fraction of the incoming ozone. This means that the dust farther from the inlet slit (closer to the FLEC outlet) experiences a lower ozone concentration. Thus k$_{Dust}$ should be considered an average rate of the reactions taking place from the inlet slit to the outlet of the FLEC. The lowest ozone concentration (O$_3$ outlet [ppb]) in the gradient at steady state was 1.0–1.6 ppm for Dusts 1–4. Thus all dust on the sample plate has been exposed to a substantial amount of ozone. However, the gradient was steeper in the initial stages in the experiment where O$_3$ outlet ~0 at time t=0.

3.2.2. Steady state reaction rate, k$_{Dust}$

The dust samples could not be tested within reasonable time at high total concentration of reactive organic compounds. All previous studies, except Mueller et al., 1973, and Sabersky et al., 1973, reported ν$_d$ values at much lower ozone concentrations (20–341 ppb) than used in the present study. The dust samples could not be tested within reasonable time at realistic indoor ozone concentration (app. 50 ppb) because high O$_3$ inlet was required. The experiments with an empty FLEC cell showed that the reaction could be treated as a first order reaction, independent of the ozone concentration. The same was indicated for k$_{Dust}$ since it remained unchanged at 2.2 and 1.6 ppm ozone for one dust sample. This is further supported by k$_{Dust}$ values at high ozone concentrations which are comparable to those measured at lower ozone concentrations (see Table 2). This also justifies the use of ozone concentrations at levels much higher than realistic for indoor air conditions.

3.2.3. Maximum reaction rate

An example of a d[O3]/dt plot for determination of the maximum reaction rate is shown in Fig. 2. The maximum reaction rates...
are summarized in Table 1. The maximum reaction rate for Dust 2 was significantly higher than for the other dust samples ($p = 0.0001–0.0022$); none of the other dust samples differed significantly ($p = 0.19–0.58$). This dust sample had the lowest $k_{\text{Dust}}$ at 50% RH, which indicates that the reactive compounds on the surface was removed fast and the replenishment was lower compared to the other dust samples; or it contained fewer catalytic active sites. The combination of the high maximum reaction rate and the low $k_{\text{Dust}}$ indicates that Dust 2 contains the smallest amount of reactive organic compounds of the four investigated dust samples. This is consistent with the low organic fraction (Table 1), though this fraction does not take the reactivity of the organic compounds into account.

Dust 3 had the lowest maximum reaction rate, though not statistically significant, which indicates that the reactive organic compounds on the surface were only removed slowly. Dust 3 had the highest $k_{\text{Dust}}$, which indicates an effective replenishment of reactive compounds, or a high number of catalytic reactive sites, and thereby, as opposed to Dust 2, the highest amount of reactive organic compounds. This is consistent with the fact, that it is younger, and thus a smaller amount of reactive compounds have been lost due to evaporation and reaction with oxygen during storage.

### 3.2.4. Rejuvenation of reaction sites in dust

Fig. 3 shows the ozone absorption time profile for Dust 4 for exposure of previously unexposed dust (First exposure) and dust
rejuvenated for one week and subsequently exposed to ozone (Second exposure). Steady state was achieved after ca. 85 h (First exposure) whereas this was achieved already after app. 5 h in the rejuvenated dust. The total ozone consumption during the ozone exposure of the rejuvenated dust was 3% of the first exposure. In comparison the empty FLEC consumed only 0.4%.

The shorter time of the rejuvenated dust to reach steady state (second exposure) indicates that the major reason for the slow increase of O$_3$ out, during the first exposure is mainly removal of ozone by chemical reactions with compounds readily available on the surface of the dust. During the rejuvenation period some compounds are transported to the surface, which results in a low concentration of reactive compounds compared to the unexposed dust. O$_3$, and thus $k_{Dust}$ reached the same level during the first and second exposure as indicated by the extended x-axis in Fig. 3.

3.2.5. Effect of humidity on the steady state reaction rate

No markedly differences were found for $k_{FLEC}$ as a function of humidity. At 25% RH, $k_{Dust}$ was found to be ca. 3 times higher than at 50% RH and ca. 6 times higher than at 0% RH (see Table 1). All three RH levels differed significantly ($p = 0.0072–0.021$). No significant differences were found for the maximum reaction rates for the different RH levels ($p = 0.35–0.67$). This indicates that the initial removal of available reactive compounds on the surface of the dust is not affected by RH, but that either the mass transport of reactive compounds from within the dust or the efficiency or amount of the catalytic reactive sites is affected.

Grøntoft et al. (2004) reported a decrease in $k_D$ from 0 to 50% RH for calcareous stone and concrete. The authors explained this decrease with an increase of occupied reaction sites by water molecules. This is consistent with the low reaction rate of dust at 50% RH compared to 25% RH, but not with the lower reaction rate at 0% RH and the fact that humidity did not influence $k_{FLEC}$. The major difference between the study by Grøntoft et al. and the present study is the chemical reactions with organic compounds in the dust. It may be speculated that the reaction with the unsaturated organic compounds requires some humidity to be effective, possibly because water might act as a plasticizer (Hansen, 1982) and aid the mass transport of VOCs to the surface of the dust.

3.3. Composition of organics in the dust before and after ozone exposure

A total of 71 compounds were identified from their EI-MS spectra (see Table S1). Some of the identified compounds are known oxidation products and reactive compounds. These included unsaturated carboxylic and dicarboxylic acids and esters thereof ($C_6$–$C_{10}$) and aldehydes ($C_7$–$C_{10}$). It is possible that some of the methyl esters originate from methylation of fatty acids during the PLE extraction with methanol.

Dust 1 and 4 generally contained more of the most volatile compounds than Dust 2 and 3. This was also the case for the less volatile compounds, but to a lesser degree.

3.3.1. Formation of compounds during ozonolysis

The formation of gas phase compounds during exposure is not considered in this study due to the high ozone concentrations that would impair results obtained by sampling on Tenax TA by formation of Tenax degradation products and further reaction of adsorbed reaction products (Kiene et al., 2002).

A few compounds increased substantially after exposure, in particular $C_7$–$C_{10}$ aldehydes (see Table 3). Aldehydes are common ozonolysis products in several previous studies on different materials, e.g. in the reactions in simulated and real aircraft environments (Coleman et al., 2008; Weisel et al., 2013; Weschler et al., 2007; Wisthaler et al., 2005); with carpets and countertops (Wang and Morrison, 2006), in homes (Rancière et al., 2011), and with green building materials (Gall et al., 2013) with nonanal as the most prominent aldehyde; from human hair decanal was the most prominent aldehyde (Pandrangi and Morrison, 2008).

The aldehydes may influence the perceived indoor air quality due to their generally low odor thresholds (Wolkoff, 2013).

The difference between the unexposed and exposed dust were in general higher for Dust 3, which was also the youngest sample due to their generally low odor thresholds (Wolkoff, 2013).

The difference between the unexposed and exposed dust were in general higher for Dust 3, which was also the youngest sample and therefore the one exposed the least to natural aging during storage.

3.3.2. Removal of compounds in the ozonolysis

No compounds consistently decreased after exposure. The only identified reactive compounds that were found in lower levels in some dust samples after ozone exposure were octadecenoic acid...
and octadecenoic acid methyl ester. The total molar concentration of the two compounds was in the range 0.21–0.84 mmol g⁻¹ dust before exposure and 0.55–0.75 mmol g⁻¹ dust after exposure (see Fig. 4). For each experiment the ozone exposure was continued until O₃ outlet was constant, and thus the different dust samples have been exposed to different amounts of ozone resulting in potentially different amounts of reacted compounds.

The unsaturated acid and its ester were expected to be highly reactive with ozone, but this was not reflected in the determined amounts before and after exposure (see Fig. 4). The amounts of octadecenoic acid was similar for Dusts 1–3 and decreased substantially after exposure for Dust 4; the amounts of octadecenoic acid methyl ester were similar in Dust 1 and increased substantially after exposure for Dusts 2–4. The increase of octadecenoic acid methyl ester in three of the dust samples could be explained by hydrolysis of lipids to form the fatty acid during PLE extraction and simultaneous esterification of the acid with methanol (Kocsisová et al., 2005). This indicates that the PLE method with methanol, high pressure and temperature creates artifacts, which might be prevented by use of a non-alcohol solvent.

Another factor to explain the relatively high concentrations of these two compounds in the exposed dust samples is the amount of ozone added to the system. If the consumption by the empty FLEC is considered the amount of ozone available for reaction with the dust (deposition and chemical reactions) was 0.0022 mmol h⁻¹ (see Fig. S6). Thus for the total exposure times (Fig. 4) the amount of available ozone was 0.046–0.18 mmol. For the four dust samples this is a factor of respectively 7, 11, 1.3 and 4 times less than the total amount of octadecenoic acid and its methyl ester in decane equivalents). In this consideration other reactive compounds was excluded so the potentially amounts of ozone available for reaction with octadecenoic acid and its methyl ester were even less. Other effective ozone scavengers are squalene and cholesterol (Petrick and Dubowski, 2009; Weschler et al., 2011). These compounds are not detected with the GC–MS method utilized in this study due to their high boiling points.

Though the concentration of octadecenoic acid and its methyl ester are determined as decane equivalents, and thus only roughly estimated, it is evident that the dust samples are not completely exhausted of reactive compounds in steady state.

In the present study, no further investigation of the ratio between chemical reaction and heterogeneously breakdown of ozone has been conducted. A previous study by Coleman et al. (2008) found that 0.07–0.24 mole of products volatile per mole of ozone consumed in the reaction between ozone (120 ppb) and aircraft materials and clothing fabrics. This supports the hypothesis that only a small fraction of the reactive compounds actually reacts with ozone before steady state is reached.

4. Conclusions

Steady state reaction rates (k_dust) and maximum reaction rates of the interaction between ozone and floor dust were determined based on ozone consumption vs. time curves for four different samples. k_dust in the range 0.039–0.14 1/s pr. g dust at 50% RH. It was shown that the steady state reaction rate was independent of O₂ inlet at 1.6 and 2.2 ppm. Ozone k_dust and k_dust-values converted from k_dust for the dust samples were in the range 0.008–0.029 cm s⁻¹ and comparable with carpet and indoor environment studies measured at lower ozone concentrations. Relative humidity was found

![Fig. 4. Octadecenoic acid and octadecenoic acid methyl ester in dust samples (Dusts 1–4, Section 3.2) before and after ozone exposure. Total exposure time is indicated for each of the dust samples. Error bars indicate standard deviation of two samples.](http://dx.doi.org/10.1016/j.chemosphere.2013.12.048)
to influence $k_{\text{diff}}$ with a maximum value at 25% RH relative to 0% and 50% RH.

From the amount of added ozone and initial amount of SVOCs it was concluded that not all unsaturated volatiles were likely to have completely reacted when the system reached steady state, and thus that the removal of ozone at this point was caused both by heterogeneous breakdown on surfaces and chemical reactions limited by mass transport of reactant molecules from within the dust particles. The major reaction products from the dust/ozone reaction included aldehydes, such as heptanal, octanal, nonanal and decanal, that may impact the indoor air quality.

The implication for indoor air is that dust can also act as an effective ozone scavenger and thus help to improve indoor air quality, however this positive effect might be counteracted by the release of aldehydes and other reaction products. Investigation of more dust samples is required for a generalization to indoor air.

Acknowledgements

This study was a part of the Centre for Indoor Air and Health in Dwellings (CISBO) study, which was supported by the REALDANIA foundation. We thank Vivi Kofoed-Sørensen (NR CWE) for technical assistance, Dr. Renie Birkedal (NRCWE) for the TGA analysis, and prof. Torben Sigsgaard from University of Aarhus for supply of dust samples.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.12.048.

References


Supplementary material

Ozone reaction characteristics of floor dust examined in the emission cell “FLEC”

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Corresponding author: Anni Vibenholt, avi@nrcwe.dk, Tel: +45 39165276
Figure S1: Dust spread on SS plate before ozone exposure.

Figure S2: Steady state reaction rate in an empty FLEC as a function of the inlet ozone concentration at the FLEC inlet.

\[ y = 2 \times 10^{-6}x + 0.1086 \]

\[ R^2 = 0.0447 \]
Figure S3: Experimental setup for the study of ozone/dust reactions.
Figure S4 – Chromatogram on-column of extracts.

Figure S5: Chromatogram of PLE extract of Dust 4 injected onto Tenax TA and analyzed with thermal desorption.
O₃=FLEC $\approx$ 1600 ppb in 500 ml air

Conversion to molecules/cm³ using the ideal gas law at 22 °C, 1 bar (pV=nRT):

$$O_3=FLEC \cdot 3.99 \cdot 10^{-11} = 1100 \text{ ppb} / 3.99 \cdot 10^{-11} = 4.0 \cdot 10^{13} \text{ molecules/cm}^3$$

Conversion to mol/ml using the Avogadro constant:

$$O_3=FLEC \cdot N_A = 4.0 \cdot 10^{13} \text{ molecules/cm}^3 / 6.022 \cdot 10^{23} \text{ molecules/mol} = 6.7 \cdot 10^{-11} \text{ mol/cm}^3$$

Conversion to mol/h at a flow of 450 ml/min (30000 cm³/h):

$$O_3=FLEC \cdot 30000 \text{ cm}^3 / h = 6.7 \cdot 10^{-11} \text{ mol/cm}^3 \cdot 30000 \text{ cm/h} = 2.0 \cdot 10^{-6} \text{ mol/cm}^3 = 0.0020 \text{ mmol/h}$$

Figure S6: Calculation of ozone available for reactions with dust.
identified compounds were reported along with the probability of a correct identification (prob ID) from the NIST database. If a possible co-eluding compounds. The deconvoluted spectra were used for identification via searches in the NIST database. All Table S1: Unknown compounds in the GC-MS chromatograms were screened and identified using the AMDIS software (Stein, 1999) and NIST database (2011). In AMDIS each significant chromatographic peak was deconvoluted to obtain spectra free from possible co-eluding compounds. The deconvoluted spectra were used for identification via searches in the NIST database. All identified compounds were reported along with the probability of a correct identification (prob ID) from the NIST database. If a

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Comments:
A: It is not determined whether it is m-, o- or p-xylene, therefore no CAS no. or prob. ID
A compound was found in one sample, all other samples were searched for this compound. The criterion for a positive identification was that both retention time and mass spectra was similar in all samples.

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<td>Decanal</td>
<td>1.5</td>
<td>0.65</td>
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<tr>
<td>2-Phenoxyethanol</td>
<td>1.1</td>
<td>0.13</td>
</tr>
<tr>
<td>Nonanoic acid methylester</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Nonanal dimethyl acetal</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Octanedioic acid dimethyl ester</td>
<td>1.57</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Table S2: Area counts of given compounds in the exposed samples compared to the unexposed for Dust 1-4 (Section 3.2). The compounds are listed in the order of increasing retention time. Abbreviations: n.d.: Not detected.
Appendix B (Paper II)

Direct quantitative analysis of PAHs, phthalates and fatty acids on Teflon filters using Low Temperature Plasma ionization MS.

Authors: Anni Vibenholt, Per Axel Clausen, Asger W. Nørgaard and Peder Wolkoff
Direct quantitative analysis of PAHs, phthalates and free fatty acids on Teflon filters using Low Temperature Plasma ionization MS

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National Research Centre for the Working Environment, Copenhagen, Denmark

Keywords: LTP-MS, PAH, Phthalate, Free fatty acid

Abstract

The quantitative properties of low temperature plasma ionization mass spectrometry (LTP-MS) were investigated for selected PAHs (including naphthalene, fluorene, anthracene, and pyrene), free fatty acids (lauric, myristic, palmitic, oleic and stearic acid), and phthalates (dimethyl, diethyl, dibutyl, benzylbutyl and bis(2-ethylhexyl) phthalate). Limit of quantitation (LOQ) was estimated for a 23 m$^3$ air sample (LOQ for PAHs: 0.86-14 ng/m$^3$; phthalates: 23-69 ng/m$^3$; free fatty acids: 190-540 ng/m$^3$). The maximum concentration within the linear range was: PAHs: 2.0-39 ng/m$^3$; phthalates: 690-2600 ng/m$^3$; free fatty acids: 8500-38000 ng/m$^3$). The method was applied to residential airborne particles sampled on Teflon filters.

Introduction

Low Temperature Plasma ionization (LTP) is a recently developed ambient ionization technique where cold plasma (ca. 30 °C) is utilized for ionization followed by mass spectrometric analysis (Harper et al., 2008). Ambient conditions permit direct analysis of samples in their native environment with little or no sample preparation, thus LTP is suited for analysis of compounds in complex matrices either in liquids or on surfaces. The desorption mechanism is governed by thermal processes (Chan et al., 2011), thus LTP works best for volatile and semi volatile compounds.

LTP-MS has been used in a range of different application, e.g. real-time monitoring of on-going reactions on surfaces (Nørgaard et al 2011; 2013), explosives (Garcia-Reyes et al., 2011), crude oil (Benassi et al., 2013), and on-line detection of indoor volatile organic compounds (VOCs) (Gong et al., 2011), structural elucidation of unsaturated fatty acids and esters (Zhang et al., 2011).

In the present study we evaluate the quantitative properties for LTP of selected organic compounds that are sampled on Teflon filters. The filters are analysed directly without sample preparation, and thus yields only a total mass spectrum without chromatographic separation. The selection of compounds was based on a screening of airborne material sampled on Teflon filters in homes. These samples were dominated by free fatty acids and phthalates. A standard mixture of polycyclic aromatic hydrocarbons (PAHs) was also
included in the investigation in order to extend future use of this method to outdoor air samples, where these are abundant compounds.

Experimental

Chemicals

Dodecanoic acid (≥99%), myristic acid (≥99%), palmitic acid (≥99%), oleic acid (≥99%), octadecanoic acid (≥98.5%), DEHP (Pestanal® grade, Fluka), methanol (LC-MS grade, Fluka), PAH mixture (EPA 610 PAH kit), phthalate mixture (EPA phthalate Esters), and Teflon filters (Zeflour™, O.D. 37 mm, pore size 2 µm) were purchased from SigmaAldrich.

LTP-MS

The LTP probe used in this study was based on the experimental set up used by Harper et al. (Harper et al., 2008) in which the plasma is generated inside a small glass tube by an alternating high voltage applied to an outer electrode wrapped around the glass tube and a low flow (< 0.3 l/min) of discharge gas (He, Ar, N₂ or air). The glass tube was pointed towards the sample and the He-plasma ionizes the compounds at the surface.

The LTP probe was kept at a 45° angle and the distance between the probe and the Teflon filter was fixed at ca. 3 mm (Figure 1). Helium (purity 5.0) was used as discharge gas at a flow rate of 0.2 L/min. The mass spectrometer, a Bruker micrOTOF-Q (Bruker Daltonics, Bremen, DE), was operated in both negative and positive mode with a potential of 1.5 kV applied to the MS inlet capillary. The mass range was m/z 45-3000. The flow rate and temperature of the dry gas were 4 L/min and 250 °C, respectively. The temperature and the relative humidity at the sampling position were 80 ± 5 °C and ca. 1%, respectively, measured by a Testo 650 (Testoterm GmbH & Co, Germany).

![Figure 1: Principle sketch of LTP-MS setup](image-url)
Evaluation of quantification on LTP-MS

Calibration, limit of detection, and recovery

Stock solutions containing a single compound; palmitic acid and DEHP and mixtures of free fatty acids, phthalates, and PAHs were prepared. The compositions of the stock solutions are summarized in Table 1. A Teflon filter was cut into quarters and a droplet (10 µl) of each standard solution was placed on the tip of each quarter for analysis. The hygroscopic property of the Teflon surface caused the formation of an uniform droplet with a diameter of about 3 mm. Each droplet was allowed to dry under ambient conditions before placed in front of the LTP-probe. A blank filter was analysed prior to each standard and used for background subtraction.

Table 1: Summary of the quantitative properties for PAHs, free fatty acids and phthalates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Stock solution [pg/µl]</th>
<th>Calibration (linear regression)</th>
<th>Recovery [%]</th>
<th>Quantiﬁcation range [ng/m^3]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[M+H]^+</td>
<td></td>
<td></td>
<td>LOQ - Max</td>
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<tr>
<td></td>
<td></td>
<td>r²</td>
<td>Response factor [counts/(ng/µl)]</td>
<td>Intercept [ng/µl]</td>
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<td>PAH mix</td>
<td></td>
<td></td>
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<tr>
<td>Naphtalene</td>
<td>129.0699</td>
<td>100</td>
<td>0.82</td>
<td>5.5·10^3</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>153.0699</td>
<td>2000</td>
<td>0.94</td>
<td>3.8·10^3</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>155.0856</td>
<td>1000</td>
<td>0.96</td>
<td>6.0·10^3</td>
</tr>
<tr>
<td>Fluorene</td>
<td>167.0856</td>
<td>200</td>
<td>0.82</td>
<td>1.0·10^3</td>
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<tr>
<td>Anthracene</td>
<td>179.0856</td>
<td>100</td>
<td>0.66</td>
<td>3.2·10^3</td>
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<tr>
<td>Phenanthrene</td>
<td>203.0855</td>
<td>200</td>
<td>0.71</td>
<td>5.3·10^3</td>
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<tr>
<td>Fluoroanthene</td>
<td>229.1012</td>
<td>100</td>
<td>0.38</td>
<td>2.1·10^3</td>
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<tr>
<td>Pyrene</td>
<td>253.1012</td>
<td>200</td>
<td>0.69</td>
<td>2.5·10^3</td>
</tr>
<tr>
<td>Pyrene</td>
<td>277.1012</td>
<td>100</td>
<td>0.005</td>
<td>1.9·10^3</td>
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<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>279.1168</td>
<td>200</td>
<td>0.009</td>
<td>5.6·10^4</td>
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<tr>
<td>Free fatty acid mix</td>
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<tr>
<td>Lauric acid</td>
<td>199.1693</td>
<td>1400</td>
<td>0.98</td>
<td>1.9·10^4</td>
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<td>Myristic acid</td>
<td>227.2066</td>
<td>1800</td>
<td>0.96</td>
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<td>Palmitic acid</td>
<td>255.2319</td>
<td>1200</td>
<td>0.97</td>
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<td>Oleic acid</td>
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<td>2000</td>
<td>0.93</td>
<td>7.3·10^3</td>
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<tr>
<td>Stearic acid</td>
<td>283.2632</td>
<td>1400</td>
<td>0.96</td>
<td>2.2·10^4</td>
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<tr>
<td>Phthalate mix*</td>
<td>[M+H]^+</td>
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<td></td>
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<td>Dimethyl phthalate (DMP)</td>
<td>195.0652</td>
<td>2000</td>
<td>0.56</td>
<td>8.9·10^3</td>
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<td>Diethyl phthalate (DEP)</td>
<td>223.0965</td>
<td>2000</td>
<td>0.63</td>
<td>1.0·10^4</td>
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<td>Dibutyl phthalate (DBP)</td>
<td>279.1391</td>
<td>2000</td>
<td>NA</td>
<td>NA</td>
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<td>Benzyl butyl phthalate (BBP)</td>
<td>313.1434</td>
<td>2000</td>
<td>0.89</td>
<td>8.3·10^4</td>
</tr>
<tr>
<td>Bis(2-ethylhexyl) phthalate (DEHP)</td>
<td>391.2843</td>
<td>2000</td>
<td>0.94</td>
<td>1.6·10^4</td>
</tr>
<tr>
<td>Individual compounds</td>
<td></td>
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<tr>
<td>Palmitic Acid</td>
<td>0.95</td>
<td>3.1·10^4</td>
<td>-1.6·10^4</td>
<td>107±41 (n=6)</td>
</tr>
<tr>
<td>Bis(2-ethylhexyl) phthalate (DEHP)</td>
<td>0.90</td>
<td>1.4·10^4</td>
<td>3.8·10^3</td>
<td>147±3.7 (n=2)</td>
</tr>
</tbody>
</table>

NA: Not applicable, see text. *: Quantifier ions: 163 (DMP), 177 (DEP), 313 (BBP), and 391 (DEHP). #: LOQ recalculated for 23 m³ air samples (see text); linear range from LOQ to maximum concentration before saturation.
Calibration curves were obtained by consecutive dilution of the stock solution with methanol until the signal was comparable to the background signal. All calibration curves were carried out in duplicate with two spots for each concentration. For calibration only data points within the linear range was used. The maximum of the linear range was determined as the concentration of the highest standard within the range. For each data point in the calibration range, a third analysis was performed to evaluate the recovery of the method. Recoveries were thus calculated for the whole concentration range within the linear range. Limit of quantitation (LOQ) was estimated as 10 times the standard deviation of 20 repeated analyses of the second lowest standard.

The free fatty acids were analysed in negative ion mode with \([\text{M-H}]^-\); PAH mixture in positive ion mode with \([\text{M+H}]^+\) as quantifier ions and phthalates in positive ion mode with quantifier ions as given in Table 1.

**Sampling and analysis of indoor air samples**

Particles were sampled onto Teflon filters using a KTL PM$_{2.5}$ cyclone as preseparator (Jantunen et al., 1998) and a BGI400 pump (BGI, inc., Waltham, MA, USA). The sample flow was 4.0±0.2 L/min. Each filter was sampled for 4 days, yielding a total sample volume of about 23 m$^3$. A total of 40 samples were collected. The filters were LTP exposed and analysed for 1.5 min in 3 spots and spectra were recorded at a rate of 1 Hz. Each experiment was initiated with a 0.5 min analysis of a blank filter for background correction.

The quantification on filters from the residential sampling was based on three assumptions: The analytes within the droplet of standard were evenly distributed over the whole area of the dried droplet; the analytes on the residential air samples were sampled evenly over the whole filter and the droplet of standard was larger than the sampling area of the LTP probe tip, thus sampling only occurred where the standards were present at the filter. The analytical signal was thus expected to correlate with the concentration pr. area of the filter. The diameter of each droplet of standard solution was 3 mm and the quantification limit in ng/µl could be converted to concentrations in ng/mm$^2$ by the following equation:

$$C_A = \frac{C_s \cdot V_d}{A_d}$$

Where: $V_d$: Volume of droplet [µl]; $A_d$: Area of droplet [mm$^2$]; $C_s$: Concentration in standard solution [ng/µl]; $C_A$: Concentration in ng/mm$^2$. To determine LOQ in 23 m$^3$ air samples the concentration in ng/mm$^2$ was multiplied by the total area of the filter and divided by 23 m$^3$. 

Results and discussion

Evaluation of quantitative properties of LTP-MS

Selection of quantifier ions

The mass spectre of the free fatty acids were dominated by molecular ions, which allowed simultaneous analysis by use of [M+H]$^+$ ions of the compounds without interference. The phthalates showed a high degree of fragmentation. The phthalic anhydride ion ($m/z$ 149) is characteristic for phthalates in general and also well suited for qualitative analysis, but causes interference between phthalates in LTP-MS. [M+H]$^+$ ions are less abundant in most phthalates; however with the fragmentation and structural likeness of the phthalates, some fragment ions were the same as [M+H]$^+$ ions derived from other phthalates. The quantification was therefore performed both with a solution containing only DEHP and a solution containing a mixture of 5 phthalates (Table 1). In the mixture [M+H]$^+$ was a suitable quantifier ion for DEHP and BBP, the fragment ion at $m/z$ 163 for DMP, and $m/z$ 177 for DEP, whereas DBP was found to have no characteristic fragment ions. The PAHs showed a low degree of fragmentation, thus [M+H]$^+$ ions were the most abundant. Some of the PAHs are isobaric isomers, and indistinguishable from each other, thus each set of isobaric isomers were treated as one compound, and their response factors were assumed to be similar.

PAHs

The response factors depended on the molecular mass (Figure 2) and was highest for fluoranthene and pyrene at $m/z$ 203. The signal for all compounds below $m/z$ 203 peaked early in the run (Figure 3). Fluoranthene and pyrene ($m/z$ 203) reached a maximum fast and maintained a high signal for about 1 min, while the compounds with $m/z$ above 203 started at zero and increased slowly throughout the run time. This different behavior could be the difference in boiling point/vapor pressure and thereby vaporization on the sampling table. The lower boiling compounds vaporized fast and were completely evaporated, whereas the higher boiling compounds only were released slowly from the filter, thus indicating that gas phase concentration has a major impact on the ionization efficiency.

![Figure 2: PAH response factors as a function of molecular mass for background subtracted LTP-MS averaged over 1.5 min](image-url)
No correlation was found in the calibration for the three highest boiling PAHs; Benzo[ghi]perylene (b.p. 500°C), indeno[1,2,3-cd]pyrene (b.p. 497°C) and dibenzo[a,h]anthracene (b.p. 524°C) due to the low volatility. This shows that a minimum vapor pressure is necessary for efficient LTP ionization.

The quantitative properties of the PAH mixture are summarized in Table 1. Due to the simultaneous analysis of the 16 PAHs, the system reached saturation at relatively low concentration and the maximum of the linear range would probably be higher for individual compounds.

**Phthalates**

Both molecular and fragment ions were used for the calibration, thus comparison of response factors as a function of molecular mass as for PAHs is not applicable for phthalates. BBP ($m/z=313$) and DEHP ($m/z=391$) showed satisfactory calibration and recovery, whereas DMP ($m/z=163$) and DEP ($m/z=177$) showed poorer calibration, but good recoveries (Table 1). For DEHP analyzed as an individual compound the maximum concentration within the linear range was about 5 times higher than for DEHP in the mixture and the response factor a factor of about 10 higher.

**Free fatty acids**

A similar dependence between molecular mass and response factors as for PAHs was observed for the mixture of free fatty acids. The optimal molecular mass was about 250 g/mol; similar to that of PAHs. All free fatty acids showed satisfactory calibration and recovery (Table 1). As for the phthalates, the linear range was larger for palmitic acid analyzed as an individual compound compared to the mixture by a factor of app. 10 for the maximum concentration within the linear range.

**Analysis of residential Teflon filters**

The dominating peaks in the LTP-MS of residential Teflon filters were $m/z$ 255 originating from palmitic acid and $m/z$ 149 from phthalates. The average standard deviation between 3 sampling points on each filter was
16% for m/z 149 and 18% for m/z 255, indicating that the variation between different areas of the filter is acceptable. However it has not been investigated whether the variation originated from inhomogeneity of the sampling or the variations from the ambient ionization.

No PAH were detected on any of the filters.

Table 2: Summary of free fatty acids and phthalates determined with LTP-MS on Teflon filters.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>n detected (S/N&gt;3)</th>
<th>n (C&gt;LOQ)</th>
<th>n quantified (max C&gt;C&gt;LOQ)</th>
<th>Concentration [ng/m^3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric acid</td>
<td>24</td>
<td>10</td>
<td>10</td>
<td>330-2000</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>32</td>
<td>18</td>
<td>18</td>
<td>320-9500</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>37</td>
<td>35</td>
<td>28</td>
<td>970-7500</td>
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<td>Oleic acid</td>
<td>30</td>
<td>23</td>
<td>21</td>
<td>550-12000</td>
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<td>Stearic acid</td>
<td>34</td>
<td>33</td>
<td>33</td>
<td>536-34000</td>
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<tr>
<td>DMP</td>
<td>30</td>
<td>6</td>
<td>6</td>
<td>37-140</td>
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<tr>
<td>DEP</td>
<td>35</td>
<td>17</td>
<td>17</td>
<td>33-589</td>
</tr>
<tr>
<td>BBP</td>
<td>38</td>
<td>19</td>
<td>19</td>
<td>8-550</td>
</tr>
<tr>
<td>DEHP</td>
<td>38</td>
<td>11</td>
<td>11</td>
<td>32-780</td>
</tr>
</tbody>
</table>

Conclusions

In LTP-MS quantification of phthalates and free fatty acids on Teflon filters, great care should be taken about the linear range. The system reached saturation within only a factor of 10-100 of LOQ. For compounds with little fragmentation, e.g. free fatty acids and PAHs, the chromatographic separation can be substituted with the high resolution mass spectral separation, but this poses a major problem for simultaneous analysis of compounds with a higher degree of fragmentation, e.g. phthalates. The maximum concentration within the linear range was substantially decreased for compounds analyzed in a mixture, and this would most likely also be the case for compounds in a complex matrix.

The correlation between boiling point/vapor pressure and response factor for PAHs and free fatty acids shows that the LTP ionization efficiency of the compounds may depend on their volatility and the time subjected to heat; thus indicating that the ionization takes place in the gas phase after evaporation rather than the plasma itself causes desorption from the surface.

The method is more suited for a fast screening of high vs. low concentration prior to a more conventional quantification or for applications where only a fast qualitative method is required.

Some of the uncertainties in the quantitation might arise from the manual deposition of standards onto the filter and thus the distribution of the compounds. This uncertainty could be minimized with a well-controlled gas phase deposition onto the filter or if an autosampler system was developed for the LTP.
Perspectives

A comparison with determination of phthalates and free fatty acids on the residential filters with a Thermal Desorption (TD) GC-MS, raised several questions with respect to the assumptions made in the LTP-MS quantification, and some of these needs a further investigation prior to submission of this manuscript. Similar the method could be improved with respect to LOQ and maximum concentration before saturation.

Acknowledgements

This study was a part of the Centre for Indoor Air and Health in Dwellings (CISBO) study, which was supported by the REALDANIA foundation. We thank Vivi Kofoed-Sørensen from NRCWE for technical assistance.

References


App. C: Example of diary page for one sampling day

```
Sophus Schandorphs Vej 3
3. Måleuge
Dag: Torsdag
23.09.2010

I ca. hvilket tidsrum er vinduerne i følgende rum åbne? Hvis vinduet er åbent skrivet et "A", er vinduet på klem skrevet et "K". Hvis vinduet er åbent/på klem i mere end en time indikerer tidstrækket med en streng i de felter som repræsenterer dette tidsrum. (Se eksempel)

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Kommentarer til åbning af vinduer kan noteres på bagseiten

Hvornår er der en eller flere personer tilstede i boligen OG i hvilket tidsrum bliver følgende aktiviteter udført

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Kommentarer til aktiviteter kan noteres på bagseiten

Hvornår opholder du dig i soveværelset følgende nat. Start tidspunktet er når du går i seng. I tilfælde af overnattende gæster noteres venligst i hvilket tidsrum samt deres højde og vægt (see eksempel).

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Kommentarer kan noteres på bagseiten
Appendix D: Structures and boiling points of PAHs, phthalates and free fatty acids.

- **Naphthalene**
  - b.p.: 218 °C

- **Fluoranthene**
  - b.p.: 375 °C

- **Benzo[b]fluoranthene**
  - b.p.: 481 °C

- **Aecnaphthen**
  - b.p.: 279 °C

- **Pyrene**
  - b.p.: 404 °C

- **Benzo[a]pyrene**
  - b.p.: 495 °C

- **Acenaphtylene**
  - b.p.: 280 °C

- **Benz[a]anthracene**
  - b.p.: 438 °C

- **Benzo[ghi]perylene**
  - b.p.: 500 °C

- **Fluorene**
  - b.p.: 295 °C

- **Chrysene**
  - b.p.: 448 °C

- **Dibenzo[a,h]anthracene**
  - b.p.: 524 °C

- **Phenanthrene**
  - b.p.: 332 °C

- **Benzo[k]fluoranthene**
  - b.p.: 480 °C

- **Indeni[1,2,3-cd]pyrene**
  - b.p.: 536 °C

- **Anthracene**
  - b.p.: 340 °C
Appendix D: Structures and boiling points of PAHs, phthalates and free fatty acids.

Dimethyl phthalate (DMP)
\[ \text{b.p.: 283 °C} \]

Diethyl phthalate (DEP)
\[ \text{b.p.: 295 °C} \]

Dibutyl phthalate (DBP)
\[ \text{b.p.: 340 °C} \]

Benzyl butyl phthalate (BBP)
\[ \text{b.p.: 370 °C} \]

di-2-ethylhexyl phthalate (DEHP)
\[ \text{b.p.: 385 °C} \]

Lauric acid (C12:0)
\[ \text{b.p.: 299 °C} \]

Myristic acid (C14:0)
\[ \text{b.p.: 326 °C} \]

Palmitic acid (C16:0)
\[ \text{b.p.: 351 °C} \]

Oleic acid (C18:1 cis-9)
\[ \text{b.p.: 360 °C} \]

Stearic acid (C18:0)
\[ \text{b.p.: 376 °C} \]