Oxidation of terpenes in indoor environments
A study of influencing factors

Linda Pommer

Akademisk avhandling

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Abstract

In this thesis the oxidation of monoterpenes by O$_3$ and NO$_2$ and factors that influenced the oxidation were studied. In the environment both ozone (O$_3$) and nitrogen dioxide (NO$_2$) are present as oxidising gases, which causes sampling artefacts when using Tenax TA as an adsorbent to sample organic compounds in the air. A scrubber was developed to remove O$_3$ and NO$_2$ prior to the sampling tube, and artefacts during sampling were minimised when using the scrubber. The main organic compounds sampled in this thesis were two monoterpenes, α-pinene and Δ$^3$-carene, due to their presence in both indoor and outdoor air. The recovery of the monoterpenes through the scrubber varied between 75-97% at relative humidities of 15-75%.

The reactions of α-pinene and Δ$^3$-carene with O$_3$, NO$_2$ and nitric oxide (NO) at different relative humidities (RHs) and reaction times were studied in a dark reaction chamber. The experiments were planned and performed according to an experimental design where the factors influencing the reaction (O$_3$, NO$_2$, NO, RH and reaction times) were varied between high and low levels. In the experiments up to 13% of the monoterpenes reacted when O$_3$, NO$_2$, and reaction time were at high levels, and NO, and RH were at low levels. In the evaluation eight and seven factors (including both single and interaction factors) were found to influence the amount of α-pinene and Δ$^3$-carene reacted, respectively. The three most influencing factors for both of the monoterpenes were the O$_3$ level, the reaction time, and the RH. Increased O$_3$ level and reaction time increased the amount of monoterpenes reacted, and increased RH decreased the amount reacted.

A theoretical model of the reactions occurring in the reaction chamber was created. The amount of monoterpenes reacted at different initial settings of O$_3$, NO$_2$, and NO were calculated, as well as the influence of different reaction pathways, and the concentrations of O$_3$ and NO$_2$, and NO at specific reaction times. The results of the theoretical model were that the reactivity of the gas mixture towards α-pinene and Δ$^3$-carene was underestimated. But, the calculated concentrations of O$_3$, NO$_2$, and NO in the theoretical model were found to correspond to a high degree with experimental results performed under similar conditions.
The possible associations between organic compounds in indoor air, building variables and the presence of sick building syndrome were studied using principal component analysis. The most complex model was able to separate 71% of the “sick” buildings from the “healthy” buildings. The most important variables that separated the “sick” buildings from the “healthy” buildings were a more frequent occurrence or a higher concentration of compounds with shorter retention times in the “sick” buildings.

The outcome of this thesis could be summarised as follows;
- A scrubber was developed to remove O₃ and NO₂ prior to the sampler to avoid sampling artefacts.
- Levels of O₃, NO₂, NO, different interactions and RH were found to influence the oxidation of α–pinene and Δ⁴–carene.
- Calculations of the developed theoretical models underestimated the reactivity of α–pinene and Δ⁴–carene, but the calculated levels of O₃, NO₂ and NO corresponded well with experimental results.
- By using a multivariate method using chemical measurements of indoor air and building data as input variables it was possible to separate “sick” buildings from “healthy” buildings.

**Keywords:** Monoterpene, Ozone (O₃), Nitrogen dioxide (NO₂), Nitrogen oxide (NO), Relative humidity (RH), Modelling, Scrubber, Experimental design, Interaction, Volatile organic compounds (VOC), Sick buildings syndrome (SBS), Principal component analysis (PCA), Indoor air, Ventilation, Tenax TA, Sodium sulphite.

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**List of papers**

This thesis is based on the papers listed below, which are referred to in the text by the corresponding Roman numeral (I-IV).

**I.** Development of a NO₂ scrubber for accurate sampling of ambient levels of terpenes.
Linda Pommer, Jerker Fick, Barbro Andersson, and Calle Nilsson

**II.** The influence of O₃, relative humidity, NO and NO₂ on the oxidation of α-pinene and Δ₃-carene.
Linda Pommer, Jerker Fick, Calle Nilsson and Barbro Andersson
*Submitted to Atmospheric Environment*, 2002.

**III.** Modelling the reaction of α-pinene and Δ₃-carene with O₃ and NO₂. Comparison between theoretical and experimental results
Linda Pommer, Jerker Fick, Calle Nilsson and Barbro Andersson
*Submitted to Atmospheric Environment*, 2003.

**IV.** Class Separation of buildings with high and low prevalence of SBS by Principal Component Analysis.
Linda Pommer, Jerker Fick, Barbro Andersson, Jan Sundell, Calle Nilsson, Michael Sjöström and Berndt Stenberg
*Indoor Air*, In press.

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Abbreviations

AMCH 4-acetyl-1-methyl cyclohexene
ATD Automatic thermal desorption
DoE Design of experiments
FID Flame ionisation detector
FLEC Field and laboratory emission cell
GC Gas chromatography
I/O Indoor levels/Outdoor levels
KI Potassium iodide
MLR Multiple linear regression
MnO₂ Manganese dioxide
MS Mass spectrometer
N₂O₅ Dinitrogen pentoxide
Na₂SO₃ Sodium sulphite
NO Nitric oxide
NO₂ Nitrogen dioxide
NOₓ Nitrogen oxides, the sum of NO₂ and NO
NO₃⁻ Nitrate radical
O₃ Ozone
OH⁻ Hydroxyl radical
PAN Peroxy acetyl nitrate
PC Principal component
PCA Principal component analysis
PLS Partial least squares projection to latent structures
PLS-DA Partial least squares projection to latent structures – discriminant analysis
ppb Parts per billion
RH Relative humidity
RSD Relative standard deviation
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>Sick building syndrome</td>
</tr>
<tr>
<td>SD</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>SIMCA</td>
<td>Soft independent modeling of class analogy</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>Sulphur dioxide</td>
</tr>
<tr>
<td>TVOC</td>
<td>Total of volatile organic compounds</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compounds</td>
</tr>
</tbody>
</table>
Table of contents

List of papers..................................................................................................................I
Abbreviations................................................................................................................. III

1. Introduction................................................................................................................. 1
   Aim of this thesis........................................................................................................ 3

2. Gas-phase contaminants in the environment ........................................ 5
   Volatile organic compounds (VOC) .........................................................................5
   Monoterpenes............................................................................................................. 6
   Ozone (O₃).................................................................................................................. 9
   Nitrogen dioxide (NO₂) and nitric oxide (NO).........................................................9

3. Atmospheric chemistry ....................................................................................... 11
   The chemistry of ozone, nitrogen dioxide and nitric oxide................................. 11
   Reactions of monoterpenes in the gas-phase ......................................................... 12
   Factors influencing the reactions of monoterpenes.............................................. 14
   Modelling in atmospheric chemistry..................................................................... 14
   Modelling indoor air compartments...................................................................... 15

4. Test atmospheres ............................................................................................. 19
   Static chambers .................................................................................................... 22
   Dynamic chambers .............................................................................................. 22
   Experimental chamber used in Papers I and II................................................... 23
   Standard generation ............................................................................................ 24

5. Sampling of VOC and atmospheric oxidants........................................... 25
   Concentration and sampling of VOC.................................................................... 25
   Diffusive sampling and active sampling .............................................................. 27
   Adsorbents suitable for thermal desorption...................................................... 27
      Tenax TA........................................................................................................... 28
   Sampling in the present studies........................................................................... 29
      Conditioning the sample tubes........................................................................ 29
      Sampling .......................................................................................................... 29
      Statistics about the performance of the sampling method....................... 29
6. Sample analysis and continuous monitoring
   Analysis of VOC .................................................. 33
   Continuous monitoring of atmospheric oxidants ............. 34
   O₃ ........................................................................... 34
   NO₂ and NO ....................................................... 35
   7. Interference of oxidants during sampling .................. 37
   Degradation of the adsorbent ....................................... 37
     Effects of O₃ on Tenax ......................................... 37
     Effects of NO₂ on Tenax ....................................... 38
   Oxidation of sampled VOC on the adsorbent .................. 38
     Oxidation caused by O₃ ......................................... 38
     Oxidation caused by NO₂ ....................................... 40
   Removing oxidants prior the sampling tube .................... 41
     O₃ scrubbers ...................................................... 41
     NO₂+O₃ scrubbers .............................................. 42
   8. Multivariate methods ............................................ 45
     Principal Component Analysis (PCA) ......................... 46
     Design of Experiments (DoE) .................................. 47
   9. Sick building syndrome ........................................ 51
     Definition .......................................................... 51
     SBS and VOC ..................................................... 52
     SBS and ventilation ............................................. 54
   10. Multivariate methods and atmospheric chemistry ....... 57
   11. Theoretical modelling – possibilities and difficulties .... 61
   12. The effect of changing relative humidity and pollution load ... 65
     The role of relative humidity .................................. 65
     Change in pollutant load ....................................... 67
   13. Conclusions and future work .................................. 69
   14. Acknowledgement ............................................... 71
   15. References ...................................................... 73
   16. Summary of papers ............................................. 83
Introduction

The air is a fundamental media for the existence of humans. Hypothetically, you can say that we are the air that we are breathing. One of the most important things for us is to have access to unpolluted air together with unpolluted water and soil.

The quality of the air around us, and its influence on our health has attracted much attention since incidents with high air pollution occurred in the middle of the 20th century. In the smog episodes in London in 1873 and 1952, pollutants were emitted due to burning coal for domestic heating in the winter. The pollution consisted of volatile organic compounds (VOC), sulphur dioxide (SO2) and particles, which together are referred to as smoke. On days with inversion, i.e. low temperatures and fog, the pollution was trapped over the city, and the smoke and fog combined to form smog. The effect of the smog episode in 1952 was an excess of 12 000 deaths in London, which were presumably due to both acute and persisting effects1. This episode initiated actions to reduce pollution in cities such as the use central heating and legislation promoting the use of cleaner coal, and the use of higher chimneys to disperse the pollution.

Urban air pollution problem attributable to automobile exhaust appeared in Los Angeles in the 1940s. An episode with a high concentration of pollutants occurred in the summertime during warm days with bright sunlight, low wind speed and low inversion height. These conditions were ideal for the formation of photochemical smog. The aerosol produced is neither smog nor fog, but reactants and products formed from the chemical reactions between organic gases, nitrogen oxides (NOx) and most importantly, ozone (O3). Both organic gases and ni-
tno oxides are mainly exhaust from cars. The presence of photochemical smog has re-introduced air pollution as a major environmental health issue.

The problem with the quality of outdoor air has resulted in restrictions of emissions from different pollutant sources in order to improve the air quality. Despite legislation, improvement of different combustion sources (e.g. fuel combustion) and improved cleaning of exhaust air, the levels of pollutants in urban areas are still a problem effecting health. On days with high levels of particles, for example, persons with asthma can experience limited breathing. Health effects such as cancer, eye irritation, headache, irritation of mucous membranes and limited breathing are also reportedly caused by enhanced levels of O₃, VOC, soot, SO₂, and nitrogen dioxide (NO₂). Increased mortality has also been observed at a 25 ppb increase in the O₃ concentration. Associations between NO₂ and mortality were also found, but NO₂ was suggested to represent a mixture of traffic related air pollution. In an estimation of Brunekreef and Holgate, 40 000 deaths per year were attributable to air pollution in Austria, France and Switzerland combined (population ~74.5 million people).

In air quality guidelines set by the World Health Organisation (WHO), the European Union (EU) and in Sweden, the maximum allowed concentration of O₃ and NO₂ averaged over time are set to promote high air quality (Table 1).

<table>
<thead>
<tr>
<th></th>
<th>O₃</th>
<th>NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8 h</td>
<td>8 h</td>
</tr>
<tr>
<td></td>
<td>(µg/m³)</td>
<td>(ppb)</td>
</tr>
<tr>
<td>WHO</td>
<td>120</td>
<td>61</td>
</tr>
<tr>
<td>EU</td>
<td>120b</td>
<td>61</td>
</tr>
<tr>
<td>Sweden</td>
<td>120b</td>
<td>61</td>
</tr>
</tbody>
</table>

* average of the concentration during 1, 8, 24 h or during 1 year, b the guidelines will take effect in 2010, c the guidelines will take effect in 2005.

Today we know more about the health effects of outdoor air pollution than the effects of contaminants in the indoor air. This is in spite of the fact that we only spend only 5-6% of our time outdoors. The interest in indoor air quality accelerated in the 70s, but was still low compared to the public concern of outdoor air.
Introduction

pollution. This is unfortunately the fact today as well, but the concern of the quality of indoor air has increased as the prevalence of sick building syndrome (SBS) has in the community.

The concentration of many indoor air pollutants is often higher than the concentrations of the corresponding compounds outdoors. This higher concentration indoors together with the fact that we spend most of our time indoors puts a further emphasis on the importance of improving the indoor air quality. The concentration of a pollutant indoors depends on several factors, such as:

- Outdoor air concentration of the pollutant
- Indoor sources, the rate of production or emission of a pollutant
- Type of ventilation (mechanical or natural)
- Air exchange rate
- Air volume of the room or building
- Rate of removal of a pollutant
- Nature of the pollutant (reactive or unreactive)

Today there is no straightforward explanation as to why people experience discomfort indoors. It could be a combination of two or several conditions e.g. the presence of moulds due to humidity in the construction, decomposition of damped materials, well insulated buildings, electromagnetic fields, different psychosocial aspects, etc.

Aim of this thesis

The aim of this thesis was to better understand the possible associations between chemical reactions in the air during transport into a building and the concentration of VOC in indoor air. This overall aim included:

- The development of an accurate sampling method for environments containing O₃ and NO₂.
- Studying the influence of different factors on the reactions of monoterpenes.
- Make theoretical calculations to verify experimental results.
- Examining if a multivariate approach could facilitate data evaluation.
• Studying the possible relations between chemicals in indoor air, building variables and sick building syndrome (SBS).
Gas-phase contaminants in the environment

In the gas-phase several types of organic compounds are present. They are divided into three classes, very volatile organic compounds (VVOC), volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC), depending on their boiling point and consequently the ease of volatilisation. The organic compounds studied in this thesis are considered to be in the class of VOC.

Volatile organic compounds (VOC)

This category of organic substances has a boiling point that ranges between 50-260°C. These compounds have high vapour pressures and vaporise easily, and those with the lower boiling temperatures, are the most volatile.

In the indoor environment a myriad of chemical compounds are present in the air and more than 900 different chemical compounds have been identified. The concentrations of these different compounds in a typical indoor environment are three to four orders of magnitude below the odour threshold. The concentrations are, however, variable, since the conditions in the rooms change during the day, between days, and between locations. This variation depends on the type of activity in the room, number of persons, furniture, flooring etc., and other factors mentioned in the introduction, such as transport of outdoor contaminants indoors.
VOC are typically present at higher concentrations in indoor air than in outdoor air\textsuperscript{5,7}. The indoor concentrations of 12 VOC frequently exceeded outdoor levels by at least two-fold\textsuperscript{7}. Brown et al.\textsuperscript{5} presented indoor/outdoor ratios of 2-20 for VOC frequently detected in indoor air. The averages of the geometric means in established buildings were less than 1 ppb to over 25 ppb for different VOC\textsuperscript{5}. In newly built houses the geometric mean concentration of 54 VOC varied between 0.5 ppb and 100 ppb\textsuperscript{9}.

**Monoterpenes**

The main organic compounds studied in this thesis are two monoterpenes, $\alpha$-pinene and $\Delta^3$-carene (Figure 1). They are biogenic, i.e. natural compounds (non-anthropogenic), and are the main compounds emitted from Scots pine and Norwegian spruce\textsuperscript{10}.

![Chemical structures of two monoterpenes](image)

*Figure 1. Chemical structures of two monoterpenes.*

The presence of monoterpenes in plant tissues can vary between different plant families. Both Pinaceae (e.g. pine, fir and spruce) and Eucalyptus families have high levels of monoterpenes in most of their members\textsuperscript{11}. Because of the ubiquity of monoterpenes in Pinaceae, all coniferous ecosystems have a considerable potential to emit terpenes. The emissions of monoterpenes from plants are usually independent of light but are strongly dependent on the temperature\textsuperscript{11}.

The monoterpenes are synthesised by the head to tail condensation of dimethylallyl pyrophosphate (5 carbons) and isopentenyl pyrophosphate (5 carbons) forming geranyl pyrophosphate, which is converted to a monoterpene with the help of the enzyme monoterpene cyclases\textsuperscript{11}. In a simplified manner, the formation of terpenes can be described as the condensation of different number of iso-
prene units (2-methyl-1,3-butadiene) (Figure 2). The boiling points of α-pinene and Δ^3-carene are 155-156°C and 168-169°C, respectively.

Figure 2. The structures of terpenes are derived from a number of isoprene units by head to tail condensation.

The levels of α-pinene and Δ^3-carene in a forest of Scots pine can vary between 0.01-8 ppb in Sweden depending on the time of the day and location. The concentration of α-pinene also has a seasonal variation with low levels in the winter (0.4 ppb) and higher levels during the summer (1.8 ppb) in the rural Southeast United States. The two monoterpenes are also present in indoor air since floors,
walls, ceilings and furniture can be made of wood that emits monoterpenes. The indoor/outdoor ratio of $\alpha$-pinene was reported to be 23 according to studies summarised by Brown et al.\textsuperscript{5}. In newly renovated or newly built buildings the concentrations of $\alpha$-pinene and $\Delta^3$-carene were 2.8-50 ppb and 1-5 ppb, respectively\textsuperscript{8,14,15}.

The work of this thesis embraces more compounds than the two monoterpenes mentioned. Four other monoterpenes and seven alkenes have been used in different experiments (Figure 3).

![Chemical structures](image)

*Figure 3. Structures of the studied alkenes.*

The common feature of the compounds studied in this thesis is that they all contain a carbon-carbon double bond. This double bond makes the compound very reactive to oxidising gases such as O$_3$ and NO$_2$, both of which are present in the environment at enhanced levels due to different human activities such as mobile exhaust.
**Ozone (O₃)**

O₃ was discovered in the middle of the 19th century by C. F. Schönbein, and was coined from the Greek word ozein, which means to smell\(^{16}\). O₃ is present in both rural and urban areas but in different concentrations. In rural areas the levels vary between 50-120 ppb and in urban areas the levels could be as high as 400 ppb\(^{16}\). The level of O₃ in the troposphere has increased 1-2% in average concentration per year during the last 30 years. This increasing concentration of O₃ is explained by the more and more widespread emissions of VOC and NOₓ, which together with sunlight are the controlling factors for O₃ production\(^{17}\).

O₃ is present indoors as well. The indoor concentration of O₃ follows the outdoor concentration closely, which indicates that the source to indoor O₃ originates from outdoor air. Already in the 70s the indoor O₃ concentration was reported to be a significant fraction (20-80%) of that outdoors\(^{18}\). The indoor concentration of O₃ is dependent on the ventilation rate and with increased air exchange rates the concentration of outdoor pollutants increase indoors\(^{18,19}\).

**Nitrogen dioxide (NO₂) and nitric oxide (NO)**

The main emission sources of NO₂ to the environment are through different combustion processes where N₂ and O₂ combine to form nitric oxide (NO)\(^{16}\). In combustion NO is the primary pollutant together with small quantities of NO₂. In the atmosphere, NO is then converted to NO₂. Enhanced levels of O₃ and photochemical reactions favour this conversion process\(^{20,21}\). The levels of NOₓ (sum of NO₂ and NO) in outdoor air can vary from 0.2-10 ppb in a rural area to 10-1000 ppb in an urban region\(^{16}\).

The concentration of NO₂ indoors was 40-80% of those outdoors when no indoor sources, such as gas cooking or smoking, were present\(^{22}\). The NO₂ concentration was then determined by the outdoor concentration of NO₂ and the ventilation rate\(^{22,23}\). With indoor sources the concentration indoors could be about three times higher than in buildings without indoor sources\(^{22}\).
Atmospheric chemistry

This thesis deals with compounds present in the gas-phase. To understand the various reactions between compounds in the air, a limitation of the compounds studied makes it easier. This section presents an introduction to the chemistry between O₃, NO₂, NO and monoterpenes.

The chemistry of ozone, nitrogen dioxide and nitric oxide

O₃ formation occurs as a result of the photolysis of NO₂ and the reaction of the oxygen atom with an oxygen molecule (Equation 1-2). This reaction is the only O₃ source in the atmosphere⁷.

\[
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad \text{Equation 1}
\]
\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad \text{Equation 2}
\]

In the Equations above, \( h\nu \) represents energy from sunlight, and M represents N₂, O₂ or another third molecule in the air that absorbs the excess energy in the reaction and thereby stabilises the O₃ molecule formed. As mentioned earlier NO and NO₂ are mainly formed as a result of different combustion processes.

In an air mixture containing O₃, NO₂ and NO, two main reactions occur²¹.

\[
\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2 \quad \text{Equation 3}
\]
\[
\text{O}_3 + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}_3^\cdot \quad \text{Equation 4}
\]
The formed NO₃·, called the nitrate radical, is a reactive species that can react with NO, NO₂ and with monoterpenes, as mentioned in the next section. Note that both of these reactions consume O₃.

**Reactions of monoterpenes in the gas-phase**

One of the common features of monoterpenes is that they have a carbon-carbon double bond in their structure. This double bond makes the molecules reactive towards oxidising agents such as O₃ and NO₂ that are normally present in the air (Figure 4). The oxidation products formed in these reactions are more irritating than the monoterpenes. In the reaction of monoterpenes and O₃, new reactive species are formed, the carbonyl oxide (a biradical) and the OH radical (OH·), which both can react with the monoterpenes.

![Figure 4. Species that react with α-pinene forming different alkyl radicals and carbonyl oxides (the O₃ reaction pathway).](image-url)
Atmospheric chemistry

In the reaction of $\alpha$-pinene with NO$_2$, NO$_3^-$ and OH$^-$, alkyl radicals are formed that at once react with oxygen present in the air thereby forming alkylperoxy radicals. The reaction of $\alpha$-pinene with NO$_2$ is shown below.

\[
\begin{array}{c}
\text{alkyl radical} \quad \text{alkyl peroxy radical}
\end{array}
\]

The alkyl peroxy radical then reacts with NO and finally with O$_2$ to form a nitroketone.

\[
\begin{array}{c}
\text{alkyl peroxy radical} \quad \text{alkyl peroxy radical with NO and O}_2
\end{array}
\]

This simplified reaction scheme presents the main mechanisms in the oxidation of monoterpenes by NO$_2$. The mechanism concerning the reactions of monoterpenes with NO$_3^-$ and OH$^-$ occur in a similar manner in producing compounds with two functional groups with either a carbonyl and a nitrate or a carbonyl and a hydroxy group. The further reactions of carbonyl oxide are presented in Paper II. As can be seen in the schedule above, NO have an important role in the conversion of the alkyl peroxy radicals. The role of NO$_2$ in the formation of O$_3$ is another key reaction occurring in the atmosphere. NO$_x$ are according to Seinfeld and Pandis among the most important molecules in atmospheric chemistry.
Factors influencing the reactions of monoterpenes

The reaction of two monoterpenes in the gas-phase was studied experimentally in Paper II. To the gas mixture containing the monoterpene, O₃, NO₂ and NO were added. It was found that increased concentrations of O₃, NO₂ and NO increased the amount of monoterpene reacted. Extended reaction time as well as decreased relative humidity (RH) also increased the amount of monoterpene reacted. In the evaluation of the data four additional factors that influenced the reaction of the monoterpenes were found. These factors were different interactions between O₃, NO, reaction time and RH. The two interactions present for both α-pinene and Δ^{3}-carene were the interactions between O₃ and reaction time, and between NO and reaction time. These interactions were interpreted as the effect of OH· formed in the gas mixture and the effect of a change in the concentration of O₃.

Modelling in atmospheric chemistry

The first air quality simulation models using chemical mechanisms were used more than 20 years ago, and since then there have been an enormous growth in our understanding of chemical processes. The extent of different models in atmospheric chemistry today could vary a lot. There are some very large mathematical models that have assignments for up to 400 types of VOC that can be used to estimate reactivities for as many as 550 VOC categories, e.g. the SAPRC-99 mechanism and the Master Chemical Mechanism. Other models are more limited and study the chemical reactions of one or a few compounds. The theoretical models could also have different directions e.g. modelling homogeneous reactions in air (Paper III), homogeneous and heterogeneous reactions in air, or indoor compartments with surface chemistry and homogeneous reactions in air.

The advantages of studying a number of compounds and including several reaction pathways and reaction steps of the reaction products are that the models become more similar to conditions in the environment or in experimental chambers that can be used for comparison. The disadvantage with more reactions in the model could be that more uncertainties are incorporated in the model. However,
Atmospheric chemistry

this disadvantage is probably outweighed by the advantages of including more reactions in the models.

**Modelling indoor air compartments**

When modelling indoor compartments physical parameters are often included. Nazaroff and Cass\(^4\) modelled the concentration of chemically reactive pollutants in indoor air. In that model the effect of amongst others, ventilation, filtration, and to some extent heterogeneous removal (e.g. removal on surfaces), were accounted for. The authors found that the concentration of many species was affected by chemical reactions, especially when outdoor air pollutants were combined with indoor emissions. Their results also indicated that a dominant route of removal of highly reactive species was deposition on walls. Concerning the surface chemistry, the authors implied that further research in this area was needed.

Dimitroulopoulou et al.\(^5\) calculated the indoor air exposure of NO\(_2\) in different microenvironments as a function of outdoor concentrations, building characteristics and indoor source emissions. The variation of NO\(_2\) concentration during the day as well as the annual mean NO\(_2\) exposure was calculated, and the model provided results that were consistent with the indoor/outdoor ratios reported. The authors concluded that the exposure indoors is critically dependent on physical features in the indoor environment such as furniture and surface materials, which are currently poorly characterised.

In a model by Weschler and Shields\(^6\), the variation of the concentration of a pollutant indoors depended on whether the pollutants in question originated from an outdoor or indoor source, and on the ventilation rate. In a scenario where the pollutant originated outdoors, the concentration indoors increased as the air exchange rate was raised. The concentrations of the decomposition products, however, decreased. The concentration indoors of pollutants with large diurnal variation and the variation of the decomposition products formed showed a pattern that also was affected by the air exchange rate. At low air exchange rates the concentration of the pollutant was low, and the concentration of the decomposition product was high and increased with time. At high air exchange rate the concentration of the pollutant varied at the same diurnal pattern as outside, and
the concentration of the decomposition product followed the variation of the pollutant. In the theoretical model described in Paper III, the reactions of one monoterpene at a time were studied. The calculations of the model were focused on the extent of the oxidation of monoterpenes, and did not take the further oxidation of the reaction products or aerosol- and particle formation into consideration. It was demonstrated that the change of initial settings of \( \text{O}_3 \), \( \text{NO}_2 \) and NO had a large influence on the calculated amount of monoterpene oxidised (Table 2).

Henceforth the word setting is used when initial levels of \( \text{O}_3 \), \( \text{NO}_2 \) and NO in the theoretical models are in view. When discussing levels of \( \text{O}_3 \), \( \text{NO}_2 \) and NO in the experimental set-up, or levels in the environment, the word level or concentration is used.

**Table 2. The calculated amount of oxidised \( \alpha \)-pinene and \( \Delta^3 \)-carene reacted at different initial settings of \( \text{O}_3 \), \( \text{NO}_2 \) and NO.**

<table>
<thead>
<tr>
<th>Initial settings (ppb)</th>
<th>( \text{O}_3 )</th>
<th>( \text{NO}_2 )</th>
<th>NO</th>
<th>% Reacted</th>
<th>( \alpha )-pinene</th>
<th>( \Delta^3 )-carene</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 75 75 1.5 1.1</td>
<td>75 75 25 5.5 4.5</td>
<td>75 25 75 1.4 0.9</td>
<td>75 25 25 4.4 3.0</td>
<td>25 75 75 0.2 0.1</td>
<td>25 75 25 0.9 0.7</td>
<td>25 25 75 0.2 0.1</td>
</tr>
</tbody>
</table>

It was demonstrated that the amount of reacted monoterpene increased when the initial setting of \( \text{O}_3 \) was high and the setting of NO was low. The calculated amount of monoterpene reacted was compared to the experimental results performed in similar conditions, and the best correlation was found at the high setting of \( \text{O}_3 \) and the low setting of NO.
Atmospheric chemistry

The influences of four different reaction pathways were also studied at the different initial settings and are presented in Table 3. The size of a reaction pathway was calculated as the number of molecules that passed through a specific reaction per second. This concept took both the reaction rate constant and the concentrations of the involved compounds into consideration in the calculations. The O$_3$-monoterpene and NO$_3^\cdot$-monoterpene reaction pathway were the dominating pathways at all initial settings of O$_3$, NO$_2$ and NO for both α-pinene and ∆$_3$-carene (Table 3). The importance of the NO$_3^\cdot$-α-pinene and NO$_3^\cdot$-∆$_3$-carene reaction pathways increased the longer the reaction time.

The influence of the initial setting of NO could be seen when comparing the influence of the different reaction pathways at high and low initial setting of NO. It was obvious that the O$_3^\cdot$, OH$^\cdot$- and NO$_3^\cdot$-monoterpene reaction pathways increased markedly when NO was at low initial setting.

Table 3. The influence of four different reaction pathways (O$_3$, OH$^\cdot$, NO$_2$ and NO$_3^\cdot$) in the reaction with α-pinene after 213 s.

<table>
<thead>
<tr>
<th>Initial settings (ppb)</th>
<th>Reaction pathways with α-pinene (molecules/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O$_3$</td>
</tr>
<tr>
<td>75    75    75</td>
<td>5.0*10$^9$</td>
</tr>
<tr>
<td>75    75    25</td>
<td>1.2*10$^{10}$</td>
</tr>
<tr>
<td>75    25    75</td>
<td>5.0*10$^9$</td>
</tr>
<tr>
<td>75    25    25</td>
<td>1.2*10$^{10}$</td>
</tr>
<tr>
<td>25    75    75</td>
<td>9.8*10$^8$</td>
</tr>
<tr>
<td>25    75    25</td>
<td>2.9*10$^9$</td>
</tr>
<tr>
<td>25    25    75</td>
<td>9.8*10$^8$</td>
</tr>
<tr>
<td>25    25    25</td>
<td>2.9*10$^9$</td>
</tr>
</tbody>
</table>

At the high initial setting of O$_3$ the number of molecules passing the four reaction pathways was higher than at the low setting of O$_3$. This indicated that despite the low gas-phase rate constants of the reactions between O$_3$ and α-pinene and between O$_3$ and NO$_2$ (to form NO$_3^\cdot$), the reaction pathways of O$_3$ and NO$_3^\cdot$ with monoterpene were most important.
Test atmospheres

The work in this thesis is based on experiments performed in conditions that somewhat could correspond to conditions in a full-scale ventilation system. The experimental set-up is a simplified model of a ventilation system and is made of Teflon and glass. An introduction to ventilation systems is presented below along with a presentation of how chemical compounds enter ventilation systems and a short overview of various experimental chambers.

A schematic view of a building with a mechanical ventilation system with a heat exchanger is shown in Figure 5. Outdoor air is transported into the building by the force of under-pressure created by a fan. The intake air passes through a filter to remove particles. After the filter the air flows through a heat exchanger. Two common types of heat exchangers are the rotating and the cross flow heat exchanger. It is in this part of the ventilation system that the cold intake air is heated by the warm exhaust air from indoors. This transmission of heat occurs through the heating and chilling of adjacent layers in the heat exchanger. In a rotating heat exchanger these heated surfaces are continuously rotated to get in contact with the intake air to release the heat, and hence, warming up the incoming air. Beyond the heat exchanger there can be a complementary heater, which adjusts the temperature of the supply air if the temperature of the outdoor air is low. The supply air is then transported through ventilation ducts of decreasing size until it reaches the rooms of the buildings.
Test atmospheres

The composition of chemical compounds in the indoor air is partly influenced by indoor sources. Also contributing are chemicals present in the supply air, which are influenced by the quality of outdoor air. Four types of processes can occur in the ventilation system that affects the composition of the supply air.\(^\text{36}\)

- Primary emission of compounds from materials in the ventilation system
- Sorption and desorption processes between pollutants and surfaces
- Pollutants removal by deposition
- Reactions between pollutants and surfaces

These four processes can be complemented with a fifth process, chemical reactions in the gas-phase.

Morrison et al.\(^\text{36}\) studied the emission of VOC from four different duct materials and concluded that they were not dominating contributors to the indoor concentrations due to either low emissions or low surface areas. The exposure of the duct components to O\(_3\) increased the emission of aldehydes and reduced the O\(_3\) concentration with less than 4% after a period of 10 days. An ageing process was observed for all of the materials tested, which was demonstrated by decreased O\(_3\) removing capacity with time.\(^\text{36}\)
In a study by Sundell et al.\textsuperscript{37}, the change in concentration of the sum of total volatile organic compounds (TVOC) from intake air via supply air to room air was studied in “healthy” and “sick” buildings. Their main findings were that the TVOC concentration in room air was lower than the corresponding level in supply air in the “sick” buildings, but not in the “healthy” buildings. They also found that a raised concentration of formaldehyde in room air was significantly correlated with raised prevalence of occupant symptoms in the buildings.

By removing O$_3$ from the ventilation air, a large number of chemical reactions possibly occurring in the ventilation system and indoors can be avoided. This also makes it possible to raise the air exchange rates without increasing the I/O ratio of O$_3$\textsuperscript{19}. Ten different commercial filters were tested for the removal of O$_3$ at ambient concentrations, and the initial efficiencies were found to vary (5-98\%) depending on the material in the filter and its properties\textsuperscript{38}. The amount of material used in the tested filters was under dimensioned to facilitate the comparison between filters, which could explain the low removal efficiencies. The O$_3$ removing capacity and the effects on the filters caused by O$_3$ (e.g. decreased pore size of the material in the filter) were the factors used for the comparison between the different filters.

In a study by Weschler et al.\textsuperscript{39}, it was demonstrated that a charcoal filter could efficiently remove O$_3$ for a lifetime of three years, if the filter was protected from submicron particles. The exposure of the filter to VOC also decreased the lifetime of the charcoal filter since VOC are removed from the air stream as well as O$_3$\textsuperscript{40-42}. By the use of chemically treated adsorbent air purifiers NO$_2$, SO$_2$ and formaldehyde could be removed from the ventilation air as well as O$_3$\textsuperscript{43}.

When studying the chemical reactions in air, in the environment, in full-scale ventilation systems, or in a small experimental chamber, it is in all cases of crucial importance to have system where the conditions and concentrations of the studied compounds are controlled. The use of static and dynamic chambers is suitable for these purposes.
Test atmospheres

Static chambers

A static chamber can be used for generating a test atmosphere with pollutants in known initial concentrations. In static chambers a volume of purified air and pollutants are added in the beginning of the experiments, or the chamber is purged with the air mixture of interest. Then the chamber is sealed. The concentrations of the compounds and/or the formation of new compounds in the chamber are then studied for a specific reaction time. A static chamber can be constructed of different materials e.g. Teflon, glass and stainless steel, in different sizes. An example of an inflatable chamber is given below.

This inflatable chamber is constructed of Teflon FEP film. The Teflon film is transparent, which enables the study of photolytical reactions. It can also be covered with black plastic to enable the study of dark reactions. These chambers can be both large and small and have a fully inflated chamber volume of 3.9-260 m$^3$. The surface to volume ratio for chambers of 3.9 m$^3$ and ~80 m$^3$ are 3.8 m$^{-1}$ and 1.4 m$^{-1}$, respectively. In a typical experiment, a known amount of the pollutant of interest is injected into the chamber containing purified air. The concentrations of the added compounds and some reaction products are then measured both on-line and by off-line collected samples.

Dynamic chambers

In a dynamic chamber the air is continuously replaced. The input air can contain all the pollutants that are studied or part of the pollutants since emission sources can be placed inside the chamber as well.

In the case of the Field and Laboratory Emission Cell (FLEC), with an interior of stainless steel, the emission cell is placed on a test material and is sealed to be airtight. There is although a continuous airflow through the cell. With this cell it is possible to study, e.g. the emission rate of the test material, or the O$_3$ removal rate of the test material.
Another type of dynamic chamber consists of an exposure chamber made of glass, where air is introduced to maintain a total flow of \(~25 \text{ l/min}\). The pollutant is volatilised from a permeation tube, diluted and introduced in the chamber together with the main air stream.

**Experimental chamber used in Papers I and II**

The reaction chamber used in Papers I and II was also a dynamic chamber. It had a continuous airflow of 37-38 l/min and the air was flowing through a 6 or 12 meter long (i.d. 25 mm) reaction chamber (Figure 6). The air added to the evaporation chamber was humidified to a determined RH at a specific temperature before it was added.

![Diagram of reaction chamber](image)

*Figure 6. Reaction chamber used in the experiments. A – syringe that injects the organic compounds, B – evaporation chamber, C – mixing chamber, D – reaction chamber (6 or 12 m), E – sampling part.*

The VOC were injected into the evaporation chamber with a micro-syringe injector that injected the compounds at a constant speed during the experiments. Passing \(\text{O}_2\) through an \(\text{O}_3\) generator produced \(\text{O}_3\), which was added together with
Test atmospheres

concentrated NO₂ and NO from gas cylinders to the airflow in the mixing chamber. The concentrations of VOC in the air stream were in the low ppb range (<40 ppb), and the concentrations of the inorganic compounds were approximately 0, 10, 20, 25, 50 and 75 ppb in the different experiments.

The reaction chamber was made of Teflon with fittings of borosilicate glass. The major part of the reaction chamber was made of Teflon to avoid reactions on the surface since the focus of this work was to study gas-phase reactions. The factors that could be varied in this system were:

- The concentration of the organic compound
- The concentrations of O₃, NO₂ and NO
- RH
- The reaction time

By changing these factors, the effect on the chemical reactions by each of these factors and interactions between the factors could be studied.

Standard generation

The method for generation of the standards used in the thesis could also be regarded as a dynamic system. The VOC in question was dissolved in methanol, and 2 µl of the solution was injected on silanized glass wool fitted in a glass tube in a stream of nitrogen (100 ml/min) at a RH of ~0%. In the stream of nitrogen the VOC was completely volatilised within 2 minutes, and was sampled during that time. This method enabled quantification of the levels in the reaction chamber.
Sampling of VOC and atmospheric oxidants

In the air several different classes of compounds are present. The air is a heterogeneous system, which contains compounds present in the gas-phase as aerosols (a colloidal dispersion of solid or liquid particles in a gas) and as particles. Besides that, chemical reactions can occur between the different pollutants. These characteristics of air make it to one of the most difficult environmental matrixes to sample.

Several research groups, however, work with the sampling of different air mixtures in the evaluation of the air quality in the environment. In order to make statements about the contamination or concentrations of different compounds in the air, the sampling must be accurate and representative for the air mixture sampled.

Concentration and sampling of VOC

In general, two sampling strategies are used to sample VOC in ambient air, concentration and whole-air sampling. The sampling of airborne compounds is preferably done with concentration on an adsorbent, since whole-air sampling is more expensive, and more interfering parameters are present. A concentration step is often required to reach acceptable detection limits of the analytical technique. A widely used concentration technique is the use of adsorption to enrich the compounds of interest on solid sorbents, e.g. chemi sorbents and adsorbents. The focus here concerning solid sorbents is mostly on adsorbents.
There are a number of different adsorbents available that are suitable for VOC sampling, which were reviewed by Nunez and Gonzalez\textsuperscript{52}, Camel and Caude\textsuperscript{50}, and Dettmer and Engewald\textsuperscript{53}. To guarantee an accurate determination of VOC an adsorbent should meet the following criteria\textsuperscript{53}:

- Complete enrichment
- Complete and fast desorption
- Homogeneous and inert surface
- Low affinity to water
- Low adsorption capacity of other inorganic constituents of air
- High inertness against reactive species
- High mechanical stability and in the case of thermal desorption also thermal stability
- Multiple usability

Today there are several adsorbents that fulfil these criteria, but they still have some differences. Care must be taken to select an appropriate adsorbent and adjust sample volumes to avoid breakthrough\textsuperscript{50}.

Desorption of the compounds from the adsorbent can be done by either solvent extraction or thermal desorption. Solvent extraction for is used e.g. charcoal, where the sampled compound is desorbed from the adsorbent with a low boiling solvent, e.g. dimethyl formamide. Using this technique the extract can be analysed using different methods\textsuperscript{50}. In trace analysis, evaporation of the solvent is mostly required to reach the detection limits. The detection limits could also be reached by sampling larger air volumes.

By using thermal desorption the sampled compounds are desorbed from the adsorbent by heating the sampling tube without using any solvents. After the thermal desorption another concentration step is done before the chromatographic column is made to achieve narrow chromatographic peaks\textsuperscript{50}. Hence, this method contains a two stage thermal process. The drawback of this method is that a sample can be analysed only once, and then it is consumed. Using thermal desorption the number of samples should preferably be increased since the sample is consumed after the analysis, and samples for backup and reanalysis could be needed. Replicates are another thing to consider when sampling. In the current
study 2-4 replicates were sampled at each sampling occasion, and sampling was repeated at least three times to verify the average concentrations of the air.

**Diffusive sampling and active sampling**

In diffusive sampling the adsorption process is controlled by the adsorption properties of the adsorbent and diffusion processes. The sampling tube is exposed to the atmosphere and the sampling times can vary between ~15 min to >40 days depending on application\(^8\). This way of sampling is simpler and cheaper than active sampling since no pumps are required. The sensitivity using diffusive sampling is in general lower than for active sampling as back diffusion occurs to a higher extent and uptake rates can decrease with time\(^8\).

In active sampling, air is sucked through the adsorbent with a pump at a specific flow rate during a proportionately short time compared to the sampling times of diffusive sampling. For active sampling the sensitivity is higher and it is possible to measure short-term means\(^8\).

**Adsorbents suitable for thermal desorption**

There are a lot of materials that can be used for adsorption of VOC. They can roughly be divided in three categories - inorganic materials, carbon based adsorbents and organic polymers\(^53\). The inorganic materials often have high affinity to water and are therefore excluded in most cases.

The carbon-based adsorbents could be sub-classified into activated carbon, carbon molecular sieves (Carboxen), and graphitised carbon blacks (Carbotrap)\(^56,53\). Sampling with activated carbon can cause irreversible adsorption, degradation of analytes, and adsorption of water\(^56,55-57\). High desorption temperatures were also required for some compounds. The carbon molecular sieves had affinity to water\(^58\) and in some cases low recovery of reactive analytes, and the graphitised carbon blacks have incomplete recovery of terpenes, which excluded them as suitable adsorbents\(^53\).
The porous organic polymers are a large group of adsorbents with different surface areas and polarities\textsuperscript{50,53}. These polymers are mostly very pure materials but have some drawbacks, e.g., limited temperature stability and artefact formation. The mostly used porous organic polymer is Tenax TA, which is in widespread use for sampling monoterpenes\textsuperscript{59}. Tenax TA is also the adsorbent used in the present thesis. Other organic polymers are XAD and Chromosorb.

**Tenax TA**

Tenax TA has the structure of a linear polymer of 2,6-diphenylphenylene oxides\textsuperscript{60} (Figure 7), and has a low artefact background when analysing blank samples\textsuperscript{61}.

![Figure 7. The chemical structure of the adsorbent Tenax TA, a linear polymer of 2,6-diphenylphenylene oxides](image)

Tenax TA adsorbs the organic compounds that are present in the air as a result of dispersion interactions supported by dipole-type interactions\textsuperscript{62}. Weak hydrogen-bond acidity was also observed, which presumably came from impurities of the Tenax adsorbent.

The adsorption on Tenax is a physical adsorption, which is appropriate for analytical purposes since it allows 100\% of the sampled compound to be recovered\textsuperscript{63}. Due to its low specific surface area (35 m\textsuperscript{2}/g), Tenax is not suitable for sampling highly volatile organics. Tenax is suitable for sampling volatile compounds with 7-26 carbons\textsuperscript{53} or 6-14 carbons according to Camel & Caude\textsuperscript{50}. According to Yang and Lo\textsuperscript{64}, Tenax TA can be used for quantitative sampling down to C\textsubscript{5}. Other characteristic that determines the adsorption of Tenax is the pore volume and the pore size. Together these three properties are used to obtain information
Sampling of VOC and atmospheric oxidants

concerning the adsorption mechanisms connected to interactions between the organic compounds to be sampled and the adsorbent.\textsuperscript{68}

**Sampling in the present studies**

**Conditioning the sample tubes**

To guarantee that the Tenax TA tubes were clean before they were used to sample test atmospheres, the tubes were heated to 300°C in a conditioning rig in a stream of nitrogen (80-100 ml/min during >30 min) to desorb possible contaminants. The Tenax TA tubes were removed from the conditioning rig when they were still warm (50-100°C) to avoid adsorption of impurities in the N\textsubscript{2}. To minimise contamination after the conditioning, Swagelok couplings with Teflon ferrules were used to seal the tubes. The Swagelok couplings were removed only during sampling and analysis to avoid contamination from the environment.

**Sampling**

The size of the air sample collected by Tenax TA (200 mg packed in stainless steel tubes) from the experimental chamber was approximately 1 l, and was collected during 10 minutes with a sampling rate of 100 ml/min. The sample flow was measured both before and after sampling. No breakthroughs of the sampled organic compounds were observed.

In the reaction chamber four samples were collected simultaneously. There were either four in the end of the chamber, or two at the end and two in the beginning of the reaction chamber (the split), simultaneously. This procedure was repeated three times generating twelve samples for the evaluation.

**Statistics about the performance of the sampling method**

The relative standard deviations (RSD) of four simultaneous samples of \(\Delta^3\)-carene in the split and in the reaction chamber were 1.2-2.0 and 0.2-0.6%, respectively. The level of injected alkenes in the reaction chamber varied somewhat over time (Figure 8). The first sampling was started after two hours of stabilisa-
Sampling of VOC and atmospheric oxidants

tion and the last sampling was made within an hour. The variation over time is the reason why the sampling is done simultaneously in the split and at the end of the reaction chamber. In this application it is important to be able to calculate differences between the two sampling points, thereof the interest in minimising the effect of short-term variation in the generation of the monoterpene atmosphere.

The measured sample flows before and after the sampling period did vary up to 2.3% (RSD) for one sample tube. In one sample point only one of the four parallel samples was allowed to have that high RSD. The common RSD of the sample flow was ~0.3%. The average of the measured sample flows before and after sampling for each sample tube was used in the calculations.

The RSD when analysing methanol standard spiked Tenax TA tubes (Δ1-carene in methanol) was 0.8-1.3%, which was in the same range as the RSD for the samples from the reaction chamber. This implied that the air was properly mixed in the reaction chamber. The injected level of monoterpene in the reaction chamber (calculated concentration) corresponded well with the concentration of monoterpene in the methanol standard.

Figure 8. The concentration of Δ1-carene at three sampling occasions during one experiment with four replicates at each sampling occasion.
All of the above mentioned factors contributed to the sampling error and influenced the sampling strategy used in the experiments in the present thesis. In the experiments both replicates and repeated sampling was done to diminish the effect of the sample errors. The use of Design of experiments introduced in Chapter 8 was another factor that decreased the effect of possible uncertainties in the experimental data.
Sample analysis and continuous monitoring

Analysis of VOC

After the adsorption of the compounds of interest on Tenax TA, an analysis of the amount of sampled compounds is made. An analysis is made to be able to quantify the amount sampled and to compare amounts between samples.

The analysis procedure starts with thermal desorption (ATD) of the sampled compounds from the Tenax TA tubes. The tubes are heated to 200ºC and are desorbed during 2 min in a Helium flow of 50 ml/min. The desorbed sample during that time is adsorbed on a cold trap of Tenax TA held at −30ºC. After 2 min the temperature of the cold trap is quickly raised to 250ºC, and the adsorbed sample is “injected” on the column in the gas chromatograph (GC) through a glass liner in a continuous flow of Helium.

The capillary column used for separation was a 50 m, 0.2 mm id. column with a 33 µm film thickness of (5%)diphenyl-(95%)dimethyl siloxane copolymer. This unpolar stationary phase retains the compounds to different extents due to their polarity and boiling point thereby giving them specific retention times. This column was chosen due to its low bleeding of background.

In the thesis the detection of the sampled compound was made with either a flame ionisation detector (FID) or a mass spectrometer (MS). The FID was used for quantification due to its sensitivity and long-term stability, and the MS was mainly used due to its capacity to identify the compounds eluted at different retention times.
The response of the FID results from a collected signal from the combustion of the eluted organic compounds in a hydrogen-air flame. Simply put, the overall FID response is proportional to the sum of carbons in the organic molecules. The error introduced in the analysis of the samples using GC/FID is regarded to be of minor importance compared to the sample errors mentioned in Chapter 5.

Also simply put, the mass spectral analysis could be described as follows. In the MS the neutral sampled organic compounds transported from the GC column are transformed to ions by giving the molecules sufficient energy to eject one of its electrons. The remaining positive ion, the molecular ion (M⁺), decomposes further to different fragment ions. The fragment ions could have a mass of, e.g. the M⁺-15 or M⁺-29, depending on the size of the loss in the fragmentation. The M⁺ ion and the fragment ions are then separated by their mass to charge ratio (m/z) and are analysed in the mass analyser (quadrupole) according to their abundance. Both the M⁺ and the fragment ions are analysed for each compound that enters the mass analyser, which gives mass spectra for each eluted compound showing the abundance of the different ions in relation to each other. The mass spectrum is characteristic for the compound analysed with its specific pattern, and the M⁺ and the fragmentation pattern are evaluated for the identification of the compounds sampled. For a more detailed description of the settings used in the analysis see Paper I.

**Continuous monitoring of atmospheric oxidants**

**O₃**

A variety of techniques to continuously measure the concentration of O₃ in air have been developed. Some of these are Ultraviolet (UV) absorption, differential optical absorption spectroscopy (DOAS), chemiluminescence, and chemical titration methods. In this thesis a photometric ozone analyser that measures UV absorption was used.

The instrument uses a mercury lamp as the light source that emits light in the UV region (254 nm). The emitted light is within the range of the absorption band of O₃. This means that if O₃ is present in the air sampled, it will absorb light with
the wavelength of 254 nm since it absorbs light with wavelengths up to ~310 nm. At higher concentrations of O₃ more light is absorbed. The instrument measures and computes the ratio of transmitted light, which gives an accurate and reliable measure of the O₃ concentration. The possible interference of water vapour and aromatic compounds on the photometric ozone analyser was studied, and under atmospheric conditions and moderate pollution the measurements of the instrument were accurate. In more polluted air the positive interference from aromatic compounds must be taken into consideration.

**NO₂ and NO**

There are two established techniques for continuous measurement of NO₂ and NO, the chemiluminescence and laser-induced fluorescence technique. In this thesis NO₂ and NO are measured using gas-phase chemiluminescence. This technique is based on the reaction of NO with O₃ that produces excited NO₂ molecules. As the excited NO₂ reverts to a lower energy state, it emits radiation that is measured and the concentration of NO is calculated. Nitrogen dioxide in the sampled air is initially converted to NO in the instrument and is then allowed to react with O₃ to produce excited NO₂ molecules that revert to a lower energy state, etc.

Due to the combined chemiluminescence of NO and photolysis-generated NO (conversion of NO₂ to NO) some nitrogen containing compounds may cause interferences. In an evaluation by Spicer et al. the possible interference of NO, O₃, formaldehyde, carbon monoxide (CO), nitrous acid (HONO) and nitric acid (HNO₃) using chemiluminescence instruments were studied. Both HONO and HNO₃ were shown to have positive interference on the measured NO₂ concentration. Interferences were also found for peroxyacetyl nitrate (PAN), ethyl nitrate, ethyl nitrite and nitroethane using chemiluminescence instruments with carbon or molybdenum converters. However, the above-mentioned interferences are only important at enhanced levels of the interfering compounds, e.g. in smog chambers.
Interference of oxidants during sampling

Sampling organic compounds with Tenax in environments containing the oxidants O₃ and NO₂ results in sample artefacts. These artefacts could depend on either the degradation of the adsorbent, or oxidation of the analyte after adsorption. To minimise artefacts during sampling a scrubber could be used prior to the adsorbent.

Degradation of the adsorbent

Effects of O₃ on Tenax

In several studies it has been shown that sampling an atmosphere containing O₃ with Tenax generated sampling errors due to degradation of the Tenax structure\textsuperscript{72}. The compounds resulting from the degradation were, for example, benzaldehyde, phenol and acetophenone. The formation of benzene, toluene, C₆-C₉ \textit{n}-alkanes, C₆-C₉ \textit{n}-aldehydes and different phenyl substituted carbonyl compounds have also been reported\textsuperscript{72,73}. In a recent publication by Klenö et al.\textsuperscript{74} further degradation products of Tenax were presented. The structures of most of the above mentioned degradation products are closely related to the Tenax structure (Figure 7).
Interference of oxidants during sampling

**Effects of NO$_2$ on Tenax**

It was shown that NO$_2$ causes degradation of Tenax just as O$_3$ does$^{73-77}$. The degradation products most frequent reported for NO$_2$ were benzaldehyde, aceto-phenone, phenol, 2,6-diphenyl-$p$-benzoquinone and 2,6-diphenyl-$p$-hydroquinone (Figure 9).

![Figure 9. Structures of 2,6-diphenyl-$p$-benzoquinone (a) and 2,6-diphenyl-$p$-hydroquinone (b)](image)

**Oxidation of sampled VOC on the adsorbent**

**Oxidation caused by O$_3$**

The most thoroughly studied group of compounds that are susceptible to oxidation on the adsorbent is the biogenic terpenes$^{72}$. The oxidation of this group of compounds, and other alkenes adsorbed on Tenax by O$_3$ (Figure 10), are in some cases reported to be quite extensive. This might lead to diminished analyte concentrations and to formation of oxidated reaction products in concentrations not present in the air sampled. Factors that may play an important role affecting the oxidation of the adsorbed compounds could be high surface concentration on the Tenax material, combined with high heterogeneous reaction rates$^{78}$. 

38
Interference of oxidants during sampling

Figure 10. Sampling a test atmosphere containing O₃ and NO₂ causes oxidation of adsorbed monoterpenes on Tenax sample tubes.

Hoffmann⁵¹ showed that the oxidation of limonene on Tenax by O₃ depended on the concentrations of the limonene sampled. At a low concentration limonene was oxidised to a higher extent than at a high concentration. Calogirou et al.⁷⁸ demonstrated that decreased sampling times resulted in an enhancement of the recovery of the different terpenoids, probably due to a shorter time of exposure to O₃.

The oxidation of terpenoid compounds on the adsorbent was found to be proportional to the gas-phase rate constants with O₃⁵¹,⁷⁸,⁷⁹. Calogirou et al.⁷⁸ also concluded that terpenoids with one double bond were less decomposed compared to compounds with two double bonds. The oxidation of a terminal double bond was occurring to a lesser extent than an internal one⁷⁸.

The different reactivity of double bonds reported by Calogirou et al.⁷⁸ was verified in the current thesis. When exposing a monoterpane spiked Tenax TA sampling tube to 56-75 ppb O₃ at a flow rate of 100 ml/min during 5, 10 and 20 min, the amount of recovered monoterpane differed between the tested monoterpenes depending on their structures, and decreased with increased sampling time as displayed in Figure 11 (Paper I).
Interference of oxidants during sampling

Figure 11. The amounts of adsorbed monoterpenes oxidised on Tenax TA after exposure to 56 ppb O₃. *The level of O₃ was 75 ppb for myrcene and α-terpinene.

A consequence of these reported oxidation compounds adsorbed on Tenax was that this sampling method was not accurate in environments with O₃ present. One solution is to remove O₃ prior to the sampling tube and sample the monoterpenes in O₃ free air.

Oxidation caused by NO₂

In a review of the literature no study was found concerning the potential of NO₂ to oxidise compounds adsorbed on Tenax. Several research groups have demonstrated the decomposition of Tenax caused by NO₂, but have not continued on the track concerning the reactivity of NO₂.

However, in Paper II, the oxidative effect of NO₂ on already adsorbed analytes was studied. When exposing a monoterpane spiked Tenax sampling tube to 56 or 75 ppb NO₂ at a flow rate of 100 ml/min during 5, 10 and 20 min, the amount of recovered monoterpane decreased with increased sampling time (Figure 12). The extent of the decrease in recovery for the tested compounds was in accordance with the gas-phase rate constants in the reaction with NO₂. The monoterpenes
with the highest reaction rate constants were also the compounds that were oxidised the most.

![Graph showing % Oxidised vs Sampled volume (l) with various monoterpenes marked on it.]

**Figure 12.** The amounts of adsorbed monoterpenes oxidised on Tenax TA after exposure to 56 ppb NO₂. *The level of NO₂ was 75 ppb for myrcene and α-terpinene.*

These results show that the presence of NO₂ in the environment causes sampling artefacts and that improvement of the sampling method is needed. Removal of the oxidant prior to the sampling tube and sample NO₂ free air is a solution in this case as suggested before for O₃.

**Removing oxidants prior the sampling tube**

**O₃ scrubbers**

To avoid artefacts when sampling an atmosphere containing O₃, different compounds can be used to selectively remove O₃ prior to the Tenax sampling tube. These constructions that are used to remove oxidants are called scrubbers. In a review article, Helmig⁷２ gave a comprehensive overview of compounds that could be used as O₃ scrubbers. The most frequently used O₃ scrubbers contain either KI or MnO₂.
Several different research groups have presented studies where O₃ scrubbers have been used. The effect of using a scrubber was evidenced by increased recoveries for the tested compounds⁵¹,⁷⁸-⁸¹.

Fick et al.⁸² developed and tested an O₃ scrubber with KI as the active substance. This O₃ scrubber was tested for its capacity to remove O₃, and its recovery for a set of monoterpenes and a few reaction products. With this scrubber it was possible to sample both monoterpenes and their reaction products with high recoveries in air containing O₃.

**NO₂+O₃ scrubbers**

Since the O₃ scrubber developed by Fick et al.⁸² only removed part of the added NO₂ (<80%), new scrubbers were developed (Paper I, and unpublished results) in order to avoid oxidation on the adsorbent caused by NO₂. These scrubbers contained glass fibre filter/s, on which the active chemical/s were applied. The filter/s were put into a filter cassette (used for sampling air particles) and were used in front of the Tenax sampling tube (Figure 13).

The active chemical in the first scrubber was Sodium sulphite (Na₂SO₃), which was solved in water until saturation. This solution was applied on glass fibre filters, two for each scrubber, and were then dried and put into filter cassettes. This scrubber removed both O₃ and NO₂ but was not reusable like the O₃ scrubber developed by Fick et al.⁸².

The active substance in this scrubber was Sodium sulphite (Na₂SO₃), which was applied on a filter, put into a filter cassette used for sampling air particles, and used in front of the Tenax sampling tube (Paper I). This scrubber had the capacity of removing both NO₂ and O₃ but had the disadvantage that it was not reusable like the O₃ scrubber.
Interference of oxidants during sampling

Figure 13. The parts of the NO$_2$+O$_3$ scrubber. The two filter cassette parts are put together with the one or two filters in between. During sampling a Tenax tube, which is shown to the left in the figure, is fixed after the scrubber where the air is O$_3$ and NO$_2$ free.

The recoveries of four monoterpenes (α-pinene, β-pinene, Δ$_3$-carene, and limonene) through the Na$_2$SO$_3$ scrubber were between 81 and 97%, and remained roughly unchanged at 15-42% RH, but at a high (75%) and a low RH (0%), the recovery decreased (Paper I). The recovery of myrcene and α-terpinene at a RH of 25% were 68 (SD 2%) and 80% (SD 5%) respectively. The recovery of the monoterpenes through the scrubbers is a factor that adds uncertainties in the quantification of the sample due to the variation in recovery between different scrubbers. The recovery α-pinene and Δ$_3$-carene through the scrubbers had a relative standard deviation of 1-3% at RH of 0-75%.

The second scrubber was a further development of the Na$_2$SO$_3$ scrubber in order to improve the performance. To the solution of Na$_2$SO$_3$ in water, 5% glycerol was added. This resulted in a higher capacity of removing NO$_2$ (>90% during 120 min at 640 ml/min), and that the Na$_2$SO$_3$ salt was more stuck to the filters. The recovery of the monoterpenes through this scrubber remained unchanged compared to the Na$_2$SO$_3$ scrubber. The recoveries of seven cyclic alkenes (Figure 3) were also tested and were found to be 92-100%.

In addition to the two NO$_2$+O$_3$ scrubbers mentioned above, which are the mainly used scrubbers in this thesis, a third scrubber with KI and glycerol applied on one glass fibre filter was tested. Five grams of KI and 250 µl glycerol were solved in 5 ml of water. This solution was applied on a filter (200 µl) and was dried in room temperature. This scrubber had the capacity of removing >98% of
Interference of oxidants during sampling

75 ppb NO₂ for more than 60 min at a RH of 38% and a flow rate of 640 ml/min. At low RH <15% the scrubber let 5% of the NO₂ through after 15 min. This scrubber also had the capacity of removing O₃ (>98% of 65 ppb O₃ during 170 min at a flow rate of 640 ml/min). The recoveries of α-pinene and Δ⁴-carene through the KI-glycerol scrubber were 95% and 91%, respectively. This scrubber was suitable for reuse, if purging with clean air for 5 min was performed between sampling occasions.

The recoveries through the different scrubbers for some of the reaction products formed in the oxidation of monoterpenes were also tested. In the study by Fick et al. the O₃ scrubber with KI had a recovery close to 100% for α-pinene oxide, nopinone and 4-acetyl-1-methylcyclohexene (AMCH). The authors also tested the recovery through one Na₂SO₃ soaked glass fibre filter, and reported recoveries of 28-45% for the tested reaction products. The recoveries of the reaction products through the NO₂+O₃ scrubber with KI and glycerol, were 84% for α-pinene oxide, 20-40% for nopinone and 56% for AMCH, which were improvements compared to the scrubber with Na₂SO₃ as the active substance. These results imply further development of scrubbers that have the capacity of removing both NO₂ and O₃, and have high recoveries of both alkenes and more reactive compounds.

By using one of the scrubbers mentioned above, air containing monoterpenes and both O₃ and NO₂ can be sampled without degradation of the adsorbent or oxidation of adsorbed compounds.
Multivariate methods

The curiosity of humans makes us strive to understand the world around us. To do this we measure a lot of things, which generates huge amounts of data coupled together. To be able to evaluate the data we need help from statistical computer programs. Transforming the data into models, which summarises the information of the data, facilitates understanding. In such a model the data are separated in two parts: the systematic part, explained by the model; and the remaining unmodelled part of the data - the noise.

\[
\text{Measurements (Y) = Model (b_0 + b_1x_1 + b_2x_2 + \ldots) + Noise (e)}
\]

In the equation \(b_0\) is the response of the reference (average response), \(x_{1,2,\ldots}\) represents different factors studied, and \(b_{1,2,\ldots}\) represents the influence on the response of a specific factor. In chemometrics, there are three basic categories of analysis

- Exploratory analysis (PCA) that gives an overview of all the data in order to detect trends, patterns or clusters.
- Classification analysis (SIMCA\(^*\), PLS-DA\(^*\)) that predicts a probable class membership of an observation.
- Regression analysis that is used for interpretation of relationships, prediction and optimisation (MLR\(^*\), PLS\(^*\)).

Multivariate approaches were used in both Papers II and IV, and an introduction to Principal Component Analysis (PCA) and Design of Experiments (DoE) are presented below.

\(^*\) The full text of the abbreviation is presented in the section of abbreviations.
Multivariate methods

Principal Component Analysis (PCA)

This tool is suitable when evaluating large amounts of data. It is hard to get insight about patterns and possible classes in the data only by looking at a table. By using PCA the data can be presented in a way that we can grasp, e.g. in a graph. PCA can be used in summarising and visualising a data set, multivariate classification and discriminant analysis, and in finding relationships among the variables.

Mathematically, PCA compresses a data set to its main structure and put simply, PCA search for similarities in the data, and tries to describe these trends by the help of a number of vectors called principal components (PC). In Figure 14 below an example of the responses of three different variables ($x_1$, $x_2$, $x_3$) for a number of observations are plotted. The first PC (PC1) represents the largest variation in the data in one direction, and the second PC (PC2) represents the second largest variation in the data, orthogonal to (at right angels to) the first PC, etc. In this way a large number of variables can be reduced to a few PC containing almost all the information in the data set. This makes it easier to find structures in the data describing similarities and dissimilarities between samples, and relations between samples and variables.

Figure 14. Projection of two principal components (PC), representing the largest variation in the data in two orthogonal directions.
Multivariate methods

The PC consists of two parts, the scores \((T)\) and the loadings \((P)\). The scores describe differences/similarities between observations. Plots in which scores from different principal components are plotted against each other serve as a good tool to get an overview of relationships in the data, i.e. separation of classes, or detection of outliers. The loadings explain the variation in the scores and the loading plot is a complement to the score plot. It is an essential tool in interpreting which variables are responsible for differences/similarities between observations, and also determines the size of and in which direction the variables contribute to the observed differences/similarities.

Design of Experiments (DoE)

Planning your experiments carefully can minimise the number of experiments required and can also facilitate the evaluation step. In a specific application there are often several factors that affect the process studied. The combination of factors and the settings that represents the optimum can be found efficiently using DoE. The influence of the different factors and interaction between factors are also possible to evaluate with this approach.

As a start, factors that are supposed to influence the process are selected and appropriate ranges (one low and one high level) of the factors determined. The ranges of the factors are determined at levels that expand the experimental domain as much as needed to be able to study the process of interest. By using DoE a set of experiments representing a full factorial design is selected, in which all relevant factors are varied simultaneously between experiments within the chosen ranges. In a full factorial design the chosen set of experiments represents all possible combinations of low and high levels of all the studied factors.

An example of the experiments chosen using a full factorial design with three factors \((O_3, NO_2\) and RH) is given below. The concentrations of \(O_3\) and \(NO_2\) are shifted between 25 and 75 ppb, and RH between 15 and 42%. This design requires eight experiments (represented by spheres in Figure 15) at different settings. The eight experiments represent all combinations of the levels of the factors studied. Three centre points are added as well to statistically verify the sampled system.
Multivariate methods

Figure 15. Experimental design including three factors. One corner in the cube represents one experiment.

In a fractionated factorial design the number of experiments can, for example, be reduced to half, as compared to a full factorial design (i.e. the experiments represented by grey spheres in Figure 15 are excluded from the design). In a case with five different factors, 32 different experiments are required in a full factorial design to cover all different combinations of the factors. This experimental design could be reduced to 16 experiments in a fractionated factorial design, and the three centre points. The designs could be further reduced as well, but this is not elaborated in this thesis.

The positive effect of using a fractionated factorial design is that the number of experiments is substantially reduced. The only negative effect is that confounding of effects is introduced in the design, i.e. the effects are to a certain degree mixed up with each other. In a fractionated factorial design with five factors, where the number of experiments has been halved, the confounding of effects is negligible. This conclusion can be drawn since the confounding introduced in the model is between four of the factors in the model, and are therefore of negligible importance in the evaluation.

After the experiments are performed, the responses and settings of the factors from the experiments are analysed by Multiple Linear Regression (MLR). This gives a mathematical model with statistical tools relating the changes in the factors to the changes in the response. The model will indicate which factors have
Multivariate methods

the highest influence on the response, and how different combination of factors influence the response. This can be displayed in tables, staple diagrams and as contour plots (graphic presentation) (Paper II).

The advantages of using DoE are that the experiments can be performed efficiently, a tool is provided to analyse and interpret the data, and that a platform is provided to facilitate the decision concerning further experiments.
Sick building syndrome

The concept of sick buildings and sick building syndrome was originally defined by the World Health Organisation in 1983\textsuperscript{86}, but complaints from workers concerning indoor air quality in buildings has received more attention since the 1970s\textsuperscript{87, 88}. Since then the awareness of the problem with health comfort coupled to buildings have increased, and today SBS is an acknowledged problem. A generally accepted theory is that SBS has increased as more energy efficient, well-insulated buildings have replaced the older naturally vented buildings\textsuperscript{89}.

Definition

The symptoms coupled to SBS refer to non-specific complaints such as\textsuperscript{86}:

- Eye, nose and throat irritation
- Sensation of dry mucous membrane and skin
- Erythema
- Mental fatigue
- Headaches, high frequency of airway infections and cough
- Hoarseness, wheezing, itching and unspecific hypersensitivity
- Nausea, dizziness

These symptoms appear when the person is located in a “sick” building and decrease when the person is no longer exposed to the environment that causes the complaints. The symptoms could vary widely from person to person within a building\textsuperscript{88}.
Wallace concluded that the symptoms included in different studies concerning SBS varied, which made a direct comparison of the results between the studies difficult. However, he found a few factors that were significantly associated with SBS that were common for the included studies. These were gender, dust, pre-existing allergies, ventilation, environmental pollutants, biological aerosols, chemical sensitivity, psychosocial aspects, temperature and humidity, and odours. These findings were in accordance with results reported by other research groups, who consider the problem with SBS to be of multifactorial origin; that is, several different factors together could cause the complaints of the indoor climate.

SBS and VOC

The concentration of a pollutant indoors is very variable since several factors could affect the wide variety of potential emission sources. This could be one reason as to why there are divergent results concerning the associations between VOC and SBS. Some of the factors that affect the composition of indoor air are climate, activities, lifestyles, and different building techniques between regions. In a review of the literature on VOC/TVOC and health, it was concluded that indoor air pollution most likely was a cause of health effects and comfort problems in indoor environments. It was also stated that the TVOC concept was not relevant from a health point of view. Brown et al. summarised that no conclusions could be drawn about the VOC and TVOC concentrations in complaint buildings relative to those in established buildings.

The concentrations of VOC in buildings could vary a magnitude or more depending on the age of the building. In new buildings the emissions from construction materials and building contents are the predominant factors that determine the concentration of the different compounds, and some of the VOC found in new buildings are not present in older buildings.

Several studies have demonstrated that the perception of indoor air quality is affected by the temperature and humidity in the air. When the air is more humid and warmer it is perceived as being less fresh, even though the concentra-
tions of volatile organic compounds (VOC) is constant. It is the combined effect of temperature and humidity that is essential for the perceived air quality\textsuperscript{93}. Changing the temperature and relative humidity affect the emissions from different materials in the indoor environment. The influence of these parameters was dependent on the VOC-type emitted and material studied\textsuperscript{94}.

Over the years a lot of effort has been made to measure the concentrations of different organic compounds, and to identify the VOC in indoor air. A common hypothesis was that the presence of SBS was coupled to the concentration of VOC, or the presence of specific compounds in the indoor environment. Several studies concerning the relation between SBS and levels of VOC have been made. However, up to today no straightforward evidence of such an association has been found\textsuperscript{4,5,88}. In this context Wolkoff et al.\textsuperscript{95} addressed the question of whether the relevant indoor pollutants were measured. Often the more unreactive compounds were measured and relations to SBS were looked for. Maybe it is the more reactive compounds that are responsible for the health complaints and should be measured as well\textsuperscript{96}. These reactive compounds were shown to be more irritating than their precursors. Wolkoff and Nielsen\textsuperscript{96} recommended that a broader analytical window of organic compounds should be used than the classic VOC window as defined by the World Health Organisation\textsuperscript{6} when sampling indoor air. Generally, these more reactive species are more difficult to sample. Furthermore, we might not even be aware of their existence, and they could be the compounds responsible for the health complaints reported. Maybe this could be an opening in trying to understand the causes of SBS.

An enhancement in the knowledge concerning the relation between SBS and VOC was the use of PCA in a multivariate study (Paper IV). In that study it was demonstrated that higher concentrations or the more frequent occurrence of a set of chemicals was an important aspect separating “healthy” buildings from “sick” buildings. It was mainly organic compounds with shorter retention times that were present in “sick” buildings in higher concentrations or more frequent than in “healthy” buildings. This PCA approach could be a helpful factor in elucidating the possible relations between VOC and SBS.
SBS and ventilation

The ventilation in a building is a factor that to a high degree determines the levels of contaminants indoors. Outdoor pollutants are transported indoors by the ventilation system and contaminants from indoor sources are diluted by increased ventilation. The ventilation rate also affects the temperature and RH in the building. This important role of ventilation on the indoor air quality is the factor that drew attention to the possible relation between ventilation and SBS.

However, a definitive relationship between ventilation rates and dissatisfaction with air quality indoors has not been established since mixed results have been reported\(^97\). According to Godish and Spengler\(^97\), the different outcomes of the studies could be explained by the complex relationships between ventilation rates, contaminant levels, and building related health complaints. Factors that could affect these relationships were, for example, study design and interacting variables, difficulties in controlling air exchange rates, inadequate mixing of supply air and air of occupied spaces, high source strengths, interactions between sources and ventilation rates. The conclusion of the review was that the relationship between ventilation conditions and air quality was relatively complex.

Mendell and Smith\(^98\) studied the relation between SBS and mechanical ventilation with and without air condition. These authors found an association between SBS and mechanical ventilation with air condition but no association with mechanical ventilation without air condition. This was supported in the review of Seppänen and Fisk\(^99\) and by Wargocki et al.\(^100\). Both of these works concluded that the literature indicated an increased risk of SBS in buildings with mechanical ventilation with air condition compared to naturally or mechanically ventilated buildings without air condition.

Despite this complexity some research groups have found that the effect of increasing outdoor air supply rate in an office on perceived air quality and SBS, was an improvement of the perceived air quality and decreased intensity of SBS symptoms\(^100-103\). This improvement of the air quality at increased outdoor air supply rate could relate with the modelled results of Weschler and Shields\(^19\). These authors concluded that the concentration of pollutants with indoor sources de-
increased with increased ventilation rates. The decreased concentrations and hence decreased oxidising reactions with compounds from indoor sources could contribute to the improvement of the perceived air quality. However, one should not forget, increased ventilation rate also increases the indoor concentrations of pollutants with outdoor sources.\(^\text{39}\).

Sundell et al.\(^\text{37}\) observed that a decrease of the TVOC concentration from supply to room air was associated with raised prevalence of occupant symptoms. This could be an indication that a higher degree of chemical reactions occurred or more sinks were present in buildings with high prevalence of SBS. These data were evaluated further in Paper IV and Chapter 13.
Multivariate methods and atmospheric chemistry

The use of multivariate methods in the design and evaluation of different atmospheric applications make the interpretation of the data easier. In many cases, in my opinion, the data are also more reliable because of the identification of interactions, and due to that a larger number of variables could be included in the analysis.

The air quality in our environment is an issue that is debated in society today. Measurements are performed to determine concentrations of several pollutants, temperature, humidity, etc., in order to control the exposure to people. The exposure to individual compounds present in the indoor environment is mostly well below recommended concentrations, and conclusions about the total exposure cannot be drawn. A method to calculate the effect of the total exposure of people to chemicals in the indoor air is therefore desired.

The use of multivariate methods to determine if, and how much, a pollutant, set of pollutants, or other measured factors affect the perception of air quality could be such a method. By using this approach interactions between chemical compounds and other factors can possibly be detected. These interactions could represent either synergistic effects or maybe the formation of other compounds or radicals than those measured.

Chemical reactions in air mixtures are complex. Thus theoretic aid from computer modelling is often used to facilitate the understanding and for calculating to
which extent the different reactions occur. When evaluating the results from the experiments in the thesis, two multivariate methods, DoE and PCA, were used to facilitate the evaluation of the data.

When making experiments the use of DoE facilitates the evaluation step since the influence of variation in data and some instability are reduced due to the amount of experiments included in the design. All the experiments performed were used as a basis for the calculation of the model used in the evaluation. When using DoE all experiments are related to each other, and if there is no systematic variation no model can be created. The reason for non-systematic variation could, for example be that the factors studied did not influence the reaction, or that the measured response was not accurately determined. Hence, using this method secures quality assurance. The use of DoE made it possible to study several influencing factors, and the interaction between factors and responses, simultaneously.

In Paper II, the influences of five factors on the reaction of monoterpenes were studied. In the evaluation it was found that five of the factors directly influenced the amount of $\Delta^3$-carene reacted, and that interaction between these factors influenced the reaction as well (Figure 16).

To interpret the meaning of the interactions the theory of atmospheric chemistry and relevant chemical reactions were studied. In the interpretation in Paper II, it was concluded that one of the interactions represented the effect of radicals in the air mixture ($O_3$-reaction time), and that other interactions were interpreted to represent the effect of $NO_2$ ($O_3$-$NO$), and the variation of the $O_3$ concentration ($NO$-reaction time). It cannot be expressed clearly enough that interactions between studied factors are very important to include in the evaluation of experiments.
Figure 16. Effect plot for $\Delta^3$-carene. The different columns/terms show the effect on the amount of $\Delta^3$-carene reacted when a factor was changed from a low to high setting with the other factors on their centre settings. Confidence level 95%.

By using PCA, the interactions or correlations between different factors were included as well. In Paper IV, PCA was used to evaluate a large data matrix. A systematic variation in the data was evaluated and from the original 179 variables 42-68 variables, depending on which model evaluated, were extracted as the most influencing variables in the class separation between different objects, i.e. “sick” and “healthy” buildings.

In one of the models evaluated with PCA in Paper IV, it was possible to separate 71% of the “sick” buildings from the “healthy” buildings with a statistical significance level of 99.9%. This was done by making a model of the rooms in the “healthy” buildings, and studying how well the rooms in the “sick” buildings fitted in that model. The degree of fit was expressed as bars in a distance to model plot, and the shorter the bar the better fit to the model of the “healthy” buildings (Figure 17). All bars exceeding the upper horizontal line did not fit the model at the chosen significance level, and was consequently defined as “sick” buildings by the model.
Figure 17. In this plot 71% of the “sick” buildings were separated from the “healthy” buildings by exceeding the upper horizontal line. Note that one bar in the figure represents one room and that one building is represented by 1-4 rooms. A total of 26 buildings are evaluated.

The significance level of 99.9% was chosen to make the determination of “sick” buildings more accurate and avoid misclassifications. This significance level is however quite high, and when using the lower significance level 95% (the lower horizontal line in Figure 17), the class separation increased markedly. Thirteen of the 14 “sick” buildings were classified as “sick” in the model. That is >92% compared to 71% in the model with the higher significance level.

This difference of chemical composition of the air in buildings and the difference of some building parameters were not found using other statistical tools. This demonstrated the power of using multivariate methods in the evaluation. These methods have the capacity to embrace the relations, as well as the variations in many parameters, simultaneously.
Theoretical modelling – possibilities and difficulties

Many of the theoretical models are developed to make calculations on a regional scale. Such models can be used to predict both short and long-term variation of, for example, O₃ and CO in the environment. Theoretical modelling is a valuable tool to understand how emitted compounds disperse, is transformed, and for predictions of the effects of the emitted compounds. However, theoretical models contain some uncertainties such as concerning the condensation of reactions in the models, reaction rates used, and the yields of radicals and organic species in the reactions. Therefore, it is recommended to use more than one theoretical model in order to achieve results when different ways of condensating reactions and other reaction rate constants and yields are used to deal with these known uncertainties.²⁹

The models used for regional scale predictions embrace many different classes of compounds. Limited models that only take one or a few compounds into account are also used. These limited models are valuable when studying specific reactions, and reaction mechanisms of which the knowledge today is insufficient. Such models are also valuable tools when ascertaining which reactions occur and relations between reactions in experimental chambers.

In the thesis (Paper II) the amount of monoterpane reacted was studied in a reaction chamber. The experiments were performed according to DoE, and the evaluation of the factors that influenced the amount of monoterpane reacted was interpreted in more detail than would have been possible if one experiment was
Theoretical modelling – possibilities and difficulties

performed at a time. Still it was impossible to specify how much influence different compounds had on the reaction and which reactions occurred.

However, by using a theoretical model created to correspond to conditions used in the experimental set-up, further information of the chemical reactions could be extracted. In Paper III, the calculated concentrations of O₃, NO₂ and NO at the end of the reaction chamber were compared to experimental results with the same settings, and the concentrations were found to correspond to a high degree. The influence of different reaction pathways was extracted as well, in order to study how the influence of different reaction pathways changed when changing the initial concentrations of O₃, NO₂ and NO. This matter is further discussed

Figure 18. The amount of α-pinene reacted after 213 s experimentally (black dots) and calculated theoretically (grey dots)*.

* The upper grey dots at each combination of settings of O₃ and NO₂ represents that a high initial setting of NO₂ (75 ppb) was used in the calculations. The lower grey dots represent a low initial setting of NO₂ (25 ppb).
The calculated amount of monoterpene reacted by the theoretical model was compared to the experimental results (Figures 18 and 19), as well as the levels of O₃, NO₂ and NO.

In both Figures 18 and 19 it can be seen that the predictions of the theoretical models underestimated the reactivities of the gas mixtures demonstrated in the experimental results. The theoretical models managed in most cases to predict the direction of the influence on the amount of monoterpene reacted, when changing the initial settings of O₃ and NO₂. The major shortcoming in the predictions was when the initial setting of NO was changed.

Figure 19. The amount of Δ₃-carene reacted after 213 s experimentally (black dots) and calculated theoretically (grey dots)∗.

*The upper grey dots at each combination of settings of O₃ and NO₂ represents that a high initial setting of NO₂ (75 ppb) was used in the calculations. The lower grey dots represent a low initial setting of NO₂ (25 ppb).
The difference in amounts reacted calculated in the theoretical model and found in the experimental results was also observed by Fick et al. The authors observed however, a smaller difference than that in the current study, which was probably due to the less complex atmosphere studied and hence, reduced content in their theoretical models. A divergence between theoretical calculations and measurements in the environment are also found in the large urban to regional scale chemical mechanisms mentioned earlier.
The effect of changing relative humidity and pollution load

In the thesis, data are collected from environments with varying conditions. It could be, for example, different RH, levels of VOC, NOx, or O3. It has been demonstrated that the levels of these factors affected the extent of, and the proportions between different chemical reactions occurring in air.

The role of relative humidity

In Paper II it was demonstrated that increased RH decreased the amount of monoterpene reacted. Of the factors studied RH was the third most influencing on the amount of monoterpene reacted. It was preceded by the influence of O3 and reaction time. When increasing RH from 15 to 42% the amount of α-pinene and Δ3-carene reacted after 213 s decreased from 8.1 to 6.1% and from 9.0 to 7.3%, respectively, at centre levels of O3, NO2 and NO. This significant effect of RH on the reactions of monoterpenes was not observed earlier. The focus in the literature had been on the influence of RH on the product formation and on aerosol formation. The influence of RH on the reaction between monoterpenes and the oxidants O3 and NO2 could be explained by that the carbonyl oxide formed in the reaction between O3 and the monoterpene was scavenged to a higher extent when RH was increased. The carbonyl oxide has been shown in several studies to react with water present in the gas-phase. This reaction between the carbonyl oxide and water can decrease the formation route for OH·, which starts out from the
carbonyl oxide thereby decreasing the total reaction with the monoterpene. The carbonyl oxide itself could also react with alkenes and when increasing RH the possible reaction pathway between the carbonyl oxide and monoterpenes decrease as well.

The relatively large effect of RH on the reactions of monoterpenes in an air mixture of O₃, NO₂ and NO implies that more attention must be taken when evaluating experiments performed in chambers with different relative humidities. More research is needed to examine the effect on other chemical reactions as well as details of the chemical mechanisms, to be able to include the influence of RH in theoretical studies.

As demonstrated in the thesis, RH has an important role in influencing chemical reactions occurring in air, and it was shown to be one factor that differed between “healthy” and “sick” buildings. Therefore, it is important to include RH as one parameter when studying chemical reactions, indoor air quality, and when studying the effects of chemical mixtures on the perception of air quality.

In Paper IV it was found that the RH was higher in “sick” buildings compared to “healthy” buildings. If the results from Paper II concerning the effect of RH could be considered to be valid for all alkenes, less of the alkenes reacted in the rooms and/or during transport into the “sick” buildings. As a consequence lower amounts of reaction products were formed that could act as irritating agents. If this decreasing effect of RH is thought to be valid for all the compounds sampled that are reactive towards O₃ and/or NO₂, this result was somewhat contradictory to the results presented in Sundell et al. The authors discussed the possibility that the decreased level of TVOC from supply to room air found in “sick” buildings could be explained by an increase of chemical reactions in “sick” buildings producing reactive chemicals not sampled with the method used. But, as concluded in Paper IV it is not appropriate to extract one variable from the developed model, for example, RH as discussed above, and make statements about the effect of having low or high levels. The ability of the developed model to separate the “sick” buildings from the “healthy” buildings is coupled to the co-variation of several variables included in the model.
Change in pollutant load

In the study of “healthy” and “sick” buildings (Paper IV) it was found that the “sick” buildings had higher levels of TVOC in intake and supply air as compared to the “healthy” buildings. To diminish the pollution load transported into buildings through ventilation systems, the intake air to the building should be placed away from polluted areas. By placing the air intake at the most appropriate place and using, for example, carbon filters (decreasing the levels of VOC, and in some cases O₃), the pollution load could be diminished, and a higher indoor air quality could be reached. These actions reduce the pollution resulting from outdoor sources. Reducing indoor sources requires other actions such as replacing high emitting materials or increasing the air exchange rates.

The buildings studied in Paper IV were located within different cities with different vicinity to emission sources and placements of air intakes, which could be factors that determined the level of TVOC in intake and supply air. The outdoor air concentrations of organic compounds and oxidants such as O₃, NOₓ, and SO₂ in the area around each building were unfortunately not measured in the study from which data were used in Paper IV. Information about the placement of the air intakes on the different buildings (if it was close to emissions sources like traffic and exhaust air of the buildings) was not available but could be part of the explanation to the difference of the chemical composition in intake, supply and room air between “healthy” and “sick” buildings. TVOC in intake and supply air, individual chemicals (represented by retention time intervals in Paper IV), building specific parameters (Paper IV), RH (Paper IV), and a set of psychosocial factors were shown in different studies to be correlated to the presence of SBS.
Conclusions and future work

In the present thesis a scrubber was developed to remove O₃ and NO₂ prior to sampling. Thus artefacts were minimised, which are a common problem when sampling in environments with elevated concentrations of O₃ and NO₂. Therefore, the use of such a scrubber for future investigations is recommended.

In the thesis this scrubber was used when factors that influence the reaction of monoterpenes with O₃ and NO₂ were studied. The main factors that influenced the reaction were the level of O₃, reaction time, and relative humidity. The evaluation of possible interactions between factors was facilitated by the use of multivariate methods.

A theoretical model of the reactions occurring in the reaction chamber was created, and the amount of monoterpane reacted at different initial settings of O₃ and NO₂, and NO was calculated. These theoretical results were compared to the experimental results, and the theoretical calculations were generally found to underestimate the reactivity of the gas mixture, which implies that the effects of oxidants in the air at elevated concentrations are undervalued. However, the calculated concentrations of O₃ and NO₂, and NO after 213 s were found to correspond to a high degree with concentrations from experimental results.

The presence and concentrations of organic compounds in the indoor air, along with a few building variables, were shown by the help of PCA to be associated with the presence of SBS.
The work in this thesis further reveals that there is insufficient knowledge in some areas concerning the indoor air chemistry of monoterpenes. To fully understand how different factors affect the chemical reactions, and to be able to draw more extensive conclusions from experiments, future work should focus on:

- Studying the influence of RH on chemical reactions occurring in air.
- Studying the effect of different surfaces on the chemical reactions.
- Studying the combined effect of RH and surfaces in the reaction chamber to be able to evaluate the role of surface water.
- Further elucidating the reaction mechanisms concerning the reaction of monoterpenes with \( \text{O}_3 \), \( \text{OH}^- \), \( \text{NO}_2 \), NO and \( \text{NO}_3^- \).
- Studying and re-determining the sizes of the gas-phase rate constants of the reactions of \( \text{NO}_2 \) with monoterpenes.
- Studying the effect of chemical reactions of monoterpenes investigated in the present thesis when introducing radiation.
- Making surveys of the variations in concentration of different chemicals within buildings.
- Studying patterns and interactions between different factors in a larger perspective instead of studying processes or chemical reactions one by one.
- Studying possibilities and the effect of reducing indoor concentrations of different chemical compounds, either by exchanging materials in the indoor environment, or absorbing/collecting the compounds prior to or in the ventilation systems.

Hopefully, this future work will shed additional light on the chemistry occurring in indoor air, and that conclusions can be drawn about the causes of the health complaints concerning indoor air quality.
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Summary of papers

Paper I

In experiments it was demonstrated that the adsorbent Tenax TA was degraded by NO₂, and that monoterpenes adsorbed on Tenax TA were oxidised 5-21% by NO₂. This influence of NO₂ encouraged improvements of the sampling method, and the current work was focused on the development of a scrubber to remove NO₂ prior to the sampling tube.

Fourteen different chemicals were tested as possible scrubber materials for NO₂. Sodium sulphite (Na₂SO₃) was the most suitable chemical in removing NO₂ and a scrubber was constructed that consisted of two filters applied with Na₂SO₃ inserted into a dust collector. This scrubber was able to remove both NO₂ and O₃ at relative humidity of 0-42%. The recoveries of the monoterpenes through the scrubber at different relative humidity were 75-97%.

Paper II

In this study the influence of different factors on the reaction of monoterpenes with O₃, NO₂ and NO at different relative humidities was evaluated. It was demonstrated that O₃, reaction time and relative humidity had the highest influence on the amount reacted. Increased levels of O₃ and NO increased the amount reacted and an increase in relative humidity, decreased the amount reacted. Various interactions between added chemicals, which also affected the reaction, were identified and interpreted, e.g. NO-reaction time and O₃-reaction time.
Summary of papers

Paper III

Theoretical models concerning the magnitude of the reaction of α-pinene and Δ⁢³-carene with O₃ and NO₂ in an atmosphere were constructed, evaluated and compared with experimental results. The levels of O₃, NO₂ and NO in the air after 44 s and 213 s were calculated by the theoretical model as well and were compared to experimental results. The comparison showed a good agreement between the levels calculated theoretically and the experimental results.

The best performance of the models in calculating the amount of monoterpane reacted was obtained at a high initial setting (75 ppb) of O₃ and NO₂, and a low initial setting (25 ppb) of NO or exclusion of NO. In this situation the calculated amounts of α-pinene and Δ⁢³-carene reacted were 67% and 44%, respectively, of the experimental values.

Paper IV

In this paper a multivariate approach was used in the evaluation of a large data set containing chemical measurements and building data from 29 office buildings in northern Sweden. Fourteen buildings were considered to be “healthy” and 15 as being “sick”. In one of the constructed models, 71% of the “sick” buildings were separated from the “healthy” buildings. The most important variables that contributed to the separation of the “sick” buildings from the “healthy” buildings were more frequent occurrence or higher concentration of compounds with shorter retention times, elevated relative humidity, and higher level of total volatile organic compounds.