Report No 26

Impact of Ozone-initiated Terpene Chemistry on Indoor Air Quality and Human Health

EUROPEAN COLLABORATIVE ACTION
URBAN AIR, INDOOR ENVIRONMENT AND HUMAN EXPOSURE

Environment and Quality of Life

Report No 26

Impact of Ozone-initiated Terpene Chemistry on Indoor Air Quality and Human Health

prepared by

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The mission of the IHCP is to provide scientific support to the development and implementation of EU policies related to health and consumer protection. The IHCP carries out research to improve the understanding of potential health risks posed by chemical, physical and biological agents from various sources to which consumers are exposed.

A great deal of additional information on the European Union is available on the Internet. It can be accessed through the Europa server
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MANDATE: European Collaborative Action **"Urban Air, Indoor Environment and Human Exposure"** (formerly "Indoor Air Quality & it's Impact on Man")

For more than 22 years now the European Collaborative Action ECA "Indoor Air Quality & it's Impact on Man" has been implementing a multidisciplinary collaboration of European scientists the ultimate goal of which was the provision of healthy and environmentally sustainable buildings. To accomplish this task ECA is dealing with all aspects of the indoor environment including thermal comfort, pollution sources, the quality and quantity of chemical and biological indoor pollutants, energy use, and the ventilation processes which all may interact with indoor air quality. The work of ECA has been directed by a Steering Committee.

In order to provide a broader view on air pollution exposure in urban areas, both indoors and outdoors, the ECA Steering Committee decided to put more emphasis on the links between indoor and outdoor air quality and to focus its further work under a new title "Urban Air, Indoor Environment and Human Exposure". The focus of the renewed activity is urban & indoor air pollution exposure assessment, seen as part of environmental health risk assessment and also considering the needs of urban and indoor air quality management. The new approach hosts and supports the activities of the Joint Research Centre's Institute for Health and Consumer Protection in Ispra (Italy) dealing with Physical and Chemical Exposures and Health Effects.

This focussed activity proceeds within the broader framework of (i) health and comfort of the citizens, (ii) building technologies and source controls, and (iii) requirements of sustainability, energy efficiency and conservation of natural resources.

Specific examples of the working areas of ECA are:
- the relative importance of outdoor and indoor sources of pollution,
- the building-related interaction between outdoor urban air and indoor air,
- exposure to pollutants from the different urban outdoor and indoor sources and its relation to health and comfort.

By addressing such topics ECA will lay the ground for air quality management to minimise exposures to air pollutants. It will thus continue to contribute to pre-normative research needed by EC services and national authorities responsible for preventing pollution and promoting health, comfort and quality of life.

In this series the following reports have already been published.

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Abstract

ECA-IAQ (European Collaborative Action, Urban Air, Indoor Environment and Human Exposure), 2007. Impact of Ozone-initiated Terpene Chemistry on Indoor Air Quality and Human Health, Report No 26. EUR 23052 EN. Luxembourg: Office for Official Publications of the European Communities

This report summarises the state of the art concerning ozone-initiated chemistry and its impact on indoor air quality and human health and recommends prioritised research goals for the future. The focus is on terpenes (e.g., limonene, α-pinene) for reasons of high chemical reactivity and abundance.

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EXECUTIVE SUMMARY

Introduction and objectives

Hundreds of compounds have been measured in indoor air including VOCs (volatile organic compounds), NO_X (nitrogen oxides) and ozone (O_3). However, to date, the only potential sensory irritants to be identified has been formaldehyde. Until recently, most research has focussed on the compounds that are emitted indoors and relatively little attention has been paid to the significance of the reactions that are likely to occur between them, i.e. mixtures. Furthermore, it is unclear whether the concentrations observed indoors are detrimental to health, or even if the compounds that are detrimental to health are being measured. For instance, hitherto unmeasured compounds have recently been confirmed to be present in abundant amounts at ambient conditions through the reactions of ozone and terpenes. Recent work suggests that the products of VOC degradation (oxidation), in particular those of terpenes, following reaction with O_3, the OH or NO_3 radicals, may be responsible for some of the reported symptoms. When ozone reacts with these VOCs, radicals such as OH, HO_2 and RO_2 are formed, as well as stable products such as aldehydes, peroxides and condensed phase compounds, some of which are sensory eye and airway irritants. Many of these compounds cannot currently be measured by traditional analytical techniques.

In this report an attempt has been made to summarise the state of the art concerning ozone-initiated chemistry and its impact on indoor air quality and human health and to prioritise research goals for the future. The focus of this report is on terpenes (e.g., limonene, α-pinene), owing to their high chemical reactivity and abundance in the indoor environment.

Content

Chapter 1 summarises the importance of ozone-initiated terpene chemistry for indoor air quality and human health, based on the outcome of several recent events and a review of a number of scientific studies in the field of indoor environmental chemistry. This evidence leads to the conclusion that in order to be able to properly assess risks related to ozone-terpene reaction products indoors and to formulate appropriate risk management measures, the concentration and composition of terpenes in the products and materials used indoors must be quantified, as well as the consumption rates through various reactions. However, currently this knowledge is incomplete. Moreover, as stated in the INDEX project, there are insufficient exposure and toxicological data to carry out a complete risk analysis for limonene and α-pinene, especially as the effects of the products of ozone reactions could not be assessed. Finally, the need to combine multidisciplinary expertise for analysing the issue of ozone-initated indoor air chemistry and its effects on air quality and human health are underlined.

In chapter 2, the terminology used for and the main sources of terpenes are provided.

The similarities and differences between gas-phase chemical reactions occuring indoors and outdoors are critically reviewed in chapter 3. Sources, concentrations, key determinants and suggestions for reducing indoor ozone concentrations are reported. Similarly, indoor sources of common terpene compounds and I/O ratios of terpenes measured across Europe are summarised. The importance of the air exchange rate for ozone removal as a competing

factor to removal by terpenes is illustrated and mechanisms for OH, NO$_3$ and particle production from gas-phase chemistry are elucidated. There have been no studies investigating the detailed composition of indoor particles to date and such studies should be a future focus of research efforts in indoor air pollution. The final part of chapter 3 reviews several recent studies that employed chemical models for understanding chemical processes indoors. The results of these studies indicate that unlike outdoors where photolysis reactions are pivotal radical initiators, the reactions of ozone with alkenes and monoterpenes play the major role in producing new radicals indoors. One important result that has emerged from these studies is the importance of tailoring a model for its particular location. As O$_3$ and NO$_X$ concentrations have a pivotal effect on indoor chemical processing, it is essential that appropriate conditions are used to initialise a model. Many indoor studies are focussed in the US where outdoor (and consequently indoor) ozone concentrations are likely to be higher than in many parts of Europe. In addition, there is a need for future indoor air measurements of radical compounds, nitrated compounds such as PANs and organic nitrates, photolysis rates of key compounds over the range of wavelengths observed indoors and concurrent measurements of outdoor air pollutant concentrations. Finally, the issue of mixing should be considered, as there can be significant concentration gradients of both reactants and products within a room. Reactions will occur at different rates across the room depending on the concentration of the reactants at any given point and produce varying concentrations of products. These results have implications for those employed in exposure studies, whereby measuring at one point in a room may not be representative for all occupants. Ideally, measurements should be made at several points around a room in order to assess whether the 'well-mixed' assumption usually applied in modelling studies is justified.

Chapter 4 deals with the degradation of material/product surfaces (through reaction with ozone, the hydroxyl and nitrate radicals), which of increasing concern not only in terms of sustainability, but also with regards to comfort, health, and productivity. In addition, chemically reactive VOCs, which are emitted from materials and products, may produce new oxidized products, including ultrafine particles. These properties, however, are not considered within existing international standards for material and product emission testing. Chapter 4 concludes that it is not currently possible to predict the impact of new odours produced through oxidative reactions, either on perceived air quality or on productivity. Since the emission of terpenes may be substantial under certain conditions, the formation of sensory irritants could add to the perception of eye and upper airway effects, and ultrafine particles and radicals may cause lung effects.

For a complete understanding of ozone-initiated chemistry of terpene degradation the concentration of the key reactants ozone and terpene have to be monitored as well as possible reaction partners for the Criegee-intermediates (e.g. water, aldehydes and acids). For all of these compounds there are several well established techniques available. Following the formation of reaction products is less straightforward, since the manifold of reaction products and reactive intermediates requires more elaborate methods, especially for the short-lived radicals and thermolabile compounds like hydroperoxides and secondary ozonides. Therefore the necessary analytical techniques cover a broad range of methods, which are summarized in chapter 5. A more detailed description for each method is presented in Annex 1.

The potential health impact of indoor air chemistry, in particular, of products resulting from ozonolysis of terpenes (e.g. limonene and α-pinene), along with sensory irritation thresholds of these compounds are discussed in chapter 6. Recent findings, both epidemiological and

experimental, suggest that these ozonolysis products could increase sensory irritation, although results remain to be substantiated in full scale experiments. Both animal and human exposure studies indicate that gaseous R-limonene/ozone (LO) and α-pinene/ozone (PO) reaction products may cause trigeminal stimulation of the eyes and upper airways at ozone and terpene concentrations that are close to high-end values measured in indoor settings. The impact of ultrafine particles on short-term symptoms like eye and upper airway irritation is unknown and their possible role in the development of effects in the lower airways is debatable. No specific experimental literature is available on potential long-term health effects. In addition, the relationship observed in epidemiological studies between ozone exposure and health effects could be hypothesized to be partially due to the action of products of ozone-initiated indoor chemistry, given that people usually spend most of their time indoors (~90%).

Finally, chapter 7 discusses the steps involved in a risk assessment for indoor ozone-initiated terpene chemistry, including hazard identification, exposure assessment, dose/response assessment and risk characterization. In summary, further knowledge is required to complete a risk assessment associated with exposure to indoor "ozone-initiated terpene chemistry". Although some associations with adverse health effects of consumer products have been observed, the causal relationship remains unclear. Observed sensory effects could be associated concomitantly with the presence of numerous chemical species, but also with as yet unknown factors/agents. Experimental insight in this field would be further beneficial as:

- current exposure data relating to ozone-terpene reaction mixtures are currently too limited for conducting an exposure assessment,

- results on acute symptoms associated with exposures to LO and PO reaction mixtures have still to be confirmed,

- full scale studies were never reported under realistic conditions, e.g. during the application of selected consumer/household products and in the presence of ozone, in order to evaluate the magnitude of exposure to the above named reaction products and the severity of symptoms,

- research on LO and PO effect levels were never confirmed/investigated on susceptible subgroups of the population, i.e. persons suffering from asthma and other respiratory diseases, infants, children or the elderly.

Conclusions

- The use of some consumer products can result in abundant indoor concentrations of terpenes.

- The chemistry of indoor air is dominated by ozone reactions with terpenes, reactions that can produce highly reactive intermediates (e.g., radicals), secondary ozonides, hydroperoxides, carbonyl compounds and also fine particles in the sub-micron range. An important product of such reactions is the OH radical, which can proceed to initiate further oxidation processes. Indeed, many reaction rates indoors have been predicted to be of a similar order of magnitude to outdoors and sometimes even larger.

- There is neither, adequate knowledge of exposure patterns of ozone-terpene reaction

products, nor dose/response relationships. There are toxicologically relevant compounds formed in ozone terpene reactions that remain unidentified. These compounds (e.g. radicals, aldehydes, acids) are potentially responsible for the observed health effects (e.g., sensory irritation, lung injuries, etc).

Recommendations

1. This report summarises our current knowledge of ozone-terpene related indoor air chemistry, although there remain significant gaps. In addition, many of the issues are exceedingly complex, both chemically and physically. It is increasingly recognised that secondary products are the cause of the ill-health effects observed indoors, however, the actual culprits have yet to be fully identified. Furthermore, model predictions of OH and NO_3 radical concentrations indoors need to be verified through experimental observation. Ideally, many of these gaps in our knowledge could be addressed by organising indoor air 'field campaigns' similar to those commonly performed outdoors. One would envisage that indoor measurements could be made *simultaneously* of the concentrations of radicals, ozone, NO_X, VOCs (particularly the reactive compounds such as the terpenes), HONO, aldehydes including HCHO, as well as aerosol size, number and composition, photolysis rates, temperature and humidity etc., in order to validate models and to identify compounds that may be deleterious to health.

2. Considering the long-term and integrated impact of material/product oxidation on exposure to indoor air, it is prudent to develop methodologies for emission testing of construction materials and consumer products (in particular spray products) under oxidative and realistic conditions for future standardization.

3. Both ozone and formaldehyde concentrations should be measured in micro-environments suspected to have strong sources of terpenes, owing to product usage or personal activities.

4. Analytical methods to measure potentially toxicologically relevant compounds indoors e.g. radicals should be further developed for practical use.

5. New metrics/proxies that are health relevant should be identified and developed, both with regard to acute/semi-acute effects and longer-term effects.

6. Risk characterization of the mixed terpene-ozone system calls for more toxicological knowledge:

    - Acute and longer-term exposure effects to eyes and upper and lower airways.

    - Evaluation and assessment of selected consumer products, in particular spray products in the presence of ozone, through the use of bioassays and full scale human exposure studies under realistic conditions.

1   INTRODUCTION

Several recent events have demonstrated that indoor environmental chemistry is an emerging issue with regard to its impact on human health (Weschler *et al.*, 2006, Carslaw and Wolkoff, 2006). In addition, the Fourth Ministerial Conference on Environment and Health organised by WHO-Europe in 2004, stressed the importance of preventing and reducing respiratory disease owing to outdoor and indoor air pollution, in the hope of reducing the occurrence of childhood asthma. For example, a recent study by Bristol University indicates that the development of childhood asthma could be related to the use of various cleaning materials and fragrances in the home (Sherriff *et al.*, 2006).

Moreover, at a meeting of the UK Air Quality Forum (DEFRA, 2003), the Brit. Med. Assoc. expressed concern about the health effects of indoor air pollution related to emissions from products and materials used in indoor environments.

On June 9, 2004 the European Commission within the frame of its Environment and Health Strategy launched the Environment and Health Action Plan (2004-2010) including an action on indoor air quality with the aim to initiate and promote activities to evaluate the impact of indoor air on human health, with primary focus on vulnerable groups such as children and elderly people. All this clearly demonstrates that there are some important issues in relation to indoor air quality and health that warrant further investigation.

Hundreds of compounds have been measured in indoor air including VOCs (volatile organic compounds), NO_X (nitrogen oxides) and ozone (O_3), without successful identification of potential sensory irritants, except formaldehyde. Although substantial research has been carried out on indoor air quality, there are still many unknowns (Carslaw and Wolkoff, 2006). Until recently most research has focussed on the compounds that are emitted indoors and relatively little attention has been paid to the significance of the reactions that are likely to occur between them, i.e. mixtures (Wolkoff *et al.*, 2006). Furthermore, it is unclear whether the concentrations observed indoors are detrimental to health, or even if the compounds that are detrimental to health are being measured. For instance, hitherto unmeasured compounds have recently been confirmed to be present in abundant amounts at ambient conditions through the reactions of ozone and terpenes (Nørgaard *et al.*, 2006).

Recent work suggests that the products of VOC degradation (oxidation), in particular those of terpenes, following reaction with O_3, or the OH or NO_3 radicals, may be responsible for some of the reported symptoms (Weschler *et al.*, 2006, Wolkoff *et al.*, 2006). Ozone is generated in outdoor air and penetrates into indoor environment as a result of infiltration and ventilation. Ozone may also be emitted directly indoors from photocopiers, printers and air cleaning devices (Niu *et al.*, 2001, Rockstroh *et al.*, 2003). Typical indoor air concentrations of ozone vary between 1 and 100 µg/m³. The strategies to determine and control the indoor air concentrations of ozone are analysed in the recent ECA-STRATEX report (ECA, 2006). Terpenes are found in numerous daily life items, like adhesives, "organic" paints, houseplants, toiletries, air fresheners, and cleaning and general household products (Singer *et al.*, 2006; Nazaroff and Weschler, 2004; Wolkoff *et al.*, 1998). In addition, they are also emitted from a number of wooden-based construction materials, and furnishing (Atkinson and Arey, 2003, Iwashita, 2005, Kagi *et al.*, 2005). Isoprene is also a major exhaled human metabolite.

To be able to properly assess risks related to ozone-terpene reaction products indoors and to focus risk management measures correctly, the amount, the content, and the consumption of

terpenes in the products and materials used indoors must be known. Currently, this knowledge is incomplete. However, some information is available about the amounts of production and contents of terpens in products. It was assessed that the annual worldwide production of d-limonene and orange oil/essence oil (95% d-limonene) in 2001 would have been 73 kt (IARC, 1993). Production volume of d-limonene in Japan was about 40 kt in 1993. In 1984, the US consumption of d-limonene was 250 t. The number of industrial plants in the USA handling dipentene has increased during last decades, especially because of its use as a substitute for chlorinated hydrocarbons, chlorofluorocarbons, and other solvents. According to the Swedish National Chemicals Inspectorate, between 69 and 80 t of d-limonene in 48 products (15 for consumers) were used during 1994 in Sweden. The corresponding numbers for dipentene were 74-88 t in 106 products (26 for consumers) (WHO 1998).

The new European chemicals legislation (REACH) requires producers and importers of chemical substances on their own, in preparations or in articles to systematically collect and distribute information on the health and environmental risks related to substance use, exposure scenarios and risk management measures across the entire lifecycle of a substance. Especially, the use of household and consumer products may have a great influence on indoor air quality. When, the recently founded European Chemicals Agency has received the information required in the REACH legislation to register substances, also the amounts of terpenes such as limonene and α-pinene, used in Europe for example in household and consumer products will be known.

Outdoors, the main atmospheric oxidant is the hydroxyl (OH) radical, which is responsible for processing the major atmospheric pollutants and mediating atmospheric oxidation processes. Recent studies using models or indirect measurements, have predicted indoor OH radical concentrations only a factor of ten less than outdoors despite the much lower levels of light indoors (Weschler and Schields, 1997, Sarwar *et al*., 2002, Carslaw, 2007). Model studies predict that most 'new' OH indoors is formed through the reaction of ozone with alkenes and monoterpenes, e.g. (Destaillats *et al*., 2006, Carslaw, 2007), which are emitted from a number of sources indoors.

For example, residential α-pinene concentrations in indoor air in European cities varied from 4 $\mu g/m^3$ in Basel to 18 $\mu g/m^3$ in Milan (30-hour mean values) as reported in the EXPOLIS-study (Jantunen *et al*., 1999). Simultaneous ambient air levels were clearly lower than the indoor concentrations suggesting the critical role of the indoor sources in increasing indoor concentrations of α-pinene. Similarly, indoor concentrations of limonene were higher than ambient air levels. Residential indoor concentrations varied from 15 $\mu g/m^3$ in Basel to 78 $\mu g/m^3$ in Athens (30-hour mean values). The maximum residential indoor air concentration of 308 $\mu g/m^3$ was reported in an English study (28-day average) (Brown *et al*., 2002). The recently published INDEX project stated that there exists insufficient knowledge of exposure and toxicological data to carry out a complete risk analysis for limonene and α-pinene, especially as the effects of the products of ozone reactions could not be assessed (Kotzias *et al*., 2005).

When ozone reacts with these VOCs, radical products such as OH, HO_2 and RO_2 are formed, as well as stable products such as aldehydes, peroxides and condensed phase compounds, some of which are sensory eye and airway irritants (Wolkoff *et al.*, 2006). Many of these compounds cannot currently be measured by traditional analytical techniques.

Moreover, experimental and modelling studies show that several (stable) compounds can attain relatively high concentrations indoors including carbonyls, alcohols, acids, nitrated compounds (such as peroxyacetylnitrates (PANs) and organic nitrates), ozonides, etc, as well as ultrafine particles (e.g. Weschler and Shields, 1999, Wolkoff *et al.*, 2006, Carslaw, 2007). Many of these products arise from the degradation of oxygenated intermediate compounds, are highly condensable, and may proceed quickly to the aerosol phase. This gas-to-particle conversion is interesting from two perspectives; first, it is potentially a sink mechanism for the loss of reactive carbon from the indoor atmosphere, and second, the incorporation of oxygenated material onto existing particles may adversely change toxicological properties, (e.g., Oberdörster *et al.*, 2005). An important question still remains unsolved, whether it is the gas-phase or the particle phase that has adverse health effects, or both (cf. recent study by Mølhave *et al.*, 2005).

It is clear that a number of compounds have recognised or anticipated adverse health effects, as documented by a number of animal and human exposure studies (cf. Weschler *et al.*, 2006, Cvitaš *et al.*, 2005, Nøjgaard *et al.*, 2005). This interdisciplinary working group aims to bring together experts in the field of atmospheric and indoor environmental chemistry and health in order to summarise what we currently know about ozone-initiated chemistry and its impact on indoor air quality and human health and to prioritise research goals for the future (Figure 1).
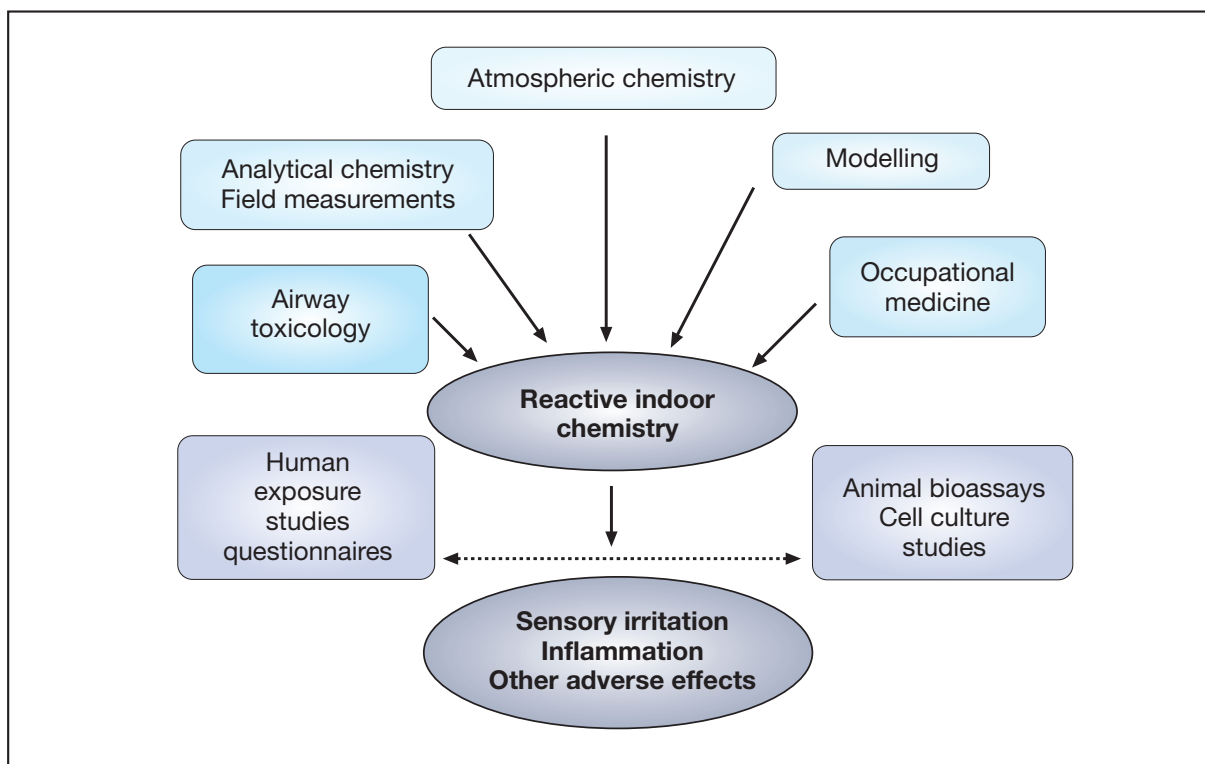
Figure 1. *A summary of the multidisciplinary expertise needed to analyse the current issue of ozone-initiated indoor air chemistry and its effects on air quality and human health.*

The focus of this report is on terpenes (e.g., limonene, α-pinene) for reasons of high chemical reactivity (NIST Chemical Kinetic Database, Atkinson, 1997) and abundance; however, other alkenes known to be present indoors may also undergo reactive chemistry.

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2   TERPENES - TERMINOLOGY
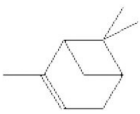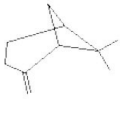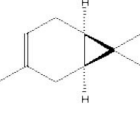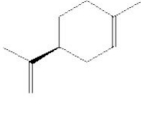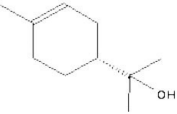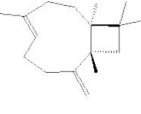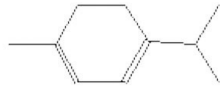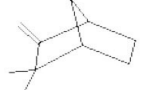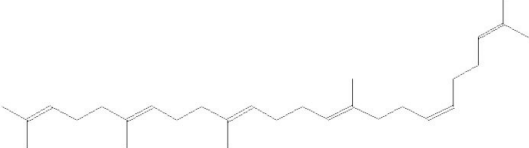
Terpenes are hydrocarbons of biological origin having carbon skeletons formally derived from isoprene [$CH_2=C(CH_3)CH=CH_2$] (isoprene rule, Wallach 1887). This class is subdivided into the C_5 hemiterpenes, C_{10} monoterpenes, C_{15} sesquiterpenes, C_{20} diterpenes, C_{25} sesterterpenes, C_{30} triterpenes, C_{40} tetraterpenes and C_{5n} polyterpenes. (IUPAC Compendium of Chemical Terminology, 2nd Edition (1997), Breitmaier, 2006). Conversion factors for α-pinene and limonene: 1 ppb = 5,654 $\mu g/m^3$ (at 20 ºC/760 mm Hg).

Terpenes are widespread in nature, mainly in plants (particularly conifers) as constituents of essential oils, though also by some insects such as swallowtail butterflies, which emit terpenes from their osmeterium. They are the major components of resin, and of turpentine produced from resin. The name "terpene" is derived from the Greek word "terpein" (pleasant smell). Terpenes and terpenoids are the primary constituents of the essential oils of many types of plants and flowers. Essential oils are used widely as natural flavour additives for food, as fragrances in perfumery, and in traditional and alternative medicines such as aromatherapy. Synthetic variations and derivatives of natural terpenes and terpenoids also greatly expand the variety of aromas used in perfumery and flavors used in food additives.

Types

○   **Hemiterpenes** consist of a single isoprene unit. Isoprene itself is considered the only hemiterpene, but oxygen-containing derivatives such as prenol and isovaleric acid are hemiterpenoids.

○   **Monoterpenes** consist of two isoprene units and have the molecular formula $C_{10}H_{16}$. Examples of monoterpenes are: pinene, geraniol, limonene and terpineol.

○   **Sesquiterpenes** consist of three isoprene units and have the molecular formula $C_{15}H_{24}$. Examples of sesquiterpenes are: nerolidol, farnesol.

○   **Diterpenes** are composed of four isoprene units and have the molecular formula $C_{20}H_{32}$. They derive from geranylgeranyl pyrophosphate.

○   **Sesterterpenes**, terpenes having 25 carbons and five isoprene units, are rare relative to the other sizes. The sester-prefix means half to three, i.e. two and a half.

○   **Triterpenes** consist of six isoprene units and have the molecular formula $C_{30}H_{48}$. The linear triterpene squalene, the major constituent of shark liver oil, is derived from the reductive coupling of two molecules of farnesyl pyrophosphate. Squalene is then processed biosynthetically to generate either lanosterol or cycloartenol, the structural precursors to all the steroids.

○   **Polyterpenes** consist of long chains of many isoprene units. Natural rubber consists of polyisoprene in which the double bonds arranged in a cis formation. Some plants produce a polyisoprene with trans double bonds, known as gutta-percha.

When terpenes are modified chemically, such as by oxidation or rearrangement of the carbon skeleton, the resulting compounds are generally referred to as terpenoids. Some authors will use the term terpene to include all terpenoids (Calogirou *et. al*, 1999).

α-pinene	β-pinene
3-carene	Limonene
Terpineol	β-caryophyllene
α-terpinene	Camphene
Squalene	

Structure and biosynthesis

Isoprene itself does not undergo the building process. Isopentenyl pyrophosphate (IPP or also isopentenyl diphosphate) and dimethylallyl pyrophosphate (DMAPP or also dimethylallyl diphosphate) are the components in the biosynthetic pathway. IPP is formed from acetyl-CoA via the intermediacy of mevalonic acid in the HMG-CoA reductase pathway. An alternative, totally unrelated biosynthesis pathway of IPP is known in some bacterial groups and the plastids of plants, the so-called MEP(2-Methyl-D-erythritol-4-phosphate)-pathway, which is initiated from C_5-sugars. In both pathways, IPP is isomerized to DMAPP by the enzyme isopentenyl pyrophosphate isomerase.

2.1. References

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IUPAC Compendium of Chemical Terminology. 2nd Edition (1997).

Wallach, Isoprene rule, 1887.

3 GAS-PHASE CHEMISTRY

3.1 Introduction

The gas-phase chemistry that occurs indoors shows many similarities to that outdoors. Many of the same reactions occur, but the emphasis on which reactions are important is different. A critical reaction outdoors is the photolysis of ozone (O_3) to produce high energy oxygen ($O(^1D)$) atoms:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad\qquad (R1)$$

Around 10% of the $O(^1D)$ atoms (under typical tropospheric conditions) react with water to form hydroxyl (OH) radicals (R2). This process is a radical initiation process in that it produces radical products without the need for radical reactants.

$$O(^1D) + H_2O \rightarrow 2OH \qquad\qquad (R2)$$

OH is the main atmospheric oxidant outdoors, and is responsible for oxidising atmospheric pollutants and mediating atmospheric oxidation processes. Despite its low abundance in the atmosphere (a few tenths of a part per trillion) it has a profound effect on many trace gas compounds such as carbon monoxide (CO), methane (CH_4) and volatile organic compounds (VOCs).

The OH radical is intimately linked to the hydroperoxy (HO_2) radical through a number of propagation (radical to radical) reactions. The HO_2 radical is the first in the homologous series known as the peroxy radicals, RO_2 (where R=H, an aryl group (C_nH_{2n+1}) or an acetyl group ($C_nH_{2n+1}CO$)). The HO_2 radical can be formed when OH reacts with carbon monoxide (CO):

$$OH + CO\ (+O_2) \rightarrow HO_2 + CO_2 \qquad\qquad (R3)$$

In addition, when OH reacts with VOCs, RO_2 radicals are formed which are subsequently propagated to HO_2 radicals (*e.g.* methane in R4-R6):

$$OH + CH_4\ (+O_2) \rightarrow CH_3O_2 + H_2O \qquad\qquad (R4)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad\qquad (R5)$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \qquad\qquad (R6)$$

The HO_2 is readily propagated back to OH through reaction with ozone and nitric oxide (NO) as shown by reactions R7 and R8 respectively:

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad\qquad (R7)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad\qquad (R8)$$

The OH and HO_2 radicals also have other photolytic sources outdoors as shown by R9 (photolysis of nitrous acid) and R10 (photolysis of formaldehyde):

$$HONO + h\nu \rightarrow OH + NO \qquad\qquad (R9)$$

$$HCHO + h\nu\ (+2O_2) \rightarrow 2HO_2 + CO \qquad\qquad (R10)$$

The fate of these radicals then depends on the NO_X concentrations. If the NO_X concentration is low, the radicals react with each other to form peroxides:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad\qquad (R11)$$

$$HO_2 + RO_2 \rightarrow ROOH + O_2 \qquad\qquad (R12)$$
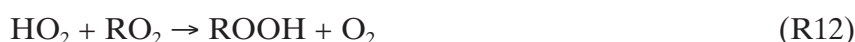
Under high NO_X conditions, the major termination route for radicals is the reaction of OH with NO_2:

$$OH + NO_2 + M \rightarrow HNO_3 + M \qquad\qquad (R13)$$

Hence in summary, OH, HO_2 and RO_2 radicals are ultimately linked in the atmosphere and photolysis processes play a key part in radical initiation.

There is much less light indoors and its spectral distribution differs from that outdoors. Much of the UV component of sunlight is filtered out by glass (below 310 nm), and the UV transmission will be further reduced if the glass is dirty, laminated or double-glazed (Quill *et al.,* 2004). Artificial lighting indoors, such as incandescent and fluorescent lighting, tends to have a low UV component: light transmission from these sources only becomes significant above ~350 nm (Quill *et al.,* 2004). Window-filtered sunlight is, therefore, the only source of UV light indoors.

Attenuation of outdoor light as it passes indoors has been little reported in the literature: there appear to be only two relevant studies. Nazaroff and Cass (1986) report that in a museum gallery, 0.7% of the visible light falling on the roof was transmitted through the skylights and 0.15% in the UV. By contrast, Drakou *et al.* (1998) report that in two laboratories in Greece with large windows, 70-80% of the visible light was transmitted indoors compared to 25-30% in the UV. Depending on the building and window design, there can be a vast difference in the amount of outdoor light that reaches the indoor environment. It is unlikely that a significant amount of UV light would penetrate the windows of many buildings, and as such, reactions requiring relatively high levels of energy to occur, such as R1, tend to be negligible indoors.

However, predicted OH concentrations indoors, both through indirect measurements (Weschler and Shields, 1997) and modelling studies (Weschler and Shields, 1996; Sarwar *et al.,* 2002; Carslaw, 2007), are only a factor of ten less than outdoors in summer and comparable to outdoor concentrations at nighttime (Faloona *et al.,* 2001) and during the daytime in winter (Carslaw, 2007). This result indicates that processes other than ozone and aldehyde photolysis are contributing to radical production indoors. Indeed, model studies predict that most OH indoors is formed through the reaction of ozone with alkenes and terpenes (Weschler and Shields, 1997; Sarwar *et al.,* 2002; Carslaw, 2007). The rest of this review is concerned with indoor ozone and terpenes, sources indoors, reactions together and resulting products.

3.2 Ozone

Ozone is a common pollutant indoors (Weschler and Shields, 1996), the most important source being transport of air from outdoors. The air exchange rate is critical in determining the indoor ozone concentration, which has a typical half-life of 7-10 minutes (Weschler, 2000). In addition, the type of ventilation system (mechanical or natural) used, the composition of indoor materials, surface removal rates and the reaction of ozone with other indoor chemicals are key determinants of the indoor ozone concentration (Weschler, 2000).

The outdoor ozone concentration varies on a diurnal, seasonal and latitudinal basis, as well as with outdoor NO_X and VOC concentrations (Weschler, 2000). Peak outdoor ozone concentrations can reach 120-400 $\mu g/m^3$ in many European regions, and are typically highest downwind of urban areas in the summer. In addition, the air exchange rate tends to be at its highest in the warmer summer months when windows are open more frequently. Consequently, there is likely to be more ozone finding its way indoors in summer. Indoor ozone concentrations track very closely those outdoors and can vary rapidly with time (Weschler, 2006).

Although most ozone indoors originates outside, there are some direct indoor emissions of ozone caused by the use of various types of electronic equipment. As early as 1978, Allen *et al*. investigated electrostatic air cleaners and photocopying machines and found that ozone concentrations up to 490 $\mu g/m^3$ could be generated in poorly ventilated rooms. Indoor ozone concentrations can also be high in close proximity to printers, photocopiers and air purifiers (Leovic *et al*., 1996; Hubbard *et al*., 2005; Britigan *et al*., 2006; Alshawa *et al*., 2007).

However, in the absence of indoor sources of ozone, numerous studies suggest that the indoor concentration is typically 10-80% of that observed outdoors owing mostly to deposition on indoor surfaces (Druzik *et al*., 1990; Zhang and Lioy, 1994; Jakobi and Fabian, 1997; Moriske *et al*., 1998; Weschler, 2000). Some further general observations from these studies were that, naturally ventilated buildings tended to have higher I/O ratios when compared to those with air conditioning systems, and that higher ratios were also associated with peak concentrations.

When monitoring personal exposure levels, they reflect the amount of time that people spend indoors and outdoors: they resemble indoor levels for people spending a large amount of their time indoors and outdoor levels for people spending more time outdoors or working outdoors (Lee *et al*., 2004). However, given that in developed countries people spend most of their time indoors (~90%), it is likely that most of their average long-term exposure to ozone occurs inside. Conversely, exposure to ozone short-term peak levels occurs mainly outdoors. Increasing attention is being paid to indoor air pollutant concentrations in aircraft cabins, owing to the recirculation of indoor air during flights (Lindgren and Norbäck 2002; Rayman, 2002, Spengler *et al*, 2004, Wisthaler *et al*., 2005).

In terms of reducing indoor ozone concentrations, it appears that the use of air conditioning and filtration lead to lower concentrations than natural ventilation. Moreover, a building with a smaller air exchange rate (ach) has lower ozone concentrations than one with a higher ach (Blondeau *et al*., 2005). Filters in HVAC (heating, ventilation and air condition) systems may reduce ozone concentrations indoors, by between 22-95% of the total removal (Zhao *et al*. 2005). Following exposure of the filters to ozone, the filtration effect declined, but recovered after a period in ozone-free air.

Based on peak European outdoor concentrations in summer reaching 120-400 µg/m^3 and I/O ratios being typically between 0.2-0.5, indoor peak concentrations may reach 25 to 200 µg/m^3 in naturally ventilated homes. The long-term outdoor objective for ozone (8-hour maximum) exceeds 120 µg/m^3 on about 15 days in the Northern Countries and on more than 25 days in Southern Europe. Assuming natural ventilation in homes, 8-hour concentrations indoors may also exceed 60 µg/m^3 for longer periods. In mechanically ventilated rooms, where I/O ratios of 0.1 are common, indoor ozone concentrations probably do not exceed 40 µg/m^3 in the absence of indoor sources. In general, reported average indoor concentrations rarely reach threshold levels.

3.3 Terpenes

The most common group of terpenes are the monoterpenes, which have the formula $C_{10}H_{16}$. The more volatile mono-and sesquiterpenes (C_{15}) are emitted in large quantities from vegetation (Guenther *et al*., 2000). For instance, alpha-and beta-pinene are monoterpenes, which are responsible for the distinctive smell of pine resin.

The presence of one or more C=C-double bonds within their structures makes the terpenes highly reactive with atmospheric constituents such as ozone, nitrate and hydroxyl radicals leading to various oxidation products. Consequently, terpenes have been considered as important precursors in photochemical ozone formation and secondary aerosol production outdoors (Andreae and Crutzen, 1997).

In confined spaces terpenes may undergo similar reactions in the presence of ozone and other reactive gases as under atmospheric conditions outdoors. Weschler and Shields (1996, 1997, 1999) have thoroughly investigated the reactions of terpenes and ozone in indoor settings as well as their role as a source of particles and hydroxyl radicals indoors. Their studies demonstrate that reactions between selected terpenes (e.g. limonene) and ozone in indoor environments can produce a significant increase in the number and mass concentration of sub-micron particles.

Over the last two decades, terpenes have become increasingly ubiquitous indoors, owing to their emission from a number of sources including timber, fragrances and cleaning products (Wolkoff *et al.,* 2000). Indeed, it has been suggested that they exist at concentrations 5-7 times higher indoors than outdoors, typically in the low ppb (parts per billion by volume) range (Saarela *et al.,* 2003). Together with aromatic compounds (*e.g.* benzene and toluene), terpenes constitute the greatest proportion of indoor VOCs.

Due to their pleasant smell, terpenes are extensively used as ingredients in many household products, in particular, in cleaning products and air fresheners. In addition, terpenes are also widely used in solvents, paintings, deodorants and varnishes. The amount of terpenes in various household products and articles varies from 0.2 to 26% (Nazaroff *et al*., 2006). Table 1 lists some of the more common monoterpene compounds and their respective indoor sources. α-pinene, β-pinene, 3-carene and limonene are the most common "indoor" terpenes, with limonene the most frequently detected indoors (Weschler and Shields, 1999).

Indoor air concentrations of the individual terpenes typically range from 6-200 µg/m^3, sometimes higher (Schleibinger *et al*., 2001; BEUC, 2005; Järnström *et al*., 2006; Singer *et al*., 2006). Although, terpene concentrations vary depending on the contents of the room, human

activities and ozone concentrations, measured concentrations of terpenes by nature are mean "steady state" concentrations. Highest concentrations tend to be found in newly built apartments with wooden floors and furniture: the so-called 'natural' paints can also contain substantial amounts of terpenes. Terpenes have been shown to constitute about 13% of the total VOC concentration when pine wood was used as the flooring material (Rosell, 1995; in Swedish).

Table 1. *Indoor sources of common terpene compounds (Nazaroff et al., 2006; Weschler and Shields, 1997; Wolkoff et al. 2000).*

Terpene compounds	Indoor sources
Limonene	Natural paints; floor wax; air freshener; cleaning agents; wood-based products.
α-pinene	Wood-based materials; textile ; cleaning agents; floor wax and polishes; air fresheners; turpentine.
β-pinene	Wood-based products; floor wax; cleaning agents.
Camphene	Cleaning agents; air fresheners.
3-carene	Wood-based materials; Cleaning agents; floor wax and polishes.
α-terpinene	Major constituent of pine oil.

Several papers report typical indoor concentrations for limonene between ~2 and ~ 500 µg/m³ (De Bortoli *et al.*, 1986; Montgomery and Kalman, 1989; Wallace *et al.*, 1991; Fellin and Otson, 1993). However, a limonene concentration as high as ~975 µg/m³ was measured after applying spray wax to a coffee table (Wainman *et al.*, 2000) and around ~ 1950 µg/m³ when peeling an orange (Langer *et al.*, 2007).

Within the framework of AIRMEX (*European Indoor Air Monitoring and Exposure Assessment Project*) (Kotzias *et al.*, 2005, The AIRMEX project's website), measurement campaigns were carried out in several European cities to monitor I/O ratios and personal exposure concentrations of selected VOCs, including limonene and α-pinene (Table 2). In total, more than 1000 samples were taken from around 80 public buildings including schools and kindergartens. In most cities, measurement campaigns were carried out during different seasons to evaluate possible variations in indoor, outdoor and exposure concentrations at different times of year.

Table 2. *I/O ratios of the terpenes sampled in cities across Europe, based on average values for all indoor and outdoor measurements in public buildings/kindergartens. The number of samples (n) that the I/O ratio is based on for each city is also shown.*

City and year	Limonene			α-pinene		
	In(n)	I/O	Out(n)	ln(n)	I/O	Out(n)
Athens, 2003	7	14.5	5	7	5.7	5
Athens, 2005	14	13.7	4	14	6.6	4
Catania, 2003	8	6.8	6	8	1.0	6
Thessaloniki, 2004	8	13.6	7		-	
Thessaloniki, 2006	15	13.0	8	7	11.3	7
Nicosia, 2004	3	49.1	3			
Nicosia, 2007	12	19.1	6			
Leipzig, 2005	10	35.4	7	10	29.8	7
Leipzig, 2006	9	19.2	7	9	85.9	7
Brussels, 2004	8	15	2			
Brussels, 2007	8	21.0	1	8	7.8	1
Nijmegen, 2004	3	48.0	2	3	3.6	2
Nijmegen, 2006	4	12.3	2	3	2.2	2
Arnhem, 2004	5	132.1	3	5	17.9	3
Arnhem, 2006	5	8.5	3	5	1.0	3
Dublin, 2007	11	48.0	6	11	15.8	6
Budapest, 2007	12	27.6	7	12	14.2	7

For d-limonene I/O ratios range from a low of 7 up to 132 while the α-pinene I/O ratios range from 1 to 85. From the available data, there is no clear evidence for a seasonal variation in the I/O ratios. Remarkable differences in I/O ratios exist between cities located in different geographical regions. With the exception of Nicosia, all other cities in Southern Europe exhibit rather low I/O ratios compared to the cities in Central and Northern Europe. This can be explained by consideration of a number of factors: the frequency of use of terpene containing products; the tightness of and the herewith associated low air exchange rates in public buildings (offices, kindergartens) and homes in Central Europe. In Southern Europe due to mild climatic conditions a much higher air exchange rate is typical for indoor environments, and therefore accumulation of components with strong indoor sources is less likely than in the Central and Northern European countries.

3.4 Ozone and terpene reactions: OH radical formation

In recent years, the reactions of terpene compounds with ozone have been studied quite extensively owing to their impact on outdoor chemistry (Aschmann *et al.* (2002) and references therein; Lee *et al.*, 2006). When ozone reacts with alkenes and terpenes, radical products such as OH, HO_2 and RO_2 are formed, as well as stable products such as aldehydes, peroxides and condensed phase compounds, some of which are potent airway irritants (Calogirou *et al.*, 1999, Wolkoff *et al.,* 2000).

In order to be important indoors, reactions must occur at such a rate that they can compete with the air exchange rate. Only a small fraction of the reactions between indoor air pollutants meet such a requirement (Weschler, 2000). Table 3 summarizes the half-life for each of a number of processes that affect the ozone concentration indoors. From chemical kinetics considerations, the half-life $t_{1/2}$ is defined as the time required for the concentration of a reactant to fall to one-half of its initial value. Some possible indoor processes for removal of ozone are ventilation (air exchange), removal by surfaces (deposition) or chemical reaction with unsaturated organic compounds such as terpenes. Ventilation and surface removal may be treated as first-order reactions and reaction with terpenes as second-order processes.

First-order kinetics of a compound A, in this case ozone, is defined as

$$A \rightarrow Products$$

with a rate coefficient k_1 (in units of time^{-1})

and a second-order process as

$$A + B \rightarrow Products$$

with a rate coefficient k_2 (in units of concentration^{-1} x time^{-1})

Given these assumptions, the half-life of ozone can be calculated:

First-order process: $\qquad t_{1/2} = 0.693/k_1$
Second-order process: $\qquad t_{1/2} = 0.693/k_2 [B]$
where [B] is the concentration of the other reactant, in this case limonene or α-pinene.

Table 3. *Half-life of indoor ozone for a number of processes.*

Process	Rate coefficient	Range of half-lives (min)
Air exchange rates	0.2-2.0 (h^{-1})[a]	21 – 210
Removal by surfaces	1.4-7.6 (h^{-1})[a]	6 - 30
Reaction with limonene	4.9 x 10^{-6} (ppb^{-1}s^{-1})[b]	60 - 500
Reaction with α-pinene	2,1 x 10^{-6} (ppb^{-1}s^{-1})[b]	130 – 1100

[a] Weschler (2000)
[b] Based on a range of assumed terpene concentrations 5–40 ppb and rate coefficients from the NIST Chemical Kinetic Database.

When one considers the alkenes and terpenes collectively, ozone removal through these reactions occurs on a similar or sometimes faster timescale, to removal by air exchange and surface deposition and depending on the indoor conditions (ozone concentration, air exchange rate, surface area etc.). The half-life for reaction between typical indoor concentrations of ozone and other VOCs such as the aromatics, alkanes and oxygenated compounds such as the aldehydes, are much too slow to be competitive (Weschler, 2000). When considering indoor air chemistry, therefore, these reactions are the key focus.

The first step in reactions between alkenes/terpenes and ozone involves addition of ozone across the carbon double bond to form an ozonide, as shown in Figure 2 for a generic alkene compound (Aschmann *et al.,* 2002):
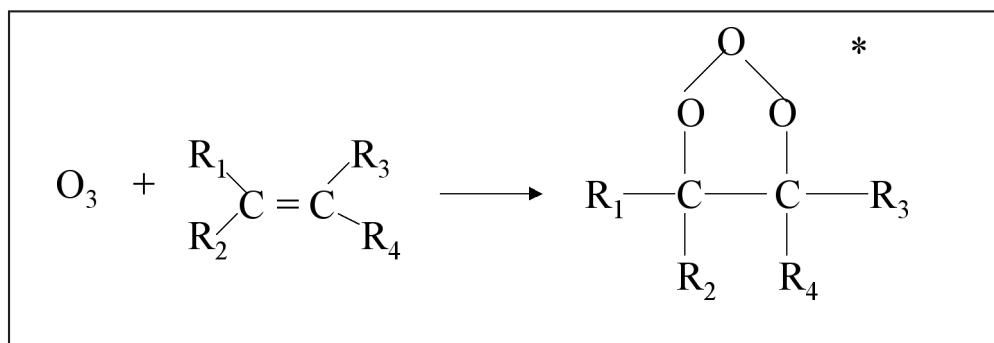
Figure 2. *Schematic representation of the preliminary step in the ozonolysis of a generic alkene to form an ozonide (denoted by the *).*

It is believed that many ozonide compounds are very unstable and quickly decompose to products. For instance, the ozonide depicted in figure 2 forms stable carbonyl products ($R_1C(O)R_2$ and $R_3C(O)R_4$), but also radical intermediates known as Criegee intermediate compounds (Aschmann *et al.,* 2002). The Criegee intermediates then undergo further decomposition, such as to yield an OH radical (through the 'hydroperoxide' channel, R14a) and/or react with water vapour to form α-hydroxyhydroperoxides through R14b (Aschmann *et al.,* 2002):

$$R_1CH_2C(R_2)OO^* \rightarrow [R_1CH=C(R_2)OOH] \rightarrow R_1CHC(O)R_2 + OH \qquad (R14a)$$

$$R_1CH_2C(R_2)OO^* + H_2O \rightarrow R_1CH_2C(R_2)(OH)OOH \qquad (R14b)$$
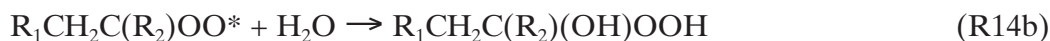
Some values of the OH yield are close to unity (e.g. 0.86 for 3-carene). Depending on the parent hydrocarbon, the α-hydroxyhydroperoxide formed in R14b can remain as a stable gas-phase compound, or can decompose further, either to a carbonyl compound and hydrogen peroxide, (R15a) or to a carboxylic acid and water (R15b) (Aschmann *et al.,* 2002):

$$R_1CH_2C(R_2)(OH)OOH \rightarrow R_1CH_2C(O)R_2 + H_2O_2 \qquad (15a)$$

$$R_1CH_2C(R_2)(OH)OOH \rightarrow R_1CH_2C(O)OR_2 + H_2O \qquad (15b)$$

More recent work by Nøjgaard *et al.* (2006a) has shown that the secondary limonene endo-ozonide formed following the reaction between ozone and R-limonene, is stable at ambient temperature. There are likely to be similar stable products formed from the reactions of other monoterpenes with ozone, which may mean that our representation of the breakdown of these compounds in chemical mechanisms will have to be revised.

The OH formed indoors can initiate oxidation reactions as in the outdoor environment, leading to more oxidative chemistry indoors than might have been expected. OH will react with NO_2, alkanes, alkenes, alcohols, aromatic compounds, carbonyl compounds and nitrated compounds as well as the monoterpenes. Reaction of OH with such compounds is much

faster than deposition onto indoor surfaces and exchange with outdoor air, both of which are negligible processes for OH indoors (Weschler and Shields, 1996). The result is a complex chemical mixture not dissimilar to that observed outdoors, but with the emphasis on different reactions.

3.5 NO_3 radical formation

Reasonably high NO_2 and O_3 concentrations indoors also allow the nitrate radical (NO_3) to be formed indoors, through R22:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad\qquad (R22)$$

The lifetime of NO_3 outdoors is around 5 seconds owing to a rapid photolysis reaction and as a consequence, it can only reach significant concentrations at nighttime (Carslaw *et al.,* 1997). However, indoors, it may be possible for the NO_3 radical to reach significant concentrations during the day, particularly in areas with little or no illumination.

Once formed, the NO_3 radical reacts rapidly with NO to reform NO_2:

$$NO_3 + NO \rightarrow 2NO_2 \qquad\qquad (R23)$$

It will, therefore, only exist in significant quantities indoors in the absence of indoor sources of NO (such as combustion). In the absence of high NO concentrations indoors, the nitrate radical reacts with NO_2 to form dinitrogen pentoxide, with which it rapidly forms an equilibrium:

$$NO_3 + NO_2\ (+M) \leftrightarrow N_2O_5\ (+M) \qquad\qquad (R24)$$
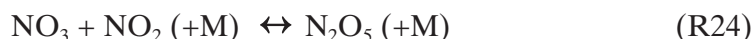
Once formed, the N_2O_5 can react on moist surfaces to form nitric acid, HNO_3:

$$N_2O_{5(g)} + H_2O_{(l)} \leftrightarrow 2HNO_{3(l)} \qquad\qquad (R25)$$
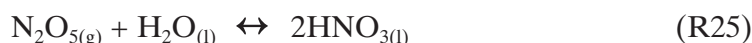
to produce dissociated nitric acid (H^+ and NO_3^-) in aqueous films (Weschler and Shields, 1997).

The NO_3 radical can oxidise compounds in an analogous manner to the OH radical. For instance, modelling studies have indicated that at concentrations of only 1 ppt, NO_3 can compete with OH and O_3 in terms of reactions with the terpene compounds (Nazaroff and Weschler, 2004). Many NO_3 oxidation reactions lead to the formation of a number of nitrated compounds.

3.6 Particle production from gas-phase chemistry

The reactions between monoterpenes and ozone were discussed earlier in the context of producing radicals. However, these reactions can also produce secondary organic aerosol (SOA) (Griffin *et al.,* 1999; Weschler and Shields, 1999; Sarwar *et al.,* 2003; Jenkin, 2004; Lee *et al.,* 2006; Nøjgaard *et al.,* 2006b). Indeed, observations of the 'blue haze' formed in the atmosphere from compounds emitted by trees date back nearly 50 years (Went, 1960). The

aerosol yield from such reactions is defined as the amount of SOA formed from the oxidation of a given hydrocarbon to the amount of the parent hydrocarbon reacted (Griffin *et al.,* 1999). For organic mass concentrations between 5-40 µg m^{-3}, the oxidation of monoterpenes by OH, O_3 and NO_3 produced aerosol yields in the range from 2-23% during one experimental study (Griffin *et al.,* 1999). The aerosol yield is dependent on the experimental conditions, the starting concentration of the parent monoterpene, and on the oxidant used (*e.g.* OH, O_3 or NO_3): dark ozonolysis experiments appear to give the highest aerosol yields (Jenkin, 2004), conditions akin to those experienced indoors. Indeed, Lee *et al.* (2006) found yields of up to 54% for the ozonolysis of terpenes, with highest values for those compounds with one or more double bonds internal to the ring structure such as α-pinene (aerosol yield of 41%). Nøjgaard *et al.* (2006b) found that the addition of NO_2 to a limonene/ozone or α-pinene/ozone mixture led to the formation of the nitrate radical, which affected particle formation, since the nucleation potential of NO_3 is much lower than O_3. The terpene ozonolysis reactions indoors can explain the previously observed discrepancy (range of 19-42%) between measured concentrations of indoor particles and specific sources of such particles (Sarwar *et al.,* 2003).

Weschler and Shields (1999) found that particles were formed from the reaction of limonene with ozone, with yields in the region of 10-15%. They used adjoining, identical offices with one office used as a control, whilst ozone and limonene were added to the other. Particle production was significantly enhanced in the office with the ozone and limonene sources, and the difference was greatest for the really fine particles in the 0.1-0.2 µm diameter size range. The authors discovered a lag (~30 minutes) between peak ozone and particle concentrations, which reflected the time required for primary and secondary reactions in the ozone-limonene system to occur. These processes occurred at times that were faster than typical air exchange rates in the office setting they used.

Sarwar *et al.* (2003) observed rapid fine particle growth through the reaction of ozone with α-pinene, and subsequent gas-to-particle partitioning of the products in a stainless steel chamber. Shortly after introducing α-pinene to the chamber, they noted a burst of particles in the 0.02-1 µm range, the number of which decreased and then attained a steady concentration. They noted that the same happened in the subsequent size range and continued up to particles with diameters up to 0.5-0.7 µm, creating an effective particle growth wave. The authors also found that the secondary particle mass increased substantially as the air exchange rate was lowered and the residence time was effectively increased.

The nature of the particles formed has been the subject of a few studies. For instance, laboratory studies have suggested that bi- and multi-functional carboxylic acids, such as pinic and pinonic acid are generated from the ozonolysis of α-and β-pinene (Glasius *et al.,* 2000; Jenkin, 2004). Outdoor field studies have suggested that as well as the above compounds, norpinonic acid, pinonaldehyde and nopinone contributed to the fine particle mass (Jenkin, 2004). Glasius *et al.* (2000) also identified a range of ketoaldehydes, hydroxyketoaldehydes, ketones and hydroxyketones in SOA following the reactions of various terpene compounds with ozone. However, there have been no studies investigating the composition of particles formed indoors to date: such studies should be a future focus of research efforts in indoor air pollution.

Finally, it has been noted that the behaviour of particles indoors is highly dependent on ventilation rates: low ventilation rates lead to a larger concentration of SOA (Sarwar *et al.,* 2003; Weschler and Shields, 2003). The longer residence times at lower ventilation rates allow the particles more time to form in the first place, but also more time to accrete organic material and grow in size (Weschler and Shields, 2003).

3.7 Modelling of gas-phase chemistry

Several recent studies have employed chemical models to attempt to understand chemical processing indoors (Weschler and Shields, 1996; Sarwar *et al.*, 2002; Carslaw, 2007). Despite the significant attenuation of light indoors, all of these model studies predict that there is only around 10 times less OH at noon compared with typical outdoor values. Carslaw (2007) used a detailed chemical model to investigate OH concentrations and chemistry, and found a maximum concentration of $\sim 4.0 \times 10^5$ molecule cm^{-3} at around 11:00 h which decreased to $\sim 1.2 \times 10^5$ molecule cm^{-3} at nighttime. This day time value is lower than that outdoors in summer (typically 2×10^6 molecule cm^{-3}), but is comparable with daytime values outdoors in the winter (typically 5×10^5 molecule cm^{-3}) (Emmerson *et al.*, 2005) and with nighttime values of OH observed outdoors ($1 \times 10^5 - 1 \times 10^6$ molecule cm^{-3}) (Platt *et al.*, 2002; Faloona *et al.*, 2001). These results indicate that unlike outdoors, non-photolytic sources are important in producing OH indoors.

The predicted OH concentration is higher than that of Sarwar *et al.* (2002) who report a noontime value of 1.2×10^5 molecule cm^{-3} and of Weschler and Shields (1996), who predicted a steady-state OH concentration of 1.7×10^5 molecule cm^{-3}. However, in the former study, higher NO_X suppresses radical formation relative to the present work, and in the latter study, a limited set of chemical reactions was used (NO_X conditions are not explicitly stated), with concentrations largely based on those outside, owing to a lack of available measurements indoors. Weschler and Shields (1997) reported an inferred OH concentration of $\sim 7.0 \times 10^5$ molecule cm^{-3}, by observing the decay rate of 1,3,5-trimethylbenzene after mixtures of O_3 and d-limonene were introduced to an experimental system. The results from all of these studies therefore support the notion that the indoor OH concentration is likely to be in the range of $1-7 \times 10^5$ molecule cm^{-3} depending on the precise indoor conditions.

The detailed chemistry in the model employed by Carslaw (2007) also allowed other conclusions to be drawn regarding the accumulation of certain compounds indoors. Concentrations of PAN-type compounds and organic nitrates were found to reach concentrations of a few ppb. It was estimated that around 72% of the total organic nitrates and 30% of the PAN compounds were likely to associate with the aerosol phase and form secondary organic aerosol (SOA). This result is potentially worrying in terms of health effects, as it may represent a pathway for nitrated compounds to penetrate the respiratory system. Measurements of nitrated compounds indoors should be made to confirm these model results.

Sensitivity tests highlighted that the most crucial parameters for modelling the concentration of OH are the light intensity levels, the air exchange rate and outdoor concentrations of O_3 and NO_X (Carslaw, 2007). Very few studies have addressed how light propagates indoors, and further information on the propagation of light indoors at different wavelengths would enable a significant area of model uncertainty to be removed.

The reactions of ozone with alkenes and monoterpenes have been predicted to play a major role in producing new radicals (Weschler and Shields, 1996; Sarwar *et al.*, 2002; Carslaw, 2007), unlike outdoors where photolysis reactions are pivotal radical initiators. In terms of radical propagation, the reaction of HO_2 with NO has the most profound influence on OH concentrations indoors. Cycling between OH and RO_2 is dominated by reaction with the monoterpene compounds, whilst alcohols play a major role in converting OH to HO_2 (Carslaw, 2007). Surprisingly, the absolute reaction rates are similar to those observed outdoors in a suburban environment in the UK during the summer.

One important result that has emerged from these studies is the importance of tailoring a model for its particular location. As O_3 and NO_X concentrations have a pivotal effect on indoor chemical processing, it is essential that appropriate conditions are used to initialise a model. Many indoor studies are focussed in the US where outdoor (and consequently indoor) ozone concentrations are likely to be higher than in many parts of Europe. These studies have also highlighted the need for future indoor air measurements of radical compounds, nitrated compounds such as PANs and organic nitrates, photolysis rates of key compounds over the range of wavelengths observed indoors and concurrent measurements of outdoor air pollutant concentrations.

Finally, the issue of mixing should be considered. Sørensen and Weschler (2002) used a computational fluid dynamics model to show that there can be significant concentration gradients of both reactants and products within a room. Effectively, reactions will occur at different rates across the room depending on the concentration of the reactants at any given point and produce varying concentrations of products. These results have implications for those employed in exposure studies, whereby measuring at one point in a room may not be representative for all occupants. Ideally, measurements should be made at several points around a room in order to assess whether the 'well-mixed' assumption usually applied in modelling studies is justified.

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4. MATERIAL OXIDATION CHEMISTRY

Ozone initiated chemistry in the gas-phase is relatively simple - the reactions can be described by gas-phase kinetics and mechanisms. The matter of indoor air reactive chemistry becomes more complicated when one need to consider surfaces and materials because of the chemical variety of the materials themselves. Reactions in the gas-phase occur upon collision of (most often) two molecules. For an accurate description of surface reactions, more parameters must be taken into account such as absorption/adsorption and deposition of the reactive compounds.

Usually measurements of the primary emissions (i.e., physical release of e.g. residual solvents, un-reacted raw materials and impurities) from building materials and products is made by exposing the products to clean air. It is difficult, however, to evaluate and predict the effects of building materials and products on health and comfort indoors during their entire lifetime based on studies of the primary emissions alone. For that reason, potential secondary emissions also need to be taken into account (Wolkoff, 1999). Secondary emissions are defined as compounds produced by chemical reaction in the product or in the indoor environment (Salthammer and Kephalopoulos, 2000).

As already mentioned in Chapter 3.2, indoor ozone primarily originates from outdoor air brought indoors by 20-70% infiltration (Weschler, 2000) and formation by electrostatic equipment, like photocopiers. The main reason that indoor ozone concentrations are lower than those outdoors is the interaction of ozone with ventilation ducts, building materials (construction products) and household products that have been applied onto a surface. This interaction may occur by two routes:

i)   *Gas-phase chemistry reactions* (homogeneous) between ozone and chemically reactive VOCs that are emitted from the material/product surface (Weschler, 2000; Mueller *et al*., 1973), or directly sprayed into the indoor air, e.g. air fresheners (Nazaroff and Weschler, 2004).

ii) *Surface chemistry reactions* (heterogeneous) between ozone that is deposited on the material/product surface and the surface structure (Cano-Ruiz *et al*., 1993). This may either proceed by oxidative degradation of the surface structure or by reaction between ozone and chemically reactive VOCs, like terpenoid compounds that are adsorbed or directly applied onto the surface (e.g. vinyl flooring). In addition, ozone may be decomposed by a catalytic action on the surface to molecular oxygen and an oxygen atom, which may diffuse into the surface structure. It is possible that reactive atomic oxygen may initiate auto oxidative degradation of e.g. unsaturated constituents in materials, like linseed oil (cf. Pryor *et al*., 1976).

4.1 Deposition rate of ozone

The deposition rate of ozone has been reported for a number of different materials, and is largest for fleecy surfaces and gypsum board (Nicolas *et al*., 2007; Knudsen *et al*., 2003; Klenø *et al*., 2001; Cano-Ruiz *et al*., 1993; Sabersky *et al*., 1973). The mean decay rate of ozone has been measured in residences to be about 2.8 ± 1.3 h^{-1} with a mean deposition rate of 0.049 ± 0.017 cm/s (Lee *et al*., 1999). The decay rate was highest in buildings with high surface-area-to-volume ratios, while the ratio of indoor-to-outdoor ozone was lowest in buildings with mechanical ventilation.

4.2 Deposition behaviour of ozone

The fact that ozone removal is replicable by the same test piece indicates a reverse aging process of the material surface during the pre-conditioning period of 44 hours in a pure nitrogen atmosphere at a relative humidity of 50 % (Klenø *et al.*, 2001) as observed in other studies (Mueller *et al.*, 1973; Sabersky *et al.*, 1973). Little is known about the reverse ageing process. One explanation could be re-sorption of chemical compounds, for example soil or skin oils that are re-oxidized (Wisthaler *et al.*, 2005).

Otherwise, the deposition rate decreases upon extended ozone exposure (Sabersky *et al.*, 1973), which confirms the observation that the deposition rate decreases as the ozone concentration increases (Nicolas *et al.*, 2007). Deposition rates on hard surfaces generally decrease with increasing relative humidity (Sabersky *et al.*, 1973). An exception is wooden surfaces (Nicolas *et al.*, 2007; Grøntoft *et al.*, 2004), where multilayer water adsorption may compete with deposition of ozone molecules.

4.3 Gas-phase chemistry reactions

For many building materials, and in particularly low emitting materials, homogeneous reactions appear only to be of minor importance (cf. Nicolas *et al.*, 2007; Knudsen *et al.*, 2003). However, for cleaning agents and other household products the emission of terpenoid compounds may be substantial (Destaillats *et al.*, 2006; Singer *et al.*, 2006b), thus resulting in a number of oxidized products (Singer *et al.*, 2006a). The homogeneous reactions (ozonolysis) both produce and remove odorous compounds (e.g. Nicolas *et al.*, 2007; Morrison and Nazaroff, 2002; Weschler *et al.*, 1992) thus affecting the perceived indoor air quality, e.g. odour intensity and odour preference (Knudsen *et al.*, 2003). In addition, those VOCs including building product surfaces that are oxidised by ozone may result in low molecular weight aldehydes, ketones, and aliphatic acids of which many are characterised by low odour thresholds or low airway irritation estimates (Wolkoff *et al.*, 2006).

4.4 Surface chemistry reactions

Usually, building materials with a large surface area, like carpets, should be considered potential secondary emission sources of new VOCs that are formed through oxidative reactions. The occurrence of heterogeneous reactions between ozone and adsorbed VOCs, like terpenes on gypsum board (Tirkkonen and Saarela, 1997) or VOCs on carpets (Chang *et al.*, 1998) is possible, which increases the sink effect of the material surface, and consequently the probability of oxidative reactions.

Heterogeneous reactions on building material surfaces form secondary emissions of odour active aldehydes (e.g. Tamás *et al.*, 2006; Wang and Morrison, 2006; Morrison and Nazaroff, 2002; Morrison *et al.*, 1998; Reiss *et al.*, 1995; Weschler *et al.*, 1992). The new VOCs formed are generally both saturated and unsaturated aldehydes and ketones, including formaldehyde (Nicolas *et al.*, 2007; Moriske *et al.*, 1998), and aliphatic acids. Some of the new VOCs may be slowly emitted from the surface, for example, it has been suggested that spinning oils in textile carpets are oxidized to unstable epoxides, which degrade slowly to nonenal (Morrison and Nazaroff, 2002). Many of these compounds are characterized by very low odour thresholds. For some building materials that are exposed to ozone, e.g. textile carpets, the immediate odour preference may alter (significantly higher odour intensity showed), which means that the emitted profile of VOCs has changed compared to that before the material was exposed to ozone (Knudsen *et al.*, 2003).

Building materials can also be sources of secondary emissions due to the deposition of dirt and dust which contain unsaturated substances. Human debris, e.g. skin oils, contains i.e. unsaturated hydrocarbons, like squalene, saturated and unsaturated fatty acids and esters (Nicolaides, 1974), including fatty acid salts (Clausen *et al.*, 1998). These substances in the form of deposited particles on building product surfaces may react with oxygen and/or ozone to form aldehydes (C_{6-7} and C_9), including ketones, and small aliphatic fatty acids, e.g. (Wisthaler *et al.*, 2005). Although the reaction of ozone is much faster than molecular oxygen with chemically reactive compounds (e.g. olefinic bonds), autooxidation promoted by an initial ozone attack should also be considered a likely candidate for formation of i.e. aldehydes from e.g. methyl esters of (poly) unsaturated fatty acids (Hancock *et al.*, 1989; Pryor *et al.*, 1976).

4.5 Formation of ultrafine particles

Ozone reacts with chemically reactive compounds in the gas phase to produce ultrafine particles, so-called secondary organic aerosols (Nøjgaard *et al.*, 2006; Zhang *et al.*, 2006; Rohr *et al.*, 2003; Weschler and Shields, 1999). They are a mixture of carboxylic acids, diacids, aldehydes, ketones and mixed combinations thereof, and hydroperoxides (e.g. Glasius *et al.*, 2000).

Ultrafine particles are produced from the ozonolysis reaction of emitted terpenes from wooden materials (Aoki and Tanabe, 2007), natural paints (Lamorena *et al.*, 2006), air fresheners, cleaning agents, and household products (Destaillats *et al.*, 2006; Singer *et al.*, 2006a; Liu *et al.*, 2004; Long *et al.*, 2000). The formation of ultrafine particles depends on a number of factors, not only the ozone/terpene ratio and the rate constant of the terpene, but also the presence of nitrogen dioxide (Nøjgaard *et al.*, 2006; Zhang *et al.*, 2006), and the relative humidity (Jonsson *et al.*, 2006).

4.6 Combined oxidation reactions

The combined impact of ozone on surfaces is difficult to predict, because the oxidative degradation reactions as well as gas phase ozonolysis of emitted chemically reactive VOCs may remove as well as produce new odour active VOCs, which alter the VOC profile, thus the IAQ (odour) perception. Sensory irritants like formaldehyde are formed.

4.7 Conclusions

There is an increasing concern about oxidative degradation of material/product surfaces, not only from the point of sustainability, but also from a comfort, health, and productivity point of view (SCHER, 2007). The surfaces may degrade by the action of ozone, the hydroxyl and nitrate radicals. In addition, chemically reactive VOCs, which are emitted from materials and products, may also produce new oxidized products, including ultrafine particles. These properties, however, are not part of existing international standards for material and product emission testing.

At present, it is not possible to predict the impact of new odours produced through the oxidative reactions, either on perceived air quality or their impact on productivity. Since the emission of terpenes may be substantial under certain conditions, the formation of sensory irritants could add to the perception of eye and upper airway effects, and ultrafine particles and radicals may cause lung effects.

4.8 References

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5. METHODS OF MEASUREMENTS

For a complete understanding of the ozone-initiated chemistry of terpene degradation the concentration of the key reactants ozone and terpene have to be monitored as well as possible reaction partners for the Criegee-Intermediate like water, aldehydes and acids. For all of these compounds there are several well established techniques available. Following the formation of reaction products is less straightforward, since the manifold of reaction products and reactive intermediates requires more elaborated methods, especially for the short-lived radicals and thermolabile compounds like hydroperoxides and secondary ozonides. Therefore the necessary analytical techniques cover a broad range of methods, which are summarized in this chapter. A more detailed description for each method is presented in Annex 1.

Gas-phase measurements
Ozone is often measured by UV-absorption with a time resolution of 10-20 s. Possible interferences with other absorbing compounds are negligible except in very polluted environments, mainly due to the presence of aromatic compounds (Parrish and Fehsenfeld, 2000). More sensitive methods are based on chemiluminescence allowing fast response ozone measurements in the range of 1 s, but are more difficult to perform.

Two sampling techniques are used to measure concentrations of *terpenes*: pre-concentration on different adsorbents or "instantaneous-sampling" (whole-air sampling) using stainless steel or glass containers, followed by gas-chromatographic separation of the compounds. The whole-air collection can result in molecular rearrangements of the unsaturated terpenes due to surface reactivity. Therefore, the analysis of terpenes is carried out preferably by sampling on solid adsorbents and subsequent thermal desorption of the compounds. Due to the unsaturated character of the analytes, care must be taken to maintain sample integrity during pre-concentration or storage of the samples. The presence of ozone and the high rate constants of the ozonolysis reaction of unsaturated hydrocarbons results in considerable loss of the terpenes if no ozone removal techniques (e.g. an ozone scrubber) are applied (Larsen *et al.,* 1997).

The reaction products of ozonolysis cover the whole range from volatile (e.g small aldehydes) to non-volatile (e.g. dicarboxylic acids, oligomers) compounds, which partition to a differing extent between the gas and aerosol phase. Volatile products can be measured in the same manner as the parent terpenes (see above), limited only by the availability of analytical standards. More sensitive techniques use derivatisation of aldehydes and ketones with 2,4-dinitrophenyl-hydrazine (DNPH) yielding the coreresponding 2,4-dinitrophenyl-hydrazones, which can be easily detected by UV or mass spectrometric methods (Slemr, 1991). Real-time measurements have been also performed using proton-transfer-reaction mass spectrometry (PTR-MS) (Wisthaler *et al*., 2001; Wisthaler *et al*., 2005). Methods for analysis of non-volatile compounds, which are mainly in the aerosol phase are summarized below.

The analysis of labile compounds like secondary ozonides (SOZs) is not as straightforward as the methods above for stable compounds and only a few studies report the formation of SOZs in the gas-phase. Long-path FTIR spectroscopy has been used in the case of SOZs formed through the ozonolysis of simple alkenes (Neeb *et al*., 1996) and β-pinene (Winterhalter *et al*., 2000) and very recently, mass spectrometric methods have been used for limonene ozonolysis (Nøjgaard *et al*., 2007; Nøjgaard *et al*., 2007; Nøjgaard *et al*., 2007).

Another class of unstable, yet very important compounds are the hydroperoxides and peroxides. Several methods can be used to measure H_2O_2 and total organic peroxides (Reeves and Penkett, 2003), but the measurement of individual organic peroxides, in particular higher organic peroxides originating from terpenes, is still an analytical challenge. An established method uses the horseradish-peroxidase catalyzed reduction of H_2O_2 and other peroxides with para-hydroxyl-phenyl acetic acid (POPHA), yielding a dimer, which can be detected with a fluorescence detector (Lazrus *et al.*, 1986; Sauer *et al.,* 1999; Li *et al.,* 2002; Fan *et al.,* 2005; Francois *et al.,* 2005; Valverde-Canossa *et al.,* 2005). The lack of analytical standards for higher peroxides limits the applicability of the HPLC/Fluorescence method for the study of terpene-ozone reactions. The development of mass spectrometric methods using soft ionisation techniques might be a promising alternative for the identification of higher peroxides (Nilsson *et al.,* 1996; Warscheid and Hoffmann, 2002; Reinnig *et al.*, in preparation).

Measurements of OH radical concentrations are difficult and often indirect methods using tracer or scavengers have been used in laboratory experiments. (Atkinson *et al.,* 1992; Paulson *et al.,* 1998). In indoor environments 1,3,5-trimethylbenzene has been used as a tracer (Weschler and Shields, 1997). Measurements of tropospheric OH-radical concentrations have been performed directly by spectroscopic methods such as laser induced fluorescence (LIF) spectroscopy at low pressure (FAGE) and long path differential optical absorption spectroscopy (DOAS) (Heard and Pilling, 2003). These methods have the advantage of high time resolution of the measurements compared to the indirect methods, but require elaborate (and expensive) experimental equipment. HO_2 radicals can be measured after conversion of HO_2 to OH through addition of NO and determination of the generated OH-radicals.

Secondary organic aerosol (SOA)
The first step in the analysis of particle bound compounds is the separation of particles from the gas-phase with filters or impactors and can lead to positive (condensation of gas-phase compounds) and negative artefacts (vaporisation of particle bound compounds), which have to be carefully addressed in order to make quantitative measurements (Mader *et al.*, 2003). The second step of analysis is then *extraction* with an appropriate solvent depending on the class of compounds and application of a separation technique like gas chromatography (usually requires a derivatisation step) or liquid chromatography (LC), which is going to become a widely used method for the analysis of individual compounds in organic aerosols (Hoffmann *et al.*, 1998; Glasius *et al.*, 1999; Anttila *et al.*, 2005; Römpp *et al.*, 2006; Warnke *et al.*, 2006). LC is especially appropriate for the separation of high-molecular-mass or very polar molecules without derivatisation. The coupling to mass spectrometers is well established, and electrospray ionisation (ESI) is the ionisation method most widely used for organic aerosol characterisation. Atmospheric pressure chemical ionisation (APCI) is also a standard ionisation method, which is particularly suited for more polar and lower molecular weight substances. Other methods applied are ion chromatography or electrophoretic methods (see annex 1). Another method for identification and quantification of organic compounds present in SOA is so called Direct Thermal Extraction of samples collected on appropriate filters followed by gas chromatography – mass spectroscopy/flame ionization detection for the analysis. This method has been successfully used in e.g. analysis of monocarboxylic acids in samples of ambient aerosol (Shannigrahi *et al.*, 2007).

Another important aspect is the amount of aerosol formed from the ozone-terpene reaction. In principle the mass of aerosol can be measured gravimetrically, but since the size range of

particles relevant to health effects is below 1 μm, the particle mass is rather low and more sophisticated methods should be used. A condensation nucleus counter (CNC) measures the total aerosol number concentration larger than some minimum detectable size. CNCs are often used as detectors with other instruments such as electrical mobility classifiers. CNCs can detect individual particles as small as 3 nm. Electrical mobility analyzers classify particles according to the electrical mobility. Most common is the so-called DMPS, which includes a differential mobility analyzer (DMA) and a CNC. These systems can measure size distributions in the range of 3 to 1000 nm diameter. The primary limitation of DMPS systems at the small particle limit is detecting very low concentrations of very small particles (McMurry, 2000).

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6 HEALTH EFFECTS

6.1 Introduction

Indoor ozone concentration is mainly due to outdoor generated ozone, as a result of infiltration and ventilation. Ozone may also be emitted directly from indoor sources, such as certain types of photocopiers, printers and air cleaning devices. In the last few years, concern has grown on the potential health impact of indoor air chemistry, in particular on products resulting from ozonolysis reactions of terpenes (e.g. limonene and α-pinene).

6.2 Odour perception

Ozone and d-limonene can be detected (50 % median) at 7 and 8 ppb, respectively, under low background conditions (Cain *et al.*, 2007). It is possible that the threshold of ozone may be even lower (~6 ppb) (Cain *et al.*, 2007; Nagata, 2003). The detection sensitivity may decrease upon elevated background concentrations of either ozone or the VOC in question; i.e. elevation of the threshold. The recognition threshold for ozone appears to be of the order of 14-15 ppb (Cain *et al.*, 2007). The threshold for α-pinene is expected to be lower than that of d-limonene (Nagata, 2003).

6.3 Sensory irritation thresholds for ozone, α-pinene, limonene, and formaldehyde

A mouse bioassay has been used to measure airway effects, i.e. sensory and pulmonary irritation, and bronchoconstriction, of ozone, limonene and α-pinene. The obtained RD50 values (the concentration causing a 50 % reduction of the respiratory rate) are useful for estimating protective levels for the general population (Kuwabara *et al.*, 2007; Nielsen *et al.*, 2007b). RD50 values for ozone, α-pinene, and limonene are listed in Table 4. The RD50 values multiplied by 0.03 gives a crude estimate of the related OEL (occupational exposure limit); formaldehyde, a known product from ozonolysis of terpenes (Atkinson and Arey, 2003), is added for comparison.

Table 4. *RD50 values (ppm) of ozone, α-pinene, and limonene and tentative indoor guidelines (ppm).*

Compound	RD50	0.03xRD50	Pulmonary irritation	Tentative indoor guideline
Ozone	NA[a]		yes[b]	
(-)-α-pinene	6302	189[c]	no	2[e]
(+)-α-pinene	2125	64[c]		0.6[e]
				0,8[f]
S-(-)-Limonene	1467	44[d]	no	0.4[e]
R-(+)-Limonene	1076	32[d]		0.3[e]-0.8[f]
Terpenes				0.04 or 0.4[g]
Formaldehyde	4[a]	0.1[b]	no	0.1[h]

[a] Not applicable. [a] 0-10 min. [b] (Nielsen *et al.*, 1999). [c] (Nielsen *et al.*, 2005). [d] (Larsen *et al.*, 2000).
[e] Default uncertainty factor 100 used; Ausschuss der gesundheitlichen Bewertung der Bauprodukten 2005.
[f] (Kasanen *et al.*, 1999).
[g] (Umweltbundesamt, 2007). [h] (Appel *et al.*, 2006; Paustenbach *et al.*, 1997; Lang *et al.*, 2007).

6.4 Airways effects of ozone-terpene mixtures

Bioassay studies
The airway effects of the monoterpene oxidation products have been evaluated by use of a mouse bioassay (see above). The results from this assay, suggested that reaction mixtures of R-limonene/ozone (LO) (Clausen *et al.*, 2001) and α-pinene/ozone (PO) (Wolkoff *et al.*, 1999) generate sensory irritants of known and unknown structures. The sensory irritation effect is significantly higher than that exhibited by the identified reaction products and residual concentration of the reactants, i.e. the pure compounds. The biological response of this reaction mixture can only be explained partially by the compounds measured (Wolkoff *et al.*, 2006).

Moderate-lasting pulmonary effects have been observed in mice (Rohr *et al.*, 2002) and pulmonary inflammation in elderly rats (Sunil *et al.*, 2007).

Human exposure studies
In a study, male subjects have been exposed in one eye for 20 min with limonene and ozone, at concentrations of 91 ppb and 101 ppb respectively, whereby 32% of the ozone reacted. The eye blink frequencies of the subjects were recorded as a physiological measure of trigeminal stimulation (Klenø and Wolkoff, 2004; Nøjgaard *et al.*, 2005). Mean blink frequencies increased significantly only during exposure to LO compared with that of clean air, and the findings coincided with qualitative reporting of weak eye irritation symptoms. The blink frequency was unaffected by exposure to limonene or ozone separately. The blink frequency showed a decreasing trend with increase of the relative humidity from 20% to 50% for LO mixtures (Nøjgaard *et al.*, 2005). A similar effect for LO was observed in the mouse bioassay in which the bioresponse was highest at low relative humidity (Wilkins *et al.*, 2003). The results demonstrate an effect of the mixture, although the concentrations are in the high end of typical indoor settings. However, such high levels are possible, e.g. during cleaning activities (Singer *et al.*, 2006b; Singer *et al.*, 2006a). The effect should also be considered in view of the short exposure time.

In a study (Laumbach *et al.*, 2005), 130 healthy, non-smoking women were exposed to a VOC mixture of 23 VOCs at 25 mg/m^3 for two hours with and without ozone admixed to a chamber level of 40 ppb. To avoid confounding from odour, the study masked the control air exposure by adding a small amount of the VOC mixture (~2.5 mg/m^3) during the first minutes of exposure. The exposures caused neither sensory irritation nor inflammation of the upper airways as evidenced by polymorphonuclear cells, protein, IL-6 and IL-8 in nasal lavage fluid. Also, the mixtures did not affect pulmonary function (FEV$_1$, FVC and FEF$_{25-75}$) and lower respiratory tract symptoms (Fiedler et al., 2005). The VOC mixture probably had a low airway irritation effect and the odour cue of the mixture may have triggered the reported symptoms at this level, cf. (Wolkoff *et al.*, 2006; Nielsen *et al.*, 2007a).

The above findings of both animal and human exposure studies indicate that gaseous LO and PO reaction products may cause trigeminal stimulation of the eyes and upper airways at ozone and terpene concentrations that are close to high-end values measured in indoor settings (see Chapter 3). The impact of ultrafine particles on short-term symptoms like eye and upper airway irritation is unknown and their possible role in the development of effects in the lower airways is debatable (Weschler, 2006).

Epidemiology
A few epidemiological studies have indicated that reactive chemistry may have been responsible for reported sensory irritation symptoms. For example, the sum of detectable

VOCs was found to be lower in an office building "classified" as "sick" as compared to a similar building classified as "healthy", cf. (Groes *et al.*, 1996; Sundell *et al.*, 1993; Höppe *et al.*, 1995; Subramanian *et al.*, 2000). In a study of buildings in California it was found that cleaning products and water-based paints accounted for a significant proportion of the observed association of sensory irritation symptoms (Ten Brinke *et al.*, 1998). It is possible that the identified products emit chemically reactive VOC that are ozonolyzed (cf. Nazaroff and Weschler, 2004).

A number of studies related to cleaning activities, both professional and domestic, indicate an increased prevalence of asthmatic symptoms among the personnel (e.g. Medina-Ramón *et al.*, 2005; Rosenman, 2007), including from domestic use of cleaning sprays (Zock *et al.*, 2007). A link between these associations and the use of terpene-based fragrances in the cleaning and household products and the formation of new reactive and harmful compounds in the presence of ozone is a plausible hypothesis that also may be the cause of reported childhood asthma (cf. Sherriff *et al.*, 2006).

6.5 Long-term effects

Until now, there has been little specific literature on potential long term health effects of ozone/terpene reaction products. Epidemiological studies have found associations between ozone concentrations measured at outdoor monitoring stations and long term effects such as allergy, asthma, and decreases in lung function (WHO 2003). Due to the fact that people spend most time indoors, it is possible that exposure to the products of ozone-initiated indoor chemistry is more directly responsible for the health effects observed in these epidemiological studies than is exposure to outdoor ozone itself (Weschler *et al.*, 2006).

Finally it has to be underlined that formaldehyde has been designated as a Group 1 carcinogen in the 2004 IARC evaluation (Cogliano 2005), and acrolein is listed by California as a carcinogen (Californian Office of Environmental Health Hazard Assessmnet 2006); however, typical indoor levels of formaldehyde and acrolein are low enough not to cause any potential risk of cancer (Appel *et al.* 2006; Arts *et al.* 2006).

6.6 Conclusion

There is increased concern about the potential health impact of indoor air chemistry, in particular of products resulting from ozonolysis of terpenes (e.g. limonene and α-pinene). As also has been stated recently more research is required before definite conclusions can be reached (SCHER, 2007).

Recent findings, both epidemiological and experimental, suggest that these ozonolysis products could cause increased reporting of sensory irritation, although results remain to be substantiated in full scale experiments. No specific experimental literature is available on potential long term health effects. However, the relationship observed in epidemiological studies between ozone exposure and health effects could be hypothesized to be partially due to the action of products of ozone-initiated indoor chemistry, given that people usually spent most of their time indoors.

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7. RISK ASSESSMENT

7.1 Risk Assessment for indoor ozone-initiated terpene chemistry

a. Introduction and principles

Necessary elements to be taken into account when conducting a health risk assessment are: the hazards, their dose-response relationship(s), exposure and results in science-based risk characterisation (Commission Regulation (EC) No. 1488/94; Technical Guidance Document on Risk Assessment (2003)). Where possible, the margin of safety/exposure should be defined or the exposure should be compared with relevant health based guideline values for risk characterisation. If neither of these assessments is possible, an evidence-based hazard characterisation should be attempted (SCHER, 2007).

b. Hazard identification

Unsaturated VOCs like monoterpenes (e.g. d-limonene and α-pinene) react with ozone to produce radical products such as OH, HO_2 and RO_2, as well as stable products such as aldehydes (e.g. formaldehyde), peroxides and condensed phase species (e.g. ultrafine particles) (Weschler and Shields, 1997; Wolkoff *et al.,* 2000; Atkinson and Arey, 2003).

Unknown short-lived species including radicals, that are derived from ozone-initiated chemistry and e.g. monoterpenes, are hypothesised to be responsible for the exacerbation of sensory effects in eyes and airways. For example, domestic use of consumer products and cleaning agents has been associated with lower airway effects among both pre-school children and cleaning personel, see 6.4.

Common indoor sources of ozone-reactive chemicals are: soft woods, linoleum, certain paints, polishes, cleaning products, air fresheners and health care products as well as the occupants themselves. These ubiquitous sources result in substantial quantities of indoor chemicals that can react with ozone, whenever elevated outdoor ozone penetrates indoors. The reaction products arising from this ozone initiated chemistry may be responsible for some of the short-term symptoms, health and comfort effects reported in recent indoor air studies (Weschler *et al*., 2006, Wolkoff *et al*., 2006).

c. Exposure assessment

The abundance of and hence the exposure to terpene oxidation products indoors, like limonene/ozone (LO) and pinene/ozone (PO) reaction products, depends on the identity and concentration of the reactants, their reaction rate and the air exchange rate, both of which determine the build-up of reaction products (Weschler and Shields, 2000). Emphasis on this relationship is given in chapter 3 of this report.

Human exposure to ozone-initiated reaction products has not yet been investigated. Model calculations (Weschler and Shields, 1996; 1997; Sarwar *et al*., 2002; Carslaw, 2007) predict that indoor OH levels at noon are around 10 times less when compared to those outdoors and, depending on contingent indoor conditions, are likely to be in the range of 1 to 7 x 10^5 molecule cm^{-3}. The most crucial parameters for modelling OH concentration are the light intensity, the air exchange rate and outdoor concentrations of O_3 and NO_x (Carslaw, 2007).

Few population based exposure data are available for ozone, d-limonene and α-pinene. Ozone is a common pollutant indoors (Weschler and Shields, 1996), the most important source being the transport of air from outdoors. It has been measured indoors at

concentrations from a few ppb to hundreds of ppb, and is typically 20–80% of outdoor levels (see Chapter 3). The composition of indoor materials, surface removal rates and the reaction of ozone with any indoor chemicals are key determinants of indoor ozone concentrations (typical half-life: 7-10 min) (Weschler, 2000). Indoor ozone concentrations can be higher in close proximity to printers, photocopiers and air purifiers.

Based on outdoor peak concentrations in summer, reaching 120-400 μg/m^3, the given I/O ratios (0.1 – 0.7) would give rise to indoor peak concentrations of 12 to 240 μg/m^3 in naturally ventilated homes, with no frequency distributions yet available. Ozone concentrations are not expected to exceed 40 μg/m^3 in mechanically ventilated rooms, where I/O ozone ratios of 0.1 are common.

On the other hand, mean residential air concentrations of d-limonene and α-pinene in European homes vary between 15-80 μg/m^3 and 4-40 μg/m^3 respectively (Kotzias *et al* 2005). Maximum concentrations have been reported in different studies, ranging between 140 μg/m^3 (Girman *et al*. 1999) and 387 (Bernhard *et al*. 1995) for d-limonene and between 134 μg/m^3 (Bernhard *et al*. 1995) and 250 μg/m^3 (Krause *et al*. 1991) for α-pinene.

Formaldehyde, one major terpene oxidation products, and frequently regarded as the principal sensory airway irritant in indoor environments, is present in European homes in the range 26-79 μg/m^3 (Kotzias *et al.* 2005). Short-term concentrations, however, may be considerably higher, during use of household products, e.g. (Destaillats *et al*. 2006).

d. Dose - response assessment
A few studies are available concerning health effects of ozone-terpene reaction products, and available data do not allow assessing a dose-response curve.

In experimental data from mouse bioassays, airway effects of LO and PO were shown to generate sensory irritation significantly higher than that exhibited by the pure compounds (Clausen *et al*., 2001; Wolkoff *et al*., 1999; respectively), with an increased bioresponse of LO at low relative humidity (Wilkins *et al*., 2003).

Concerning acute effects on human health, no effects (i.e. sensory irritation and inflammation) have been observed at concentrations of 25 mg/m^3 VOC mixture with and without ozone admixed to a chamber level of about 40 ppb during two hours (Laumbach *et al*., 2005). Weak symptoms of irritation (i.e. eye blink frequencies) have been observed with an exposure of 20 min to a mixture of ozone and limonene of about 100 ppb each, with 32% of ozone reacted, with a decreasing trend following a relative humidity increase from 20% to 50% (Klenø and Wolkoff, 2004; Nøjgaard *et al*., 2005).

No long term effects of LO and PO mixtures were ever studied in humans. The relationship observed in epidemiological studies on human ozone exposure and long term effects such as allergy, asthma or decreased lung function could be hypothesized to be partially due to the action of products of ozone-initiated indoor chemistry. There are only a limited number of epidemiological studies investigating the association with adverse health effects of consumer products (e.g. Farrow *et al*., 2003; Sherriff *et al*., 2005).

e. Risk characterization
The above findings of human and animal exposure studies indicate that gaseous LO and PO reaction products may cause sensory irritation at ozone and terpene concentrations that are close to the high-end values measured in indoor settings.

Odour perception of ozone, d-limonene and α-pinene occurs in the range of about 10 ppb under low background conditions (Cain *et al*., 2007; Nagata, 2003). At these levels LO and PO reaction products are not expected to produce sensory irritation; anyhow, detection sensitivity may decrease upon elevated background levels, either ozone or VOC levels.

It is assumed that measurable health effects of ozone-initiated chemistry could be induced at elevated levels of the reactants:

- High outdoor ozone levels are encountered in summer and are typically highest downwind of urban areas. Also, air exchange rates tend to be highest in summer, when windows are open more frequently and more ozone is finding its way indoors.

- High terpene levels could be attained during the application of consumer/household products or when using personal care products.

Health effects of the stable reaction products such as formaldehyde, peroxides and condensed phase species (i.e. ultrafine particles), although increasingly investigated have not yet being elucidated.

Formaldehyde has been designated a Group 1 carcinogen in a 2004 IARC evaluation (Cogliano *et al*. 2005). Acrolein is listed as an irritant as well as peroxyacetyl nitrate (eye irritant; Vyskocil *et al*. 1998), as are some of the above mentioned products of ozone/terpene and ozone/isoprene chemistry (Kleno and Wolkoff 2004; Nojgaard *et al*. 2005). Finally, the impact of ultrafine particles on short-term symptoms like eye and upper airway irritation is unknown and their possible role in the development of effects in the lower airways is debatable (Weschler, 2006).

In summary, further knowledge is required to complete a risk assessment associated with exposure to indoor "ozone-initiated terpene chemistry". Although some associations have been observed with adverse health effects of consumer products, the causal relationship remains unclear. Observed sensory effects could be associated concomitantly with the presence of numerous chemical species, but also with as yet unknown factors/agents.

 f. Future perspectives
Risk assessment in the EU is conducted in accordance with the procedures set out by the Commission Regulation (EC) No. 1488/94 and the Technical Guidance Document on Risk Assessment (2003), laying down the principles for assessment of risks to man and the environment of existing substances.

Revised principles are now coming into force with the establishment of Regulation (EC) No. 1907/2006 of the European Parliament and of the Council, known as the REACH regulation. This regulation foresees the institution of a Committee for Risk Assessment, which shall be responsible for preparing the opinion of the constituting European Chemicals Agency (EChA) on evaluations, applications for authorization, proposals for restrictions and proposals for classification and labeling and any other questions that arise from the operation of this Regulation relating to risks to human health or the environment.

According to this regulation, risk characterisation considering the human population and environmental spheres consists of a comparison of the derived no effect levels (DNELs) and predicted no effect concentrations (PNECs) and shall be carried out on exposure estimations based on single exposure scenarios (including suitable Risk Management Measures and Operational Conditions). Guidance on developing exposure scenarios, estimating emissions

and exposure, as well as for performing a risk characterisation, is being given in the Guidance on the Chemical Safety Report for individual registrants (available in early 2008; http://reach.jrc.it/chemical_safety_en.htm), describing the basic approaches.

Conditions defined in the exposure scenarios are used to calculate the exposure. Where monitoring data are used, they should reflect the situation where these elements of the exposure scenario are implemented, and the compliance check should confirm that this is the case.

The responsibility for assessing the risks and hazards of substances lies with natural or legal persons that manufacture or import substances, produce or import articles, or use it as downstream user, in case the use is not covered by the exposure scenario(s).

On the basis of available data and taking into account the new REACH regulation, experimental insight in this field is furthermore requested, since:

- current exposure data of ozone-terpene reaction mixtures are currently too limited for conducting an exposure assessment,

- results on acute symptoms associated with exposures to LO and PO reaction mixtures have still to be confirmed,

- full scale studies were never reported under realistic conditions, e.g. during the application of selected consumer/household products and in the presence of ozone, in order to evaluate the magnitude of exposure to the above named reaction products and the severity of symptoms,

- research on LO and PO effect levels were never confirmed/investigated on susceptible subgroups of the population, i.e. persons suffering from asthma and other respiratory diseases, infants, children or the elderly.

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8. CONCLUSIONS

1. The use of some consumer products can result in abundant indoor concentrations of terpenes.

2. The chemistry of indoor air is dominated by ozone reactions with terpenes, reactions that can produce highly reactive intermediates (e.g., radicals), secondary ozonides, hydroperoxides, carbonyl compounds and also fine particles in the sub-micron range. An important product of such reactions is the OH radical, which can proceed to initiate further oxidation processes. Indeed, many of the reaction rates indoors have been predicted to be of a similar order of magnitude to outdoors and sometimes even larger.

3. There is neither, adequate knowledge of exposure patterns of ozone-terpene reaction products, nor dose/response relationships. There are toxicologically relevant compounds formed in ozone terpene reactions that are not identified. These compounds (e.g. radicals, aldehydes, acids) are potentially responsible for observed health effects (e.g., sensory irritation, lung injuries, etc).

9. RECOMMENDATIONS

1. This report summarises our knowledge of ozone-terpene related indoor air chemistry to date, although there are still significant gaps. In addition, many of the issues are exceedingly complex, both chemically and physically. It is increasingly recognised that secondary products are the cause of the ill-health effects observed indoors, however, the actual culprits have yet to be fully identified. Furthemore, model predictions of OH and NO_3 radical concentrations indoors need to be verified through experimental observation. Ideally, many of these gaps in our knowledge could be addressed by organising indoor air 'field campaigns' similar to those commonly performed outdoors. One would envisage that indoor measurements could be made *simultaneously* of the concentrations of radicals, ozone, NO_X, VOCs (particularly the reactive compounds such as the terpenes), HONO, aldehydes including HCHO, as well as aerosol size, number and composition, photolysis rates, temperature and humidity *etc.,* in order to validate models and to identify compounds that may be deleterious to health.

2. Considering the long-term and integrated impact of material/product oxidation on exposure of indoor air, it is prudent to develop methodologies for emission testing of construction materials and consumer products (in particular spray products) under oxidative and realistic conditions for future standardization.

3. The ozone and formaldehyde concentrations should be measured in micro-environments suspected to have strong sources of terpenes due to product usage or personal activities.

4. Analytical methods to measure potentially toxicologically relevant compounds indoors e.g. radicals should be further developed for practical use.

5. New metrics/proxies that are health relevant should be identified and developed, both with regard to acute/semi-acute effects and longer-term effects.

6. Risk characterization of the mixed terpene-ozone system calls for more toxicological knowledge:

   ❍ Acute and longer-term exposure effects to eyes and upper and lower airways.

   ❍ Evaluation and assessment of selected consumer products, in particular spray products in the presence of ozone, through the use of bioassays and full scale human exposure studies under realistic conditions.

ANNEX 1: METHODS OF MEASUREMENTS (extended)

Ozone

Several techniques for ozone monitoring have been developed including UV absorption, differential optical absorption spectroscopy (DOAS), chemiluminescence and chemical titration methods. UV absorption provides a reasonably straightforward and accurate means to measure ozone. Most instruments rely on the 254 nm emission line emitted from a low pressure mercury discharge lamp as the UV light source. Several high quality, reliable, commercially available instruments use this method; their response times are generally of the order of 10-20 s. The chemiluminescence methods use the detection of chemiluminescence from the reaction of ozone with either NO, unsaturated hydrocarbons (e.g. ethane) or eosin (Parrish and Fehsenfeld, 2000).

For microenvironmental and personal monitoring, diffusive and pumped ozone badges have been developed. Koutrakis *et al*. (1993) developed a diffusive ozone badge with sodium nitrite impregnated filters. The nitrite reacts with ozone forming nitrate, which is analysed by ion chromatography (Koutrakis *et al*., 1993). A disadvantage of this method is that it only provides one single integrated ozone measurement over an averaging time, which is longer than the time scales in which ozone concentrations change. For fast real-time measurement a portable detector has been developed using the reaction of polybutadiene with ozone. The polybutadiene is coated on a piezo electric crystal, the frequency of which changes upon reaction of the polymer with ozone (Black *et al*., 2000).

Terpenes

In general, two sampling techniques are widely used to measure concentrations of terpenes: pre-concentration on different adsorbents or "instantaneous-sampling" (whole-air sampling) using stainless steel or glass containers, followed by gas-chromatographic separation of the compounds. The whole-air collection using different canister materials has been applied frequently for the measurements of low molecular weight hydrocarbons, but surface reactivity can result in molecular rearrangements of the unsaturated terpenes. Therefore, the analysis of airborne terpenes is preferably carried out by sampling on solid adsorbents and subsequent thermal desorption of the compounds.

Due to the unsaturated character of the analytes, care must be taken to maintain sample integrity during pre-concentration or storage of the samples. The omnipresence of ozone as well as the high rate constants of the ozonolysis reaction of unsaturated hydrocarbons raises the question if in situ reactions of the analytes with the oxidant may occur during the collection procedure. Several studies have addressed the analytical problems arising from interactions between unsaturated terpenoid compounds and ozone during sampling procedures. Saturated terpenoid compounds (1,8-cineole, camphor and bornyl-acetate) showed no losses due to ozone, while unsaturated compounds with one double bond (e.g.: camphene, α-pinene, sabinene) showed moderate loss rates (5-35 %) and compounds with two or more double bonds (e.g.: trans-ocimene, α-terpinene, trans-caryophyllene) showed very strong depletion (80-100 %) at ozone mixing ratios of 120 ppbV on Tenax TA cartridges (Calogirou *et al*., 1996). Larsen *et al*. (1997) compared results from ten European laboratories that analyzed the same monoterpene standard. The sampling was performed at various ozone levels (8, 65 and 125 ppbV). The results were usually accurate and precise at 8 ppbV ozone. However, under elevated ozone conditions (65 and 125 ppbV) significant losses (up to 100 % for some compounds) were found. Laboratories utilizing ozone mitigation techniques reported much higher recovery rates and improved accuracy.

Conclusively, these studies have shown that many terpenes are rapidly depleted at elevated ozone concentrations. Consequently, ozone removal techniques are required during terpene sampling. Several techniques for selective ozone removal have been applied to reduce these sampling losses (Helmig, 1997). Further research, with particular focus on how to minimize sampling losses of biogenic compounds, has also been published (Fick *et al.*, 2001; Komenda *et al.*, 2001; Pollmann et al., 2005; Pollmann *et al.*, 2005). The most frequently used techniques are: a) the application of sodium thiosulfate impregnated filters, b) titration of ozone with nitric oxide and c) catalytic removal of ozone with manganese dioxide coated screens.

Oxidation products
Volatile aldehydes and ketones (Formaldehyde, acetaldehyde and acetone) are mainly analysed by derivatisation with 2,4-dinitrophenyl-hydrazine (DNPH) yielding the coreresponding 2,4-dinitrophenyl-hydrazones, which can be easily detected by UV or mass spectrometric methods. For sampling, DNPH-coated silica gel cartridges are used and detection limits of 1 ppbv for HCHO in a 45 l air sample have been reported (Slemr, 1991). On-line measurements have been performed in reaction chambers and air craft cabins using proton-transfer-reaction mass spectrometry (PTR-MS) (Wisthaler *et al.*, 2001; Wisthaler *et al.*, 2005).

Important reaction products from ozone reaction are the so-called secondary ozonides (SOZ), which posses a cyclic peroxidic structure and are therefore unstable compounds. Nevertheless, they exhibit typical absorptions in the infra-red region between 1200 and 1000 cm^{-1}, and have been observed on-line by long-path FTIR-spectroscopy from the reaction of ozone with simple alkenes (Neeb *et al.*, 1996) and β-pinene in chamber experiments (Winterhalter *et al.*, 2000).

Nørgaard *et al.* (2006) identified two diastereomeric SOZs from limonene as the main reaction products using GC/MS after gas sampling on XAD-2 resin and liquid extraction with dichloromethane. The identity was confirmed by GC/MS/MS comparison with cryo-synthesized SOZ using electron impact and chemical ionisation techniques (Nørgaard *et al.*, 2006).

Recently an on-line mass spectrometric method has been developed for the analysis of SOZs from limonene and cyclohexene (Nøjgaard *et al.*, 2007; Nøjgaard *et al.*, 2007; Nøjgaard *et al.*, 2007). The authors used atmospheric sampling townsend discharge ionization (ASDTDI) in connection with a triple quadrupole mass spectrometer for the direct analysis of these labile compounds. The identity of the observed ions was confirmed by comparison with synthesized standards of the SOZs.

Hydrogen peroxide (H$_2$O$_2$), organic peroxides and hydroperoxides, are also important reaction products, which are difficult to measure and require specific methods. Several method are able to measure H$_2$O$_2$ and total organic peroxides (Reeves and Penkett, 2003), but the measurement of individual organic peroxides, in particular higher organic peroxides originating from terpenes, is still an analytical challenge. An established chromatographic method, which allows the measurement of H$_2$O$_2$ and small organic peroxides and hydroperoxides uses the horseradish-peroxidase catalyzed reduction of H$_2$O$_2$ and other peroxides with para-hydroxyl-phenyl acetic acid (POPHA), yielding a dimer .which can be detected with a fluorescence detector (Lazrus *et al.*, 1986; Sauer *et al.*, 1999; Li *et al.*, 2002; Fan *et al.*, 2005; Francois *et al.*, 2005; Valverde-Canossa *et al.*, 2005). The lack of analytical standards of higher peroxides limits the applicability of the HPLC/Fluorescence method for the study of the terpene-ozone reaction. The development of mass spectrometric methods using soft ionisation techniques might be a promising alternative for the identification of higher peroxides.

Several unstable hydroperoxides derived from the auto-oxidation of limonene have been identified by GC-MS with chemical ionization in the negative mode by comparison with synthesized hydroperoxides (Nilsson *et al.*, 1996). Furthermore the authors also developed an HPLC method with UV detection for these unstable compounds. However the hydroperoxides detected from the auto-oxidation and photo-oxidation of limonene contain all the cyclic structure of limonene. Since ring opening of limonene is the first step of the ozone initiated degradation, these hydroperoxides are different from theoretical expectations as hydroperoxides formed in the ozone reaction contain no cyclic structure.

A soft ionization MS technique (APCI-MS2) for organic peroxide analysis in the particle phase has been developed and a specific peroxide structure of a highly oxidised reaction product formed from the ozonolysis of α-pinene has been proposed (Warscheid and Hoffmann, 2002). Recent studies show that atmospheric pressure chemical ionisation in the positive ion mode [APCI(+)] as a soft ionisation technique provides information about molecular mass by producing intact quasi-molecular ions. Coupled to an ion-trap, organic hydroperoxides derived from the ozonolysis of α- and β-pinene could be identified by a characteristic loss of 34 Da (H_2O_2) in their on-line MS/MS spectra (Reinnig *et al.*, in preparation).

Also a thermal desorption particle beam mass spectrometer (TDPBMS) was used to investigate the ozonolysis of cyclohexene and some of its structural homologues, including cyclopentene, cycloheptene, and cyclooctene, in humid air. In these reactions based on mass spectra and desorption behaviour, the formation of diacyl peroxides oxidation products was predicted as well as dicarboxylic acids identified previously (Ziemann, 2002). On the basis of these results the formation of alkoxyhydroperoxy aldehydes in the presence of alcohols could be observed in SOA of these alkenes with the TDPBMS system (Ziemann, 2003).

Radicals (OH, HO$_2$ and RO$_2$)

Direct measurements of OH radical concentrations in the range of 10^5-10^6 molecules cm^{-3} are difficult and therefore often indirect methods have been used to determine OH-radical concentrations in laboratory experiments. For indirect determination either a sufficient amount of an OH-radical scavenger (e.g. cyclohexane) is added and the reaction products (e.g. cyclohexanone and cyclohexanol) are measured (Atkinson *et al.*, 1992) or the loss of a tracer compound has been monitored (Paulson *et al.*, 1998).

In indoor environments the indirect method that has been applied uses 1,3,5-trimethylbenzene as an indicator compound that reacts almost exclusively with OH during the time scale of interest. To determine an average OH concentration in a room, 1,3,5-trimethylbenzene is emitted into the indoor setting at a known rate. In the absence of OH, the steady-state concentration of 1,3,5-trimethylbenzene can be calculated from its emission rate, the air exchange rate, and the volume of the room; if the measured concentration of 1,3,5-trimethylbenzene is less than this value, the difference is attributed to OH (Weschler and Shields, 1997).

Measurements of tropospheric OH-radical concentrations have been performed directly by spectroscopic methods such as laser induced fluorescence (LIF) spectroscopy at low pressure (FAGE) and long path differential optical absorption spectroscopy (DOAS). An indirect method is the ion-assisted OH measurement technique, where OH is titrated with isotopically labelled $^{34}SO_2$ to yield $H_2^{34}SO_4$, which is measured by chemical ionisation mass spectrometry (CIMS) (Heard and Pilling, 2003). All these methods have the advantage of

high time resolution of the measurements compared to the indirect methods described above, but require on the other hand very elaborate (and expensive) experimental equipment.

HO_2 radicals can be measured after conversion of HO_2 to OH through addition of NO and determination of the generated OH-radicals by one of the above methods. As long as a significant fraction of HO_2 can be converted to OH, the instruments capable of measuring OH ought to be excellent, as HO_2 concentrations are much higher than for OH (Heard and Pilling, 2003).

A relatively new method uses a modified chemical amplifier that converts peroxy radicals to gaseous sulfuric acid via a chain reaction with NO and SO_2, with detection of the sulfuric acid by CIMS.

Secondary organic aerosol
The chemical analysis of organic aerosol constituents includes sampling, sample preparation and analysis. It depends on the sample preparation and the method of analysis, which constituents can be measured and sometimes it depends even on the sampling (e.g. sampling substrates). Because of their different chemical properties, it might be necessary for the determination of different compound classes to use different analytical procedures. It is important to know that it depends on the analytical procedure as to which organic compounds can be detected and quantified. For example, the first step of an analytical procedure is often the extraction of filter samples. Depending on the solvent, different compound classes will be extracted or they will be extracted with different efficiencies. Accordingly, extractable organic compounds are often divided into water soluble (e.g. WSOC) and solvent extractable (e.g. solvent extractable organic matter – SEOM).

Sampling
For chemical analysis of airborne particles, they have to be separated from the surrounding gas phase (the atmosphere). Often, this separation step is realised by particle collection, which at the same time represents an enrichment step of the particulate material. Basic methods for particle collection are filter sampling and the use of impactors. Fibre filters, such as quartz fibre filters, generally collect particles of all sizes, whereas impactors can be used to collect different size fractions. For the characterisation of organic aerosol components, quartz or Teflon filters are often used.

Impactors, for example, the Berner impactor (Berner and Lurzer, 1980), use the mass inertia of particles for their separation. The aerosol is accelerated by passing it through defined openings (nozzles). Usually a vacuum is applied at the 'end' of the impactor to draw the air inside. Aerosol particles are accelerated together with the air. This jet is guided against a wall, forced to change its direction rapidly (90◦). Aerosol particles, which have a high inertia (big particles) cannot follow the air stream and will collide with the wall where they will (ideally) adhere. Particles with a low inertia (small particles) are able to change direction together with the airflow and will be transported away. As a result, the smaller particles are separated from the larger ones. Changing the velocity of the airflow (usually by reducing the diameter of a nozzle) enables the size of particles being impacted to be varied. This is usually done using a series of impactors combined to a cascade impactor. Each impactor within this cascade represents one 'stage'. At the first stage, particles with a relatively large aerodynamic diameter will be impacted, the aerodynamic diameter of impacted particles will then decrease at each following stage. At the end of the cascade, a filter can be installed to collect

the finest particles which have passed the last stage. Ideally, all particles larger than a certain aerodynamic diameter will be impacted on one stage, and all smaller particles will pass to the next stage. This certain size is called, for example, cutoff, cutoff size or cutoff diameter. In reality, some particles larger than the cutoff diameter will enter the next stage, and some particles smaller than the cutoff diameter will be impacted. Therefore, the cutoff for real systems is the aerodynamic diameter with a collection efficiency of 50%.

Particles are usually impacted on special substrates, such as foils of aluminium or polymers. These will be removed after a certain period of time and can be analysed afterwards. For organic aerosol analysis, sampling times are often between 8 and 24 h. Impactor sampling suffers from different sampling errors, for example, wall losses and 'bounce off'. Particles may bounce from the collection substrate instead of getting stuck if their velocity is high and they are relatively solid. If solid particles hit the impaction surface, only part of their kinetic energy will be used for plastic deformation, and a considerable amount of the energy will be converted elastically to kinetic energy of rebound. To prevent bounce off, collection substrates can be coated with different oils or greases.
However, these coatings can heavily interfere with chemical analysis, especially for organic aerosol analysis. In a virtual impactor, the accelerated air is split in two parts, a fast one, which is the main air stream, and a slow one. The fast main stream is forced to change its direction, whereas the slower minor part of the air does not. Smaller particles can follow the main stream of air that was forced to change the direction. The larger particles will continue to move in the previous direction together with the smaller part of the air flow. Particles of both airstreams can be collected on filters. Virtual impactors have usually only one stage. The benefit of a virtual impactor is the use of conventional fibre filters that do not suffer from bounce off like the substrates for impaction in normal impactors or interferences of chemical analysis from substrate coating.

A special impactor is the so called steam jet aerosol collector (SJAC). It is not designed for the separation of different-sized particles but for the efficient collection of all particles. After passing a denuder to remove gas-phase constituents, particles grow in supersaturated water vapour to droplets which are afterwards impacted in a cyclone. A cyclone is a special design of an impactor. Here, the aerosol is injected tangentially into a cylindrical hole. Due to the geometry, the aerosol begins to rotate around before it leaves the cyclone through an opening at the upper end. Because of the centrifugal forces caused by the rotation larger particles collide with the wall and will be removed from the aerosol. The liquid from the collected droplets in the SJAC can be continuously removed from the lower part of the cyclone. Cyclones have several applications in science and technology (they are also used in some vacuum cleaners). In the SJAC, impacted droplets are much larger than the original aerosol particles. Due to the much larger diameter of the droplets, the SJAC provides high collection efficiency and additionally prevents negative artefacts due to the evaporation of semivolatile constituents. This system can be coupled online to, for example, ion chromatography (IC) for the determination of nitrate (Slanina *et al.*, 2001).

Impactors with only one stage (also cyclones) are often used to separate coarse particles from the fine particle fraction before filter sampling. They are called preseparators if used this way, making it possible to sample the smaller particles with diameters below the cut-off size of the preseparator. Preseparators are commercially available for different size classes. There exist different standards cutoff sizes for air monitoring: 1, 2.5 and 10 μm. These size classes are called PM_1, $PM_{2.5}$ and PM_{10}. Here, PM means particulate matter and the number in lower case shows the cut-off size. Preseparators are commonly used in filter-sampling assemblies.

Filters

The most commonly used method to collect particles is filter sampling. There are mainly two types of filters used: fibre filters (glass, quartz, cellulose, polymers) and porous membrane filters (cellulose esters and polymers, for example, Teflon®). The mechanism of particle filter sampling from aerosols is not simple and differs from the commonly assumed 'sieving' of particles, as it appears in liquid filtration. In aerosol particle sampling, particles much smaller than the pore size of the filters are retained. There are several mechanisms that take part in deposition of particles onto fibre filters: gravitational settling, impaction, interception, diffusion and electrostatic attraction.

Gravitational settling is only important for particles larger than a few micrometres. Impaction onto a fibre works like the mechanism in an impactor and is important for particles larger than a few hundred nanometres. Interception occurs if a particle follows a streamline of air passing a fibre. Due to its size, the particle gets into contact with the fibre and adheres. Interception is an important collection process for particles slightly smaller than those lost to the fibre by impaction. Diffusion is the main process for the collection of the smallest particles. It becomes the most important for particle diameters smaller than 100 nm, which have a considerable coefficient of diffusion compared to larger particles. Brownian motion forces small particles to hit a fibre by chance. Finally, if filters or particles are charged, electrostatic attraction can be a very efficient way for particle deposition. It is used in technical applications, for example, for cleaning of exhaust gases. Although porous membrane filters have a different constitution compared to fibre filters, the mechanisms of particle deposition are similar. As mentioned above, for the chemical analysis of organic compounds in aerosol particles, quartz fibre and Teflon filters are most widely used. These materials are chemically inert and do not interfere in the chemical analysis of trace compounds. Quartz can be cleaned very easily by heating up to 700°C, a treatment that removes all organic contaminants.

Sampling artefacts

Sampling artefacts are errors that occur during sampling due to physical or chemical processes on the sampling substrate (filters, impactor foils). Sampling artefacts can result in a lower (negative artefact) or higher (positive artefact) mass determined for certain components. Physical artefacts can either be based on the volatilisation of compounds sampled, which would result in a negative artefact, or on adsorption of gas-phase compounds on active surface sites of the sampling substrate, which would result in a positive artefact. Chemical artefacts are based on the formation or loss of compounds by chemical reactions on the sampling substrate, for example, caused by oxidants. Artefacts due to adsorption and evaporation of organics have been investigated in a series of studies (Kirchstetter *et al.*, 2001; Mader and Pankow, 2001; Mader *et al.*, 2003; Muller *et al.*, 2004). If particles and the surrounding gas phase are in equilibrium, volatile components will not evaporate if sampled. However, if the equilibrium is disturbed by changing pressure, temperature or gas-phase concentration, for example, which will regularly happen during longer sampling periods, components may evaporate (or condense). Inside filter systems or impactors, a pressure drop can cause evaporative losses. The absorption of gaseous compounds is known to be relevant, especially for quartz fibre filters. The active surface is able to adsorb compounds in a quantity that might be in the order of the particulate mass. In contrast, Teflon filters do not suffer from adsorption of gaseous compounds because of their non-active surface characteristics. Unfortunately, Teflon filters are not suited to certain analytical methods, for example, OC-measurements, due to their limited temperature resistance.

To avoid artefacts due to adsorption or evaporation a variety of sampling techniques have been developed. Most research of sampling artefacts concerns sampling for OC/EC measurements, not individual components. Sampling errors without correction might range from a positive artefact of 55% to a negative one of up to 80% for OC-measurements, depending on sample composition and sampling conditions. Unfortunately, frequently, the attempt to avoid errors produces new ones. If, for example, the gas phase is removed by a denuder to prevent positive artefacts by adsorption of gaseous compounds, the equilibrium of gas and particle phase is disturbed and semi-volatile compounds begin to evaporate, creating a massive negative artefact. A rough estimate of the positive artefact can be done by placing a backup quartz filter behind the particle collecting quartz filter (front filter). The measured OC or component mass on the backup filter can be accounted as adsorbed gas phase and subtracted from the determined mass of the front filter for correction. Nevertheless, the particle-phase compounds may evaporate from the front filter and condense onto the backup filter. A negative artefact would then be additionally subtracted, making the error even bigger. Newer attempts to eliminate artefacts use combinations of different filters and denuders in different sampling lines for measurement of the different artefacts (Mader *et al.*, 2003).

Analytical methods for characterisation of particulate organics - Sample treatment
The procedure following the particle collection step depends on the analysis that has to be carried out. The measurement of OC/EC by thermal methods can usually be done without any further treatment of the filter/impactor substrate. For most other analytical techniques, particulate matter has to be extracted from the collection substrate. The selection of the solvent depends on the chemical characteristics of the analytes of interest. It might be necessary to use several extracting steps using different solvents if the substances of interest cover a wide polarity range. Commonly used solvents are dichloromethane, methanol, water and also mixtures or additives, for example, acids to adjust the pH. Repeated ultrasonic agitation or the soxhlet extraction is applied to optimise the extraction efficiency. Another possibility is supercritical fluid extraction (SFE) using CO_2; however, this method is not widely used for atmospheric aerosol analysis (Förstner *et al.*, 1997) (Shimmo *et al.*, 2004).

The further treatment of the extracts likewise depends on the compounds of interest and the selected analytical method. If necessary, solvents can be changed after the extraction step by drying the extracts and resolving them in a suitable solvent. However, relatively volatile analytes might be lost during this treatment by evaporation. The evaporation of the solvent can also be used as enrichment after the extraction process. For gas chromatography (GC) measurements, several enrichment, clean-up and derivatisation methods are available. Derivatisation is required if the components of interest are not volatile enough for GC analysis. Derivatisation is sometimes also used for an improvement of the sensitivity. High performance liquid chromatography (HPLC) and IC analysis usually do not require derivatisation. However, the analytes have to be dissolved in suitable solvents.

Separation and detection methods
Gas chromatography–mass spectrometry (GC–MS) is the most widely used method for the separation, identification and quantification of organic compounds in aerosol samples. It is a powerful, sensitive and very selective analytical method. Occasionally, flame ionisation detectors (FID) are still used for detection (Cheng and Li, 2005). They produce lower costs, have a better dynamic range and are often better for quantification than MS-detectors; however, they feature a poor selectivity. On the other hand, many compound classes present in atmospheric aerosol particles are not accessible by a direct GC analysis. Carboxylic acids,

low volatile carbonyls, sugars and other polar substances have to be derivatised prior to analysis. There exist a variety of derivatisation techniques. Alcohols can be derivatised to trimethylsilyl ethers by, for example, N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) (Simoneit *et al.*, 1999) or N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) (Zdrahal *et al.*, 2002). Carbonyl groups can be derivatised using, for example, o-(2,3,4,5,6-pentafluorobenzyl) hydroxyl amine (PFBHA) (Yu *et al.*, 1998). Acids can also be treated with BSTFA-forming trimethylsilyl esters (Yu *et al.*, 1998) or with BF_3-methanol to yield methyl esters (Bin Abas *et al.*, 1995). Diazomethane is a long-known, universal and often-used methylation reagent that is still in use (Kubátová *et al.*, 2000).

Besides GC, liquid chromatography (LC) is going to become a widely used method for the analysis of individual compounds in organic aerosols (Hoffmann et al., 1998; Glasius *et al.*, 1999; Anttila *et al.*, 2005; Römpp *et al.*, 2006; Warnke *et al.*, 2006). LC is especially appropriate for the separation of high-molecular-mass or very polar molecules without derivatisation. The coupling to mass spectrometers is well established, and electrospray ionisation (ESI) is the ionisation method most widely used for organic aerosol characterisation. Atmospheric pressure chemical ionisation (APCI) is also a standard ionisation method, which is particularly suited for more polar and lower molecular weight substances.

Ion chromatography (IC) is usually used for the separation of inorganic ions. In organic aerosol analysis, it is applied for the analysis of very acidic, short-chain carboxylic or dicarboxylic acids, such as oxalic acid and glyoxylic acid (Jaffrezo *et al.*, 1998; Kerminen *et al.*, 1999; Rohrl and Lammel, 2001). Mass spectrometric detection is usually not applied with IC because of the necessity to use buffers that are often not suitable for MS-detection. However, there exist methods for the coupling of IC with mass spectrometric detection (Bauer *et al.*, 1999; Fisseha *et al.*, 2004).

Electrophoretic separation techniques are also used for the analysis of aerosol constituents. Capillary electrophoresis (CE) has high separation efficiency and can be coupled to mass spectrometers by ESI. However, CE/MS is usually only suited for the separation of analytes that are charged or are at least in equilibrium with a charged form, for example, carboxylic acids. CE/MS has been used in several studies mainly for the analysis of acidic organic compounds (Iinuma and Herrmann, 2003; Iinuma *et al.*, 2004).

Due to the tremendous number of substances present in aerosol samples, some scientists tried not to identify every single component but to identify and quantify compound classes (functional group analysis). For a series of atmospherically relevant questions, this information is adequate to give satisfying answers. (Decesari *et al.*, 2000) separated the water extractable organics into groups of molecules having one, two and three or more carboxylic acid functionalities by anion exchange chromatography. This way, they were able to classify up to 82% of WSOC. However, there are also uncertainties using this approach, since certain individual substances do not elute within the compound class to which they actually belong (Chang *et al.*, 2005).

Nuclear magnetic resonance (NMR) can be especially useful for functional group analysis. Applying 1H-NMR, it is possible to quantify protons of different functional groups in extracts of aerosol samples, such as OH, CH, CHO and COOH (Decesari *et al.*, 2000). This information can be used to get information about the chemical composition of the main organic components. Besides proton-NMR, solid-state ^{13}C-NMR of extracted and dried matter was also used for the characterisation of particulate WSOC (Duarte *et al.*, 2005).

Another method for identification and quantification of organic compounds present in SOA is so called Direct Thermal Extraction of samples collected on appropriate filters followed by gas chromatography – mass spectroscopy/flame ionization detection for the analysis. This method has been successfully used in e.g. analysis of monocarboxylic acids in samples of ambient aerosol (Shannigrahi *et al.*, 2007).

The analytical techniques described above are based on a time integrating sampling step (using filters, impactors, etc.) with the inherent risk of positive and negative artefacts during the multi-step analytical procedure. Moreover, this type of sampling severely limits both spatial and temporal sampling densities. Therefore, analytical techniques to monitor the organic aerosol fraction with a high time resolution are required, especially for the understanding and control of highly dynamic systems such as atmospheric aerosols. For certain atmospheric research platforms, such as aircrafts, rapid online systems are even mandatory. Consequently, several real-time analytical methodologies based on mass spectrometry for particle analysis have been developed within the last few years.

Laser-based aerosol mass spectrometers allow the real-time analysis of single particles (Johnston, 2000; Noble and Prather, 2000). Using nozzles, capillaries or aerodynamic lenses, particle beams are created and transferred into a vacuum. There, the particles are detected by the scattering of a continuous laser beam followed by vaporisation and ionisation by a second laser system. It is also possible to use different lasers to separate the ablation/desorption and ionisation step, for example, a combination of IR and ultraviolet (UV) lasers. For ion separation, time-of-flight mass spectrometers are used. However, although the organic aerosol fraction gives characteristic ion patterns with laser based aerosol mass spectrometers, the frequently observed strong fragmentation and matrix effects prevent quantification of organic aerosol components. For some specific applications, for example, the detection of high-molecular-weight compounds in laboratory-generated SOA, single particle instruments appear to be useful tools even for organic aerosol characterisation (Gross *et al.*, 2006). In these cases, the ability to also produce larger ions is probably connected with the presence of a suitable matrix in the investigated particles, which allows a MALDI-like desorption/ionisation processes.

Another (non-laser-based) online mass spectrometric technique for aerosol analysis uses thermal desorption (flash evaporation) of the aerosol components, typically followed by electron ionisation of the desorbed components (so-called aerosol mass spectrometers, AMS). At first, a particle beam is generated by aerodynamic lenses, and the particles are transferred into the vacuum region of the MS. Before the particles hit a vaporiser, they have to pass a chopper and a drift region, a set-up that generates the size information.. The vaporised compounds are than ionised by electron ionisation and analysed by quadrupole mass spectrometry (Jayne *et al.*, 2000; Zhang *et al.*, 2005). These systems have proven to be especially useful for the quantitative measurement of major inorganic compounds, such as sulphate, nitrate and ammonium. Also, valuable information about the organic aerosol fraction can be obtained; however, due to the strong fragmentation resulting from EI single compounds can hardly be identified. Currently, developments in this field are focussing on soft ionisation techniques and the use of high-resolution, time-of-flight mass spectrometers (Drewnick *et al.*, 2005). However, a rapid development in ionisation and analyser techniques will maintain this type of online aerosol mass spectrometry as an active field of analytical chemistry in the coming years.

Using a similar set-up for the introduction of particles into the vacuum, the particles can also be collected on impactor plates before they are thermally desorbed and ionised. The

volatilisation is then done discontinuously after a certain collection time either by heating the collector (Tobias and Ziemann, 1999; Tobias *et al.*, 2000) or by the use of infrared lasers followed by soft (Vacuum Ultraviolet) VUV-ionisation (Oktem *et al.*, 2004). Also, atmospheric pressure chemical ionisation (APCI) has been applied for the analysis of aerosol particles using a modified APCI-source for LC/MS. Since APCI is a very soft ionisation technique, it can provide valuable information about individual molecular compounds. Using an ion trap mass spectrometer, pseudo-molecular ions can be characterised by their MSn spectra. It is a quantitative method that has been used for the characterisation of SOA components in chamber studies (Kuckelmann *et al.*, 2000).

Physical characterisation of SOA

Condensation nuclei counter

Condensation nucleus counters (CNCs) measure the total aerosol number concentration larger than some minimum detectable size. CNCs are often used as detectors with other instruments such as electrical mobility classifiers. Particles are grown by condensation in CNCs until they are sufficiently large to be detected optically. CNCs can detect individual particles as small as 3 nm, so they provide an extraordinarily sensitive means for detecting small amounts of material. A variety of substances have been used as the condensing vapor, but water and n-butyl alcohol are currently used most often. Because the supersaturation of the condensing vapor is very high, the response of CNCs is typically insensitive to the composition of the measured particles (McMurry, 2000).

Optical particle counters

Single-particle optical counters (OPCs) measure the amount of light scattered by individual particles as they traverse a tightly focused beam of light. A fraction of the scattered light is collected and directed to a photodetector. The particle size is determined from the magnitude of the voltage pulse in the photodetector by using a calibration curve typically obtained from measurements using spherical particles of known size and composition. Pulse height and area are commonly used measures of pulse magnitude. Size distributions are obtained by measuring the distribution of pulse magnitudes obtained from a representative population of particles. OPCs tend to heat aerosols leading to a decrease in size and an increase in refractive index for hygroscopic atmospheric particles. These perturbations make it difficult to accurately measure atmospheric aerosol size distributions with OPCs (McMurry, 2000).

Electrical mobility analyzers

Electrical mobility analyzers classify particles according to the electrical mobility. Most common is the so-called DMPS, which includes a differential mobility analyzer (DMA) and a particle detector. These systems can measure size distributions in the range of 3 to 500 nm diameter. The aerosol is exposed to a bipolar charger in the DMA, where it achieves a charge equilibrium. Particles in a narrow mobility range determined by the classifying voltage and flow rates are separated from the main flow and transported to the detector. A complete size distribution is obtained by carrying out measurements at a number of classifying voltages. (McMurry, 2000). The primary limitation of DMPS systems at the small particle limit is detecting very low concentrations of very small particles. Although CNCs can measure very low concentrations, their lower detection limit is 3 nm.

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ANNEX 2: MEMBERS OF THE ECA *"Urban Air, Indoor Environment & Human Exposure"* STEERING COMMITTEE

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Abstract:

This report summarises the state of the art concerning ozone-initiated chemistry and its impact on indoor air quality and human health and recommends prioritised research goals for the future. The focus is on terpenes (e.g., limonene, α-pinene) for reasons of high chemical reactivity and abundance.

Conclusions

❍   The use of some consumer products can result in abundant indoor concentrations of terpenes.
❍   The chemistry of indoor air is dominated by ozone reactions with terpenes, reactions that can produce highly reactive intermediates (e.g., radicals), secondary ozonides, hydroperoxides, carbonyl compounds and also fine particles in the sub-micron range. An important product of such reactions is the OH radical, which can proceed to initiate further oxidation processes. Indeed, many of the reaction rates indoors have been predicted to be of a similar order of magnitude to outdoors and sometimes even larger.
❍   There is neither, adequate knowledge of exposure patterns of ozone-terpene reaction products, nordose/response relationships. There are toxicologically relevant compounds formed in ozone terpene reactions that are not identified. These compounds (e.g. radicals, aldehydes, acids) are potentially responsible for observed health effects (e.g., sensory irritation, lung injuries, etc).

Recommendations

1.   Concerning our knowledge of ozone-terpene related indoor air chemistry there are still significant gaps. In addition, many of the issues are exceedingly complex, both chemically and physically. It is increasingly recognised that secondary products are the cause of the ill-health effects observed indoors, however, the actual culprits have yet to be fully identified. Furthermore, model predictions of OH and NO3 radical concentrations indoors have yet to be verified through experimental observation. Ideally, many of these gaps in our knowledge could be addressed by organising indoor air 'field campaigns' similar to those commonly performed outdoors. One would envisage that indoor measurements could be made simultaneously of the concentrations of radicals, ozone, NOX, VOCs (particularly the reactive compounds such as the terpenes), HONO, aldehydes including HCHO, as well as aerosol size, number and composition, photolysis rates, temperature and humidity etc., in order to validate models and to identify compounds that may be deleterious to health.
2.   Considering the long-term and integrated impact of material/product oxidation on exposure of indoor air, it is prudent to develop methodologies for emission testing of construction materials and consumer products (in particular spray products) under oxidative and realistic conditions for future standardization.
3.   The ozone and formaldehyde concentrations should be measured in micro-environments suspected to have strong sources of terpenes due to product usage or personal activities.
4.   Analytical methods to measure potentially toxicologically relevant compounds indoors e.g. radicals should be further developed for practical use.
5.   New metrics/proxies that are health relevant should be identified and developed, both with regard to acute/semi-acute effects and longer-term effects.
6.   Risk characterization of the mixed terpene-ozone system calls for more toxicological knowledge:

     ❍   Acute and longer-term exposure effects to eyes and upper and lower airways.
     ❍   Evaluation and assessment of selected consumer products, in particular spray products in the presence of ozone, through the use of bioassays and full scale human exposure studies under realistic conditions.

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