

## WORKING GROUP 2

**What can the indoor and outdoor  
air chemistry communities learn  
from each other?**

## **Final Report**

**COST Action 17136 Indoor Air Pollution Network**

## The network

**INDAIRPOLLNET** (INDoor AIR POLLution NETwork) is a network of experts on indoor air, working together to solve issues related to indoor air quality and planning an optimal way of studying indoor air pollution and its effects on health of the occupants. The overarching aim of this network is to define a blueprint for the optimal indoor air chemical characterisation campaign, which is relevant for the buildings we use and for the way that we use them.

**This is the final report** of INDAIRPOLLNET COST Action 17136 Working Group 2, based on review of recent literature about outdoor measurement and modelling results. The aim of this work was to gather the existing information and expertise in outdoor air studies to be used in the development of planning indoor air campaigns.

## Authors

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**Suggested citation:** INDAIRPOLLNET (2020) *Final Report of INDAIRPOLLNET Working Group 2: What can the indoor and outdoor air chemistry communities learn from each other? Deliverables of COST Action 17136 Indoor Air Pollution Network INDAIRPOLLNET.*

This report is based upon work from COST Action INDAIRPOLLNET, supported by COST (European Cooperation in Science and Technology).

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# Final report of INDAIRPOLLNET Working Group 2

## Introduction

Outdoor air pollution research is relatively more advanced than indoor air research, with measurements made over a longer period of time and better established and validated models. Aerosol process models, such as kinetic models, thermodynamic models, and SOA partitioning models developed by the outdoor community may be useful and even directly applicable to indoor research. There are many parallels between indoor and outdoor chemistry and an important part of this Action will be to use existing expertise from outdoor air chemistry for use indoors where relevant. Further, indoor air research (e.g. O<sub>3</sub>-terpene reaction chemistry, aerosol formation, deposition onto surfaces) that could benefit outdoor air chemistry understanding will be identified. This WG will facilitate community building between the indoor and outdoor air chemistry experts.

## Key objectives

**To use existing outdoor air quality expertise and develop it for use indoors.**

In order to achieve this objective, the following tasks will be carried out through reviews of existing studies, with the results presented at the second workshop in month 12:

1. A review of outdoor measurement and modelling results to date to understand:
  - a. What have been the key challenges for outdoor air chemistry field campaigns? This will include challenges with the chemistry, the instrumentation and models, as well as climatic variation (e.g. temperature, humidity).
  - b. How have these been overcome?
  - c. What is the best way to understand the sources, transformations and sinks of air pollutants and how can this knowledge be applied to mitigation?
2. Identification of relevant areas of indoor research for outdoor community

In order to achieve this objective, the subtasks described below were carried out through reviews of existing literature and current projects.

## Approach

WG2 is aimed at providing the information from outdoor air chemistry studies that could be found relevant and useful for the indoor air chemistry community. The outdoor air pollution and chemistry measurements and models have been made for a considerably longer period of time, before the importance of the air chemistry has been recognized to be valid also for the indoor environments. The work within WG2 was not performed as a comprehensive review of the existing literature, but it was organized rather to provide information and input to other WGs, mainly WG3 “What to measure” and WG4 “How to measure”. We did not focus on measurements or modelling of actual species and their concentrations, but we preferred to identify the areas and processes, based on our own knowledge of and experience in atmospheric chemistry in general, that could be useful for the indoor community.

The task of this Working Group was divided into the following subtasks:

1. Outdoor field campaigns
2. Outdoor models
3. Simulation chamber studies
4. Linkage between WG1 and WG2

Each subtask had a subtask leader and subtask co-leader, following the general management structure of the tasks/WGs. The members of the network who expressed their interest to work within the WG2 subtasks were then requested to help with detailed reading and summarizing the findings of the selected articles or models.

The initial purpose was to review recent literature using Web-of-Science or other platforms and to focus on peer-reviewed articles, mainly review articles published during the past 10 years (2009 – 2018), following the procedure for WG1, for consistency. However, the enormous amount of literature and the scope of WG2 prevented us from an exhaustive literature review within each subtask. The subtask leaders had the freedom to define the search procedures, search terms or other ways to select relevant literature or other information to proceed with their subtasks. Details about the literature search strategy and selection procedures are provided in this report, in the specific chapter for each subtask, in the “Introduction to the subtask” section.

## Output

The following deliverables have been produced by WG2:

- A (this) report including lists of top research areas and questions, suggestions and recommendations from each subtask that the outdoor community can provide the indoor community to focus on in future work;
- Excel files, when relevant (subtasks *Outdoor models* and *Simulation chamber studies*), listing the important chemical species, compounds, and parameters or processes to be measured or studied in WG3 “What to measure”, and the methodologies and suitable instrumentation as an input to WG4 “How to measure”.

## Deliverables

### D4: Recommendations for WGs3-4 based on outdoor research

The recommendations for the WGs 3 and 4 are based on the reviews made within subtasks 1. *Outdoor field campaigns*, and 3. *Simulation chamber studies*, as these two subtasks are focused on “measurements”.

#### Outdoor field campaigns

The outdoor studies suggest and can provide advice and guidance on issues such as characterization and categorization of the organic substances in indoor environments according to their **volatility**. It encourages considerations of phase transition indoors alongside and in competition with chemical reactions in either the vapour or condensed phases. It also provides a complement to traditional classifications according to primary or secondary origin or the distinction between gaseous and particulate indoor air pollutants.

The fate of indoor air pollutants may be controlled by their oxidation. The distribution of the main atmospheric oxidants hydroxyl radical (OH), ozone (O<sub>3</sub>), nitrate radical (NO<sub>3</sub>), and chlorine atom (Cl) differs indoors compared to ambient outdoor conditions due to different access to sunlight and precursors. The outdoor measurements will provide expertise for direct time-resolved measurements of the concentrations of the **oxidants and their precursors** indoors. The measurements will indicate the relative importance of these oxidants in indoor environments and could help to validate the indoor models.

The novel mixtures of indoor oxidants, in comparison to outdoors, will benefit from studies on measured and modelled **oxidant reactivity** (overall loss rate), mainly of OH radicals. There is often a discrepancy between directly measured reactivity of an oxidant and that of identified and measured VOC towards the same oxidant. The missing reactivity, i.e., the ratio between measured reactivity and that calculated from the sum of products of measured chemical concentrations and their reaction rates will give guidance to identify missed/unknown indoor air pollutants. In this regard, published work from both outdoor measurements and simulation chamber studies are directly usable for such work in indoor environments.

Given the abundance of substances of anthropogenic (mainly BTEX) and biogenic (mainly terpenes) origin in indoor air, it can be suggested to investigate formation and concentrations of **highly oxygenated organic molecules (HOM)**. The HOM-compounds are formed by both OH- and O<sub>3</sub>-initiated auto-oxidation reactions, and products can shift the partition between the gaseous and particulate pollutants in the indoor air. There are relevant publications for guidance and expertise both on the outdoor field campaigns and the simulation chamber studies.

Understanding the **atmospheric complexity and its simplification, reduction and interpretation**, in terms of chemical composition, microphysics, particles size-distribution, and biology, is a true challenge for both the outdoor and indoor air research communities. Profiling this atmospheric complexity, while avoiding redundancy of information, requires matching the level of knowledge of the atmospheric constituents to the problem being addressed. This goal has now become feasible by the **development and implementation of powerful measurement analytical techniques** (namely, on-line and field-deployable instruments). These sophisticated technologies are big data drivers that require **sophisticated statistical approaches for mining and simplifying the atmospheric compositional information** from large-scale datasets. Combinations of novel measurement technologies with emerging data visualization strategies that seek to **make highly dimensional datasets both accessible and comprehensible**, can be applied to understand the relative contributions of sources of chemical components, biological materials and size-resolved particulate matter in indoor air.

### Outdoor models

The development and implementation of modelling activities to understand and predict indoor air quality for regulatory purposes is of utmost importance for the indoor air pollution community (including modelers, researchers, health and environmental experts, and legislative experts). **Create initiatives similar to HARMO and FAIRMODE**, which are well established tools used to support the implementation of outdoor air quality policies relevant for the local and regional European scale, **should be pursued by the indoor air community**.

The outdoor environment is also an important factor that cannot be neglected for indoor air quality studies. Indoor/outdoor air pollution studies has many challenges, but it is also an opportunity to **create links between the indoor and outdoor air pollution modelling communities**, by organizing common workshops, implementation of working groups, and research networks. For example, representative(s) of outdoor air models communities could be invited to future INDAIRPOLLNET meetings. These initiatives and the wealth of knowledge accumulated by the outdoor air modelers could help to shed light on specific indoor-relevant questions, namely: (1) **better refinement of the indoor-outdoor (I/O) ratio variability**, which is prone to many influential factors (e.g., outdoor weather and pollutant concentrations, climate change, indoor ventilation and infiltration rates, source strength, and human activities); (2) **better assessment/identification of indoor sources**; and (3) **estimation of a true individual (personal) pollutant exposure level**, focusing on a better discrimination between indoor and outdoor air pollutant exposure. Furthermore, improvement of outdoor exposure models, by including indoor factors (e.g., indoor air pollutant levels and sources), should also be pursued if those models are to be used to establish a comprehensive understanding and attribution of exposure levels to individuals spending time in those indoor environments.

## Simulation chambers

Although there is a large amount of data on the kinetics and mechanisms of the atmospheric reactions of the organic compounds, reaction rate coefficients and degradation schemes for novel or not yet considered compounds are still missing. The comprehensive assessment of **atmospheric transformation** of chemical substances can be with advantage performed in large simulation chambers for studying atmospheric processes using the devices, the associated instrumentation, and expertise of the chamber community. The data will then serve as inputs for and help to refine models.

The air pollution and chemistry in indoor environments are often treated compound by compound individually or as a complex mixture of compounds, originating from diverse emission sources. The simulation chambers have the ability to study **separate processes or sources** of indoor pollutants and also to expose the pollutants to various succeeding processing steps, such as aging by atmospheric oxidants. The chamber will enable the study of simulated processes such as cooking, cleaning, wood burning, human presence, furnishing and clothing - both primary emissions and their chemical transformation – to understand their role and partial contributions in realistic indoor environments.

The instrumentation from the outdoor measurement campaigns and the simulation chamber studies has been, by now, already successfully used in several indoor related campaigns and measurements. It mainly applies to advanced instrumentation for fast on-line measurements of organic substances by chemical ionization mass spectrometry, often with high mass resolution and various ionization processes suitable for various (groups) of compounds. In addition to standard instruments for measurement of regulated substances (ozone, NO<sub>x</sub>), there is a wide variety of particle instrumentation for both the mass and number concentrations, size distributions, and chemical composition. Another class of instruments are devices for direct measurements of concentration of the atmospheric radicals, peroxy radicals and their precursors. Mainly the WG4 “How to measure” working group, will benefit from the expertise of the simulation chamber community for **calibration and intercalibration of instruments**. Chamber campaigns for **intercomparison of instruments** for various species can provide guidance for the selection of instrumentation during indoor campaigns. The literature review on the *Outdoor field campaigns* and the *Simulation chamber studies* provides additional guidance on the selection of the best, most suitable techniques, instrumentation, and the operational expertise for the particular design of an indoor measurement campaign.

## D5: Summary of indoor air chemistry research for outdoor air chemistry community

While the field of indoor air chemistry is at an earlier stage of development than its outdoor counterpart, three research directions investigated indoors were identified as of interest for outdoor scientists, including **gas-surface processes**, **biological processes**, and the **characterization of indoor emissions**.

The indoor community has produced a significant body of literature on gas-surface interactions since surfaces, which are found everywhere in buildings, have an important impact on the loading of pollutants indoors. These surfaces acts as sources and sinks of trace gases and aerosols and are an important media for the conversion of inorganic species such as NO<sub>2</sub> (into HONO) and N<sub>2</sub>O<sub>5</sub> (into ClNO<sub>2</sub>). This knowledge could be of interest to help assess **the impact of outdoor urban surfaces** on atmospheric composition. Similarly, biological processes occurring on surfaces can impact the chemical composition of the air surrounding these surfaces. The knowledge developed by the indoor community in this field has the potential to help in the **characterization of biological aerosols in the outdoor atmosphere**. Finally, budgets of emissions from building materials, occupants and various activities performed indoors are of interest for the outdoor community to assess the **contribution of indoor emissions to the outdoor VOC budget**.

# 1. Outdoor field campaigns

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## Introduction to the subtask

The subtask relating to “Outdoor atmospheric chemistry studies” aims to identify the information forthcoming from ambient outdoor studies relevant to processes that require attention in the indoor environment. There have been countless observation campaigns in the ambient atmosphere and this subtask necessarily aims to extract examples from each of the key areas of high current scientific interest and relevance rather than being an exhaustive review.

To this end, we have identified 4 major areas of relevance to indoor air chemistry from which we have distilled the key findings from recent field studies, with particular emphasis on the novelty of the findings. Studies of ambient atmospheric processes are conducted in intensive campaign-mode observations and also through long-term monitoring programs using ground-based, airborne or shipborne platforms. We have selected studies according to the advantages of the observational mode and platform but considering satellite observations to be of limited relevance and out-of-scope.

## Brief summary of the state-of-the-art

The vast area of outdoor field campaign covers to a large extent measurements of different pollutants and monitoring of regulated substances. For the scope of the objective we have selected four areas of outdoor field campaigns with a focus on atmospheric chemistry, which we judged to be relevant for the chemistry in indoor environments.

The outdoor community has experience, competence and instrumentation for determination of *volatility* of the ambient organic compounds. The volatility of both primary organic aerosol (POA) and secondary organic aerosol (SOA) may vary with specific indoor conditions. The magnitude and ratios of POA and SOA will be an important characteristic of the indoor environment. The knowledge can be transferred to the indoor community and enable a new classification of indoor air pollutants instead of the classical approach with primary and secondary or gaseous and particulate indoor air pollutants.

Recent studies provide increasing understanding of the concentrations and role of *atmospheric oxidants and their precursors* in ambient air. Agreement between the observed and modelled concentrations of OH, HO<sub>2</sub> and total RO<sub>2</sub> have been found to be highly dependent on NO<sub>x</sub> concentrations in the rich VOC mixtures of particularly urban atmospheres. There is a lack of understanding of the chemistry of more complex and/or functionalised RO<sub>2</sub> to explain the chemistry and reactivity of these RO<sub>2</sub> towards NO<sub>x</sub>.

The outdoor studies found that the nitrous acid (HONO) may be a dominant source of OH radicals in very polluted urban atmospheres. There is similarity with the indoor environments where other sources of OH radical than direct photolytical production is to be considered.

Nitrate radical (NO<sub>3</sub>) may be the dominant oxidant for certain VOC and responsible for production and cycling of OH, HO<sub>2</sub> and RO<sub>2</sub> radicals. As indoor environments most likely resemble night-time ambient conditions owing to substantial reduction of light to trigger photolytical processes, NO<sub>3</sub>-initiated chemistry may be important indoors. Methods for direct concentration measurements of NO<sub>3</sub> are reported.

Unconventional oxidants like BrO and IO, important for regulating ozone budget in some atmospheres, have been judged as not of interest for indoor environments. On the other hand, precursors of chlorine atoms such as nitryl chloride (ClNO<sub>2</sub>) may be of importance for indoors owing to the prevalence of chlorine containing cleaning products and ClNO<sub>2</sub> prevalence in outdoor air. Criegee radicals, given their estimated ambient concentrations similar to that of OH radicals, may make a significant contribution to the outdoor air oxidising capacity and may be of interest indoors.

Oxidant (mainly OH) reactivities and *oxidant lifetimes* is another major research theme in the outdoor studies. Agreement between measured and calculated reactivity and comparison of individually detected OH sinks with the measured OH reactivity often reveals a significant missing reactivity, ranging from 20% to over 80% in some environments. Methods for measurements of the oxidant reactivity and lifetime have been developed and deployed for OH and NO<sub>3</sub> radicals and ozone but are yet to be developed for Cl.

Recently discovered *highly oxygenated organic molecules* (HOM) represent a new mechanistic pathway to atmospheric oxidation of VOC and a source of SOA precursors. HOM observations are reported from ozonolysis of monoterpenes and aromatic compounds using advanced mass spectrometry-based approaches. HOM species have been detected in both vapour and particle phases, the latter using the filter inlet for gases and aerosols (FIGAERO). The contribution of HOM to new-particle formation and the associated RO<sub>2</sub> chemistry will be of interest to the indoor community.

*Compositional complexity* in terms of the chemistry, microphysics and biology of the atmosphere is increasingly evident as powerful new measurement techniques emerge and are deployed. Sophisticated statistical analytical approaches including a wide array of new machine learning techniques are as relevant to interpreting indoor air composition as they are to outdoor air. Combinations of novel measurement technologies and advanced analytical techniques can be applied to understand the relative contributions of sources of chemical components, biological materials and size-resolved particulate matter.

## Summary of selected studies

This report is concerned with areas of relevance to atmospheric chemistry and not atmospheric composition, per se. Whilst recognising their importance to the chemistry, this largely renders primary pollutant emissions out-of-scope. Here, we are more concerned with what outdoor studies can reveal about the processes and products of relevance to indoor air chemistry, with particular emphasis on current and emerging areas of significant interest. In total, 94 articles were reviewed and summarised in this report.

### 1) Volatility of ambient organic material

One area of direct relevance to indoor air chemistry that has received considerable recent attention is the prevalence in the ambient atmosphere of organic compounds of widely varying volatility and their characterisation and categorisation. This straddles the conventional classification by primary and secondary origin and in large part, the distinction between gaseous and particulate components. Moreover, it encourages consideration of phase transition alongside (and in competition with) chemical reaction in either the vapour or condensed phases (in particles or on surfaces). A practical example of the requirement for such a consideration of direct relevance to indoor air chemistry is the volatility of organic emissions from woodburning. Whilst much of the material will be sufficiently volatile to not be sampled as particulate matter (PM) at the temperature of the flue (and under standard test conditions), at ambient temperatures, much of this material would be condensed if undiluted. However, on dilution, the material in the exhaust can remain in the vapour phase and hence be available to participate in gaseous atmospheric oxidation and subsequent secondary organic aerosol (SOA) formation. There has been similar substantial interest in the volatility of emissions from diesel and petrol vehicles and a number of chamber and laboratory studies on each which can be used to inform the ambient studies.

Goldstein and Galbally (2007) stated that “...we guess that  $10^4$ – $10^5$  different atmospheric organic species have been measured. That may be only a small fraction of the number actually present”. This includes those present in the vapour and particulate phases or both. Kim et al. (2001), Eatough et al. (2003) and Subramian (2004) all highlighted substantial difficulties associated with traditional approaches to measure PM related to the volatility of both the inorganic and organic fraction using a variety of offline sampling techniques, with both positive and negative artefacts. Grieshop et al (2009) recommended the use of isothermal dilution and thermodenuder measurements to constrain the estimation of volatility of organic components. Huffman et al. (2009) and Cappa and Jimenez (2010) reported the use of online instrumentation sampled after a thermodenuder for the measurement of chemically-resolved volatility of aerosol components in the ambient atmosphere in Riverside and during the MILAGRO experiment in Mexico City. The latter study concluded that from 50–80% of the organic aerosol (OA) is involatile and will not evaporate under any atmospheric conditions and that the amount of semi-volatile organic vapours in equilibrium with the OA could range from ~20% to 400% of the OA mass, depending on the enthalpy of vapourisation assumptions employed. Lee et al. (2010) retrieved volatility distributions from similar measurements in Finokalia, Crete in the FAME-2008 experiment, concluding that the ambient OA is approximately 2 or more orders of magnitude less volatile than fresh laboratory-generated monoterpene SOA. Louvaris (2016) and Louvaris et al. (2017) reported measurements of the volatility of OA using a similar technique in 2016 measurements in Finokalia, FAME-16, and Athens during winter 2013. The Athens measurements showed 4 discrete OA factors all with components ranging in volatility by 5 orders of magnitude, from semi-volatile to extremely low volatility. The FAME-16 measurements found that each of two discrete OA factors exhibited a similarly wide range of volatility. Paciga et al. (2016) reported comparable measurements made in Paris during the MEGAPOLI summer 2009 and winter 2009/2010 measurement campaigns and presented a seasonal contrast of the volatility of the contributory factors, with the lowest volatility oxygenated OA components more abundant during summer. Xu et al. (2019) reported volatility measurements using a similar approach from Beijing in summer 2017 and 2018. Thermogram behaviour was similar to those in previous studies, with an additional abundance of low volatility organic nitrates. SVOC comprised around 63% of the OA (between 60 and 70% for each of the OA factors) and was more volatile in general than in Western Europe and the US. Ma et al. (2016) describe the volatility of Pittsburgh aerosol during summer and winter with an alternative approach, using the organic carbon (OC) measured during different temperature fractions of OC/EC analysis of single bare quartz filter samples, presenting both measured and predicted amounts in each phase in each volatility fraction.

Thermal Desorption Aerosol Gas Chromatography System (TAG) first described in Williams et al. (2006) has been modified to enable rapid direct measurement of SVOC (Zhao et al., 2013a), using online derivatization and a dual cell configuration as described in Isaacman et al. (2014). Field deployment has demonstrated its ability to measure and quantify components in both phases, hence yielding for example, ambient gas-aerosol partitioning of tracers for biogenic volatile organic compounds (BVOC) oxidation (Isaacman-VanWertz et al., 2016). This approach is able to provide data to challenge a range of partitioning predictive approaches and populate descriptive volatility frameworks such as the VBS. Other recently developed online techniques, such as the Filter Inlet for Gases and Aerosols (FIGAERO; Lopez-Hilfiker et al., 2014) coupled to Chemical Ionisation Mass Spectrometry (CIMS) and “Chemical Analysis of Aerosol Online” (CHARON; Eichler et al., 2015) inlet coupled to Proton Transfer Reaction Mass Spectrometry (PTRMS) have similarly been deployed in ground (e.g. Müller et al., 2017; Riva et al., 2019) and airborne (Piel et al., 2019) platforms to explore the influences on component partitioning in ambient PM. Recent development (Martinez et al., 2016) and deployment of the volatility and polarity separator (VAPS) promises to further extend the capabilities to directly measure the properties of atmospheric components.

## **2) Oxidants and their precursors** (daytime and night-time; OH, NO<sub>3</sub>, O<sub>3</sub>, Cl and other halogens and Criegee)

Notwithstanding the deposition to surfaces and ventilation and exchange with outside air, the fate of indoor pollutants will largely be controlled by their oxidation. It is unclear whether outdoor oxidants will play comparable roles indoors, owing to the prevailing conditions (chemical environment, sources and precursors

etc.). Daytime outdoor oxidation is almost invariably controlled by the hydroxyl radical (OH) and ozone (O<sub>3</sub>) while night-time by the nitrate radical (NO<sub>3</sub>) and O<sub>3</sub>.

There has been increasing understanding of the cycling of OH radicals, and the tightly coupled hydroperoxy (HO<sub>2</sub>) and organic peroxy (RO<sub>2</sub>) radicals, following the commencement of direct OH measurements by LIF and CIMS, nearly three decades ago. The review of [Stone et al. \(2012\)](#) summarises measurement-model comparisons for a range of different environments sampled from the ground and aircraft, including the marine boundary layer, continental low-NO<sub>x</sub> regions influenced by biogenic emissions, the polluted urban boundary layer and polar regions. Agreement between OH, HO<sub>2</sub> and total RO<sub>2</sub> concentration measurements with box model predictions using a variety of mechanisms is found to be highly NO<sub>x</sub> dependent. For OH, agreement is best at intermediate NO<sub>x</sub> (on the order of several ppb), with agreement worsening at low and very high NO<sub>x</sub>. In central Beijing winter, NO<sub>x</sub> is extremely high, extending disagreement beyond that in other mega-cities (e.g. London; [Whalley et al., 2018](#); Los Angeles; [Griffith et al., 2016](#)). In summer by contrast, very low NO in the afternoons in Beijing, and very high isoprene (up to 8 ppb) are experienced. HO<sub>2</sub>, and especially RO<sub>2</sub>, are consistently underpredicted by models at very high NO. This has important implications for P(O<sub>3</sub>) and AQ, with significant under-prediction of instantaneous O<sub>3</sub> production, worsening with increasing NO. The origin of the model deficiencies seems to reflect a lack of understanding of the chemistry of more complex RO<sub>2</sub>, prevalent owing to the rich mix of VOCs. At very low NO<sub>x</sub>, autooxidation probably controls the fate of RO<sub>2</sub> (see section 4) which is not captured well in models. The situation is similar in rainforests: at high NO<sub>x</sub>, more complex functionalised RO<sub>2</sub> may not react with NO as might be expected (models assume they behave like simple RO<sub>2</sub>) and a key question arises concerning the persistence of RO<sub>2</sub> at high NO<sub>x</sub>.

More recent outdoor field campaigns have placed considerable emphasis on urban environments, in particular in China. Pearl River Delta and Beijing measurements in 2006 ([Lu et al., 2012; 2013](#)) indicated a strong missing source of OH. A review of radical measurements in China is provided by [Lu et al. \(2018\)](#). More recent measurements in Beijing and the N. China Plain (e.g. [Tan et al., 2017; 2018](#), [Shi et al., 2019](#)) have indicated that nitrous acid (HONO) is the dominant source of OH (and new radicals in general) in all these environments, especially in winter, leading to exceptionally high observed OH, with in-haze concentrations in winter as high as those out of haze. Difficulties in constraining HONO will lead to difficulty in predicting the radical budget. Here there is strong similarity to the indoor environment, where an abundance of surfaces and sufficient light in the HONO absorption region lead to its dominance as an OH source ([Gómez Alvarez et al., 2013](#)).

Insufficient UV flux indoors will limit primary OH production from O(<sup>1</sup>D) photolysis of O<sub>3</sub>. Potential sources of the discrepancies in radical levels predicted by models and measured are discussed in [Dusanter et al. \(2017\)](#). [Wofsy et al. \(2018\)](#) and [Wolfe et al. \(2019a;b\)](#) describe global coverage of OH and k(OH) from the DC8 ATom mission in the remote troposphere under clean conditions using HCHO to infer OH levels. It is found that the level of understanding of deposition rates of some species (e.g., gas-phase HCHO) to the ocean is the limiting factor for modelling, again illustrating the need to describe surface interactions well to constrain radical chemistry.

Night-time oxidation is frequently dominated by the nitrate radical (NO<sub>3</sub>), which is produced by the reaction of NO<sub>2</sub> and O<sub>3</sub> and rapidly establishes equilibrium with dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>). Night-time NO<sub>3</sub> reaction can be important and even dominate the fate of VOC and organic sulphur species. Oxidation by NO<sub>3</sub>, along with ozonolysis of alkenes, is responsible for the nighttime production and cycling of OH, HO<sub>2</sub> and RO<sub>2</sub> radicals. NO<sub>3</sub> reaction with biogenic hydrocarbons can lead to production of organic nitrates and secondary organic aerosol (SOA). A review of three decades of field, laboratory and modelling of night-time radical chemistry is provided by [Brown and Stutz \(2012\)](#). There has been substantial focus on airborne measurements of night-time chemistry investigating both the contribution to radical chemistry and the oxidant budget ([Brown et al., 2004; 2006; 2007; 2011; Stone et al., 2014](#)) and to aerosol composition and heterogeneous chemistry ([Osthoff et al, 2008; Brown et al., 2009; Morgan et al., 2015](#)). The importance of

night-time chemistry via  $\text{N}_2\text{O}_5$  uptake and night-time aerosol nitrate to substantial heterogeneous formation of  $\text{ClNO}_2$  in Beijing was reported in [Zhou et al. \(2018\)](#), with unpublished data showing that  $\text{NO}_3$  is seen in the daytime (Bin Ouyang; pers. comm). [Zimmerman et al. \(2013\)](#) investigated the reaction of  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$  and  $\text{NO}_2$  with ambient Los Angeles particulate samples, reporting the formation of nitro-PAH products. Such nitro- and oxygenated PAHs have been observed in urban and suburban atmosphere (e.g. [Ringuet et al., 2012](#)). Heterogeneous oxidation mechanisms for PAH are discussed in the review of [Keyte et al. \(2013\)](#). Similar processes could have implications for indoor air chemistry. Recently, a method for direct measurement of  $\text{NO}_3$  reactivity and lifetime has been developed ([Liebmann et al., 2017](#)) and deployed ([Liebmann et al., 2018a;b](#)).

Similarly, an  $\text{O}_3$  reactivity direct measurement technique was reported by [Sommariva et al \(2019\)](#). Additionally, a direct method for  $\text{O}_3$  production rate measurement has been described by [Cazorla et al. \(2012\)](#), reporting measurements in Houston between 15 and 100 ppbv/hr, and by [Sklaveniti et al. \(2018\)](#), during field deployment in Indiana, measuring rates between 6 and 20 ppbv/hr.  $\text{O}_3$  concentrations are routinely measured using established techniques (most usually UV absorption) and there is little novelty in their measurement, *per se*.

In addition to the more established daytime and night-time oxidants, there has been interest in the contributions from more unconventional species to the outdoor oxidising capacity. Halogen cycling has received particular focus and the roles of BrO and IO found to be important in regulating  $\text{O}_3$  in some environments, but are unlikely to be of interest in the indoor environment. Chlorine atoms are highly reactive species that have been postulated to play a role under tropospheric conditions, most recently via their photolytic release from nitryl chloride ( $\text{ClNO}_2$ ).  $\text{ClNO}_2$  sources are unclear; it is known to be released through the uptake of  $\text{N}_2\text{O}_5$  on aqueous chloride-containing particles and some studies have shown that  $\text{N}_2\text{O}_5$  uptake on marine aerosol is a dominant source ([Sommariva et al., 2018](#)). However, the origins of the elevated concentrations observed in Los Angeles ([Riedel et al., 2012](#)), London ([Bannan et al., 2015](#)), Hong Kong ([Brown et al., 2016](#); [Wang et al., 2016](#)) and elsewhere are unclear. In the CalNex study of [Riedel et al. \(2012\)](#),  $\text{ClNO}_2$  and  $\text{Cl}_2$  ranged from detection limits at midday to campaign maximum values at night reaching 2100 and 200 pptv, respectively. The maxima were observed in the Los Angeles urban plume and it is estimated that up to a few ppb per day ozone could be generated via  $\text{RO}_2$  from Cl atoms. Similarly,  $\text{ClNO}_2/\text{N}_2\text{O}_5$ -laden air measured by [Wang et al. \(2016\)](#) originated from transport of urban/industrial pollution, with the highest concentrations in extensively processed air containing non-oceanic chloride. [Bannan et al. \(2015\)](#) found that Cl atoms from  $\text{ClNO}_2$  in the early morning were the dominant oxidant for alkanes and, over the entire day, contributed 15%, 3%, and 26% toward the oxidation of alkanes, alkenes, and alkynes, respectively. Additional data on  $\text{ClNO}_2$  have been observed by CIMS in the coastal UK ([Bannan et al., 2017](#)), and emitted from landfill ([Bannan et al., 2019](#)), and are indicative of as yet unresolved heterogeneous processes, either on aerosol particles or other available surfaces ([Simpson et al., 2015](#)). Chlorine chemistry may be of significant interest to indoor air chemistry studies, owing to the prevalence of chlorine containing cleaning products and abundance of surfaces for heterogeneous processes.

Finally, there has been considerable recent interest in Criegee radicals following their relatively recent isolation and identification. Their kinetics are now much better resolved ([Osborn and Taatjes, 2015](#)) and consequently their role in  $\text{SO}_2$  oxidation is likely less important than previously thought. However, their abundance in the atmosphere is unknown. If suggested estimates of  $1 \times 10^4 \text{ cm}^{-3}$  to  $1 \times 10^5 \text{ cm}^{-3}$  are correct, they may make a significant contribution to the outdoor oxidising capacity and may be of interest for indoor air chemistry studies.

### 3) Pollutant reactivity and oxidant lifetimes

Early studies to report the discrepancy between directly observed reactivity of oxidant reaction partners (the inverse of observed oxidant lifetime) and that of the measured and identified VOC were those of [Kovacs et al. \(2003\)](#) in an urban environment and [DiCarlo et al. \(2004\)](#) in a biogenically-dominated environment. [Kovacs](#)

et al. (2003) reported that the measured OH reactivity was 1.4 times larger than that calculated from the sum of the products of measured chemical concentrations and their reaction rates, attributing the discrepancy to unmeasured short-lived highly reactive volatile organic compounds (VOC). In the Program for Research on Oxidants: Photochemistry, Emissions and Transport (PROPHET 2000) in a north Michigan Forest, DiCarlo et al. (2004) found that the missing OH reactivity increased with temperature, as did emission rates for terpenes and other biogenic volatile organic compounds (BVOC). Methods for both direct (e.g. Laser Induced Fluorescence; LIF and Laser Photolysis-LIF; LP-LIF and Chemical Ionisation Mass Spectrometry; CIMS) and indirect (e.g. Comparative Reactivity Method; CRM) measurement of reactivity have been deployed in the past two decades. Yang et al. (2016) provided a review of these and subsequent studies, summarising the status of understanding of OH reactivity and concluding that “comparison with individually detected OH sinks often reveals a significant missing reactivity, ranging from 20% to over 80% in some environments”. Average measured urban OH reactivity ranges from less than  $10 \text{ s}^{-1}$  to over  $40 \text{ s}^{-1}$ , with excursions as high as  $120 \text{ s}^{-1}$ . In forest environments, this ranged from  $1 \text{ s}^{-1}$  to greater than  $70 \text{ s}^{-1}$  with strong diurnal and seasonal variations. Altitude variation in OH reactivity has been investigated from airborne platforms. During INTEX-B on the NASA DC-8 in the clean Pacific, more polluted Alaska and western US coast reactivity was found to be higher in the boundary layer, averaging  $4 \text{ s}^{-1}$ , decreasing to below  $1 \text{ s}^{-1}$  with altitude up to 12 km (Mao et al., 2009). PEGASOS measurements from the Zeppelin over the Po Valley showed reactivity decreasing from about  $5 \text{ s}^{-1}$  at ground-level to around  $2 \text{ s}^{-1}$  at 800 m, with morning rush hour reactivity higher than daytime. Up to several tens per second of unexplained reactivity was identified in biogenically dominated temperate (Di Carlo et al., 2004; Hansen et al., 2014), tropical (Nölscher et al., 2016) and boreal (Nölscher et al., 2012) forest environments and is dependent on the biogenic source, time of day and season (Williams et al., 2016; Nölscher et al., 2016). Where agreement between measured and calculated reactivity has been obtained, it indicates that all relevant trace gases were measured. This was found to be the case in environments that were influenced by anthropogenic OH reactants such as in New York (Ren et al., 2003) and in the North China Plain (Fuchs et al., 2017) and in isoprene-dominated environments during daytime in a Mediterranean forest (Zannoni et al., 2016). The missing reactivity can sometimes be closed if model-calculated oxygenated VOC is considered (e.g. Chataniet et al., 2009; Lou et al., 2010; Kaiser et al., 2016; Whalley et al., 2016), though this clearly requires accurate representation of the product yields and reactivities. This is particularly relevant when considering the recent identification of novel oxidation products (see section 4 below). Use of OH reactivity measurements for OH budget analysis has also provided new results. A gap in the understanding of OH recycling processes was found in a field study in Nashville (Martinez et al., 2003), in China (Hofzumahaus et al., 2009) and in Borneo (Whalley et al., 2011). Despite the challenges associated with such measurements, comparable reactivity measurements towards other oxidants may be similarly revealing. Sommariva (2019) have recently reported a total ozone reactivity technique, but those for Cl, for example, are yet to be developed.

#### **4) Highly oxygenated organic molecules (HOM) formed by auto-oxidation of VOC**

Despite their very recent discovery, highly oxygenated organic molecules (HOM) have generated considerable interest, both from the perspective of providing a new mechanistic pathway to rapid atmospheric VOC oxidation and also a ready source of SOA precursor molecules; for example, under atmospheric conditions, monoterpene auto-oxidation can promptly form compounds such as  $\text{C}_{10}\text{H}_{14}\text{O}_9$  or  $\text{C}_{20}\text{H}_{30}\text{O}_{16}$  that can rapidly condense. Whilst there has been some confusion in the definition of HOM, Bianchi et al. (2019) have suggested that they should satisfy the following three criteria:

- i) HOM Are Formed via Autoxidation Involving Peroxy Radicals;
- ii) HOM Are Formed in the Gas Phase under Atmospherically Relevant Conditions, and
- iii) HOM Typically Contain Six or More Oxygen Atoms.

Following the early postulations of the role of auto-oxidation in atmospheric VOC degradation (Crouse et al., 2013), the importance of HOM in SOA formation has been widely established and quantified in monoterpene oxidation (Ehn et al., 2012; 2014; Jokinen et al. 2015; Berndt et al., 2016; 2018). There has subsequently been increasing evidence for, and quantification of, HOM formation across a range of systems including OH-initiated auto-oxidation of aromatic and substituted aromatic compounds (Wang et al., 2017; Molteni et al., 2018). The first HOM observations were reported in laboratory and chamber studies of monoterpene ozonolysis and the laboratory mass spectra were found to closely correspond to observations from the boreal forest (Ehn et al., 2012; 2014; Zhao et al., 2013b). As outlined in the review of Bianchi et al. (2019), there have been a number of ambient observational studies of HOM. All of these have benefited from the recent advances in mass spectrometry with atmospheric pressure interface time-of-flight mass spectrometry (API-ToF-MS) alone or coupled with a nitrate ion chemical ionisation source (NO<sub>3</sub><sup>-</sup>-CI-API- ToF-MS) almost invariably used. HOM species have been detected in both vapour and particle phases, the latter using NO<sub>3</sub><sup>-</sup>-CI-API- ToF-MS coupled with the filter inlet for gases and aerosols (FIGAERO).

Charged HOM species were first observed in the Finnish boreal forest using API-ToF-MS (Ehn et al., 2010); these observations were subsequently confirmed and expanded by Ehn et al. (2012) and Bianchi et al. (2017). Neutral HOM species have been widely observed at rural European stations by NO<sub>3</sub><sup>-</sup>-CI-API- ToF-MS (Ehn et al., 2014; Jokinen et al. 2014; Mutzel et al., 2015; Berndt et al., 2016; Kürten et al., 2016; Yan et al., 2016; Bianchi et al. 2017; Zha et al., 2018), with concentrations of the most abundant HOM species (RO<sub>2</sub>, C<sub>10</sub> monomers, C<sub>10</sub> organonitrates and C<sub>20</sub> accretion products) reaching 10<sup>7</sup> molecule cm<sup>-3</sup> and total HOM concentrations of ~10<sup>8</sup> molecule cm<sup>-3</sup>. Closed shell monomers are generally most abundant and exhibit a weak diurnal trend, though many of the individual monomers have strong diurnal variability, some having daytime and others, night-time, peaks. The total gas-phase HOM concentration shows two maxima, one around noon and another during late evening.

Using an I<sup>-</sup>-ToF-CIMS, Mohr et al. (2017) characterised accretion products (C<sub>16-20</sub>H<sub>y</sub>O<sub>6-9</sub>) of monoterpene oxidation at concentrations of ~10<sup>6</sup>-10<sup>7</sup> molecule cm<sup>-3</sup> at a boreal forest site and Jokinen et al. (2016) identified C<sub>15</sub> HOM species as sesquiterpene oxidation products. Lee et al. (2014; 2016) reported airborne and ground-based ToF-CIMS measurements of HOM over the US and Krechmer et al. (2015) reported 14 isoprene-derived auto-oxidation products measured using nitrate ToF-CIMS. Bianchi et al. (2016) and Frege et al. (2017) reported HOM and new particle formation in the free troposphere. Mutzel et al. (2015) and Brüggemann et al. (2017) suggested the presence of HOM in the particle phase from off-line measurements, but the first on-line measurements using the FIGAERO were reported in the US by Lee et al. (2016) and Lopez-Hilfiker et al. (2016) and in Finland in Mohr et al. (2017). Organosulphates are widely suspected to be formed by heterogeneous processes in aerosol of biogenic and anthropogenic origin (e.g. Meade et al., 2016). Mutzel et al. (2015) speculated the formation of highly oxidized organosulphates with O/C>1 (HOOS) from the simultaneous presence of gas-phase HOMs and particulate sulphate. Brüggemann et al. (2017) suggested that correlation between HOOS, sulphate and HOM support this hypothesis.

## 5) Atmospheric complexity and its simplification, reduction and interpretation

The abundance of sources, chemical and physical transformation processes, the variability in mixing and removal processes all lead to an overwhelming complexity in atmospheric components in both gaseous and particulate phases. The emergence, proliferation and combination of online and offline multidimensional hyphenated measurement technologies has enabled massive data generation requiring novel interpretative methods (e.g., data mining and/or machine learning algorithms). Such methodologies are applicable to resolution of biological, microphysical and chemical complexity and their combinations in both outdoor and indoor environments and allows movement beyond the historical simplification by use of surrogates, representative compounds and tracers/markers for individual processes towards a more complete appreciation of their complexity.

The indoor community have a strong appreciation of the variety of new and emerging techniques and of the consequent generation of vast amounts of data, so the aim is not to summarise their outdoor application and direct indoor air studies towards an expansion of these capabilities from outdoor studies. This section solely aims to provide a brief flavour of the wealth of studies in this area.

Relating to chemical complexity and following up on the work of [Goldstein and Galbally \(2007\)](#), [Glasius and Goldstein \(2016\)](#) discussed a number of recent discoveries and future challenges in atmospheric organic chemistry largely derived from field observations using advanced analytical techniques, concluding that “we must strive to achieve speciation to understand the complexity of trace compounds to a degree that is detailed enough to enable process level understanding of atmospheric organic chemistry”. Developing the status reviewed by [Hallquist et al. \(2009\)](#), this work largely focused on developments in understanding SOA processes over the last decade, with attention to measurements from a variety of online and offline techniques exploring mechanistic channels producing hydroperoxides, epoxides, carboxylic acids, lactones, organosulphate and organonitrate compounds as well as high molecular weight oligomers and HOM species. The review of [Nozière et al. \(2015\)](#), discussing the molecular identification of atmospheric organic compounds outlined the requirement to match the level of knowledge of the compounds to the problem to be addressed. This approach can help avoid redundancy of information and its coupling to appropriate data interrogation techniques, should focus attention onto the real needs of both outdoor and indoor pollution studies.

In addition to chemical complexity, biological atmospheric complexity, driven by the wide variety of biotic activity is expressed, for example, in primary biological aerosol particles (PBAP; [Després et al., 2012](#)). The range of PBAP, as recently revealed by real-time online fluorescence instrumentation ([Fennelly et al., 2018](#)), has led to the need for techniques to handle the vast quantities of information required for their characterisation. Additionally, single-particle mass spectrometric techniques have recently used to classify PBAP ([Zawadowicz et al., 2017](#)), having been previously deployed to investigate chemical complexity of primary sea spray particles and the complex mineralogy of airborne desert dust. Quantification of the contributions of pollen, bacteria, fungal spores, viruses and skin fragments is clearly of interest to indoor as well as outdoor air quality as is the contribution of dust from both long-range transport and local resuspension. Microphysical particle complexity accounting for the mixing of the rich variety of components from various sources has received substantial recent attention and the mixing-state of PM is reviewed extensively in [Riemer et al. \(2019\)](#), along with methodologies for its simplified representation.

Much recent effort has been invested in resolving and reducing this complexity to make the understanding of atmospheric composition tractable. *Hierarchical clustering* is a method of cluster analysis which seeks to build a hierarchy of clusters in either a bottom-up (agglomerative) or top-down (divisive) manner. Hierarchical agglomerative (HA) cluster analysis techniques have been used to classify single PBAP measured using online fluorescence ([Robinson et al., 2013](#); [Huffman et al., 2013](#); [Crawford et al. 2015](#)). *Principal component analysis* (PCA) is a multivariate data analysis method that has been widely used for some time in atmospheric applications which reduces the dimensionality of the data, whilst preserving as much ‘variability’ (i.e. statistical information) as possible. In principle, it is used for identification of components that are able to account for most variability for all measured variables and serves as a useful reduction technique (a recent example of PCA can be found in [Martinsson et al., 2017](#)). *Positive Matrix Factorisation* (PMF) has been used as a powerful alternative to conventional source-apportionment techniques to separate the major contributing temporally co-varying factors in a dataset. It was pioneered in atmospheric applications with Aerosol Mass Spectrometer (AMS) data ([Ulbrich et al., 2009](#); [Zhang et al., 2011](#)) and was subsequently used with ambient measurements by Proton-Transfer Reaction Mass Spectrometry (PTR-MS; [Vlasenko et al., 2009](#)), to combined datasets ([Slowik et al., 2010](#)) and has recently been applied to other Chemical Ionisation Mass Spectrometry (CIMS) data (e.g. to identify HOM sources, [Yan et al, 2016](#)). *Constrained factorisation* techniques can further enhance their ability for source apportionment purposes. An example is the

comprehensive use of the multilinear engine (ME2) approach to apportion organic aerosol across EUROPE (Crippa et al., 2014).

Combinations of techniques can provide powerful tools. For example, Chavent et al. (2009) used a combination of PCA and PMF for source identification and apportionment and Wyche et al. (2015) used a combination of PCA, HCA and positive least-squares discriminant analysis (PLS-DA) to interrogate chemical complexity in a coupled dataset of gaseous measurements by PTR (relating to organic reactivity) and particle measurements by AMS (relating to SOA formation).

Interpreting the complexity of the behaviour of the ultrafine particle (UFP) fraction of the size distribution by source apportionment presents particular challenges. Most receptor modelling tools are based on sampling the mass of PM, subsequent chemical analysis and the application of receptor models such as PMF, PCA, UNMIX and Chemical Mass Balance (CMB), among others. However, the mass of UFP is a small fraction of total PM and significant sampling artefacts may be produced (artificial loss or gain of mass), particularly related to SVOCs. Taking this into account, a number of studies have performed *source apportionment* analysis using impactor sampling. This has allowed apportionment of metals, elemental carbon (EC) and low volatility species concentrations in UFP or quasi-UFP (e.g. Arhami et al., 2010; Lü et al., 2012; Tan et al., 2014; Xue et al., 2018) into road traffic, oil combustion and regional (secondary PM dominated) contributions. More recently, clustering and PMF analyses have been applied to size segregated particle number concentrations (e.g. Beddows et al., 2009, 2014, Kim et al., 2004, Harrison et al., 2011, Vu et al., 2015). These analyses categorise and group particle size distributions in clusters or factors, according to the prevalence of the nucleation, Aitken or accumulation modes, relating them to source through their relationships to other pollutants, mean meteorological parameters and temporal variability (season, day of the week, daily hourly variation). In urban areas, the main UFP source is road traffic (e.g. Kumar et al., 2014, Brines et al., 2015), but in high insolation urban climates, photochemical nucleation can also contribute (e.g. Brines et al., 2015, and references therein). Most recently, CI-API-ToF-MS has been used to directly measure ion clusters leading to nucleation and new particle formation (Riva et al., 2019, and references therein).

All the above outdoor approaches to obtain source contributions of UFP might also be applied to indoor environments to apportion indoor UFP. Infiltration of UFP might be evaluated by simultaneously measuring BC as a tracer of outdoor road traffic UFP, and the contribution of indoor sources by using VOCs as tracers of the different sources. Bekö et al. (2013) used the indoor activity records to obtain such source contributions in Danish homes.

Each of the techniques outlined above for outdoor environments might usefully be used in indoor environments. Conventional measurement limitations and emerging solutions to these limitations should also be considered when resolving the complexity of the dynamical evolution of UFP. Whilst mobility instruments can indicate occurrence of these nucleation episodes and growth or evaporation dynamics, most such instruments have lower size limits greater than the freshly nucleated particles. Measurement of finer particles (1-5 nm) particles has been made possible by the Particle Size Magnifier (PSM; e.g. Vanhanen et al., 2016) and combinations of instruments should be used to enable a detailed source apportionment of the total particle number concentration across all size ranges.

The possible combinations of data analysis techniques and hence number of applications is almost endless and extremely powerful and their adoption in understanding the complexity of indoor air is as important as it is in outdoor studies.

## List of top research questions, hypotheses, recommended future steps

### Recommendations

- The nature of organic compounds in the indoor environment inevitably requires characterisation according to volatility. By design, many of the products used indoors will partition between phases. All fragrances are applied in the condensed phase and evaporate towards their equilibrium concentration in the vapour phase. This will apply to all scented products and the degree to which the vapours contribute to the available reactivity will depend upon the degree of disequilibrium after the time of application.
- Oxidant focused recommendations: Understanding of indoor HONO is needed to constrain OH given the evidence for outdoor importance in megacity studies; OH, HO<sub>2</sub> and RO<sub>2</sub> discrepancies may result from complex RO<sub>2</sub> chemistry – it is important to characterize RO<sub>2</sub> complexity. The potential importance of NO<sub>3</sub> should be explored, given the extended photolysis lifetime under indoor lighting conditions. Chlorine and Criegee radicals may have important roles in indoor oxidizing capacity.
- The indoor environment, with its novel mixtures of oxidants, VOC, SVOC and other pollutants will substantially benefit from attempts to reconcile measured and modelled reactivity.
- Given the prevalence of HOM in the ambient atmosphere and the evidence in chamber studies of both OH- and O<sub>3</sub>-initiated auto-oxidation forming HOM species, it is widely expected that they will fulfil an important role in indoor chemistry and should be investigated in the rich mixture of both biogenically- and synthetically-derived VOC in the indoor environment.
- Compositional complexity of the atmosphere is becoming increasingly evident with the emergence and deployment of powerful new measurement techniques. Sophisticated statistical analytical approaches including a wide array of new machine learning techniques are as relevant to interpreting indoor air composition as they are to outdoor air.

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## 2. Outdoor models

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### Introduction to the subtask

Environmental air pollution is a major environmental problem that also affects the indoor environment. The problem of ambient air pollution has been recognised for more than half a century and led to the development of a large scientific community working with ambient measurements and monitoring, emissions characterisation and quantification, basic research on atmospheric chemistry and physics related to air pollution as well as the air quality and atmospheric chemistry modelling. In the last few decades, the air quality situation has improved in developed countries but concurrently it has seriously deteriorated in developing countries, especially in India and East Asia.

Today, there exist a series of models and model systems in use by a large number of outdoor pollution experts. Many of them are open source community models built on cores developed by organisations such as e.g. NOAA, NCAR or the European Monitoring and Evaluation Programme, Meteorological Synthesizing centre-West (EMEP MSC-W), which then coordinate further model developments through open fora of developers and users. Thanks to this higher organization of the model development the research models nowadays often consist of modules which can be exchanged and implemented across the models. As an example, several chemistry mechanisms or treatment of aerosol can be chosen in one model, depending on the aims of the study. An extensive effort has also been spent on integration of the knowledge, benchmarking of the models and development of air quality monitoring and modelling infrastructures.

The goal of this subtask was to identify, in Europe, which of the existing and actively maintained models can provide information that can help in the frame of INDAIRPOLLNET. For this purpose, we have used information from an existing outdoor model database (AQ-MDS), modelers and users' networks (FAIRMODE, HARMO) and existing reviews of models at the country level (U.K., U.S.)

For INDAIRPOLLNET, we identified ways in which outdoor models could be used to aid indoor air modelling as follows:

1. Inform the planning of indoor air pollution studies about pollution levels to be expected in European regions and cities (CAMS, EMEP, national met-offices, FAIRMODE & HARMO, EIONET, Nordic Welfare);
2. In urban/local studies, prognostics of meteorological variables, including data from at the least meso-meteorological scales, wind velocity and direction, temperature and relative humidity fields;
3. In microscale studies, 3D wind, temperature and pressure fields, namely around buildings (CFD models);
4. Provide data input for indoor air modelling that includes outdoor pollution as a source;
5. Assess the chemistry models and schemes used to inspire indoor air modelling (Chemistry, gas-to-particle partitioning);
6. Coupling of indoor and outdoor air pollution to assess the (short- or long-term) health effects in cohorts;
7. Development and evaluation of indoor air intervention strategies that consider outdoor pollution as an important health impact.

Each potential use for indoor studies has different requirements. It is thus important to know the principle functioning of each of these models, what type of information it gives and how suitable it may be for a specific application.

## Brief summary of the state-of-the-art

Outdoor air pollution modelling has a long history, starting with the Gaussian Model in 1936. The main air quality models are stationary and non-stationary Gaussian models, reactive and non-reactive Eulerian Regional - Scale transport Models, Lagrangian Trajectory Models, Computational Fluid Dynamics models (CFD) and Large Eddy Simulation (LES) models. The Gaussian and the Eulerian models are the most common models for atmospheric air quality assessment.

Outdoor air pollution models are used as instruments for various purposes, such as regulatory, policy support assessment of potential pollution in case of accidents, source identification, or atmospheric chemistry research. Those used for regulatory purposes are subject to legislative requirements (in the EU Directive 2008/50/EC on Ambient Air Quality and Cleaner Air for Europe - the AQ Directive).

In 1991 the European Initiative on Harmonization within Atmospheric Dispersion Modelling for Regulatory Purposes (HARMO) started with focus on common tools and methodologies and aiming to improve the “modelling culture” both in Europe and at international level ([HARMO, 1992](#)). The Air Quality Model Documentation System (AQ- MDS), developed by the European Topic Centre on Air Quality (ETC-AQ) provided information and guidance to any user of air pollution models in selecting the most appropriate model for a specified application. The AQ-MDS was launched in 1997 and included 142 models, which are still accessible via the web-archive ([AQ-MDS 1997](#)).

Given the large number of outdoor air pollution models, the reference models at European level need to be comparable, well documented, and validated for their required field of applications. For this purpose, in 2007 the Forum for Air Quality Modelling in Europe (FAIRMODE) was established as a joint action of the European Environment Agency (EEA) and the European Commission's Joint Research Centre (JRC). It aims to bring together air quality modelers and users to promote and support the harmonized use of models by EU Member States, with emphasis on model applications under the European Air Quality Directives ([FAIRMODE 2007](#)). The FAIRMODE network include national experts nominated by the Member States (MS) and provides a framework for exchanging experience regarding a wide number of applications for interfaces, databases and tools to workshops, seminars and common projects or activities.

Beside these pan-European initiatives, there are also country level activities (e.g. in the U.K. and U.S.) for evaluation of the performance of air dispersion models ([Derwent 2010](#), [Bessagnet 2012](#)).

Worth mentioning is the Copernicus Atmosphere Monitoring Service (CAMS), a service implemented by the European Centre for Medium-Range Weather Forecasts (ECMWF), that provides continuous data and information on atmospheric composition. CAMS, which is part of the Copernicus Programme, describes the current situation, forecasts the situation a few days ahead, and analyses consistently retrospective data records for recent years. CAMS builds on many years of European research and development, and on existing European and national capacities, experience and know-how. The current portfolio of mature operational products was developed through a series of EU-funded precursor projects starting in 2005. CAMS has been fully operational since 1 July 2015. The current phase runs until the end of 2020, the scope of Copernicus after 2020 is currently under discussion. Expects try to secure continued provision of the existing services for the foreseeable future. CAMS tracks air pollution, solar energy, greenhouse gases and climate forcing globally and regionally for Europe. For Europe an ensemble of 7 models (CHIMERE, EMEP, EURAD-IM, LOTOS-EUROS, MATCH, MOCAGE, SILAM) delivers data in 10x10 to 25x25 km grid resolution as well as an air quality forecast

for 40 major European cities. Due to the coarse spatial resolution of the models this forecast corresponds mostly to urban background conditions (ENSEMBLE, 2016).

The main approach to this task was divided into several steps:

- Step 1: Compile these reviews and database reports into an “outdoor modelling summary” aimed to inform indoor air pollution specialists on a few pages about the lessons to be learnt. This would go together with identifying gaps (open questions) from an indoor air quality perspective, to be listed as a second main chapter.
- Step 2: Contact the experts identified (including the authors of these reports) to:
- review the summary and to provide updates to references if indicated
  - ask specific questions aimed to fill the „indoor gaps" identified
- Step 3: Conclude by writing the report that contains the following three sections:
- state of the art of outdoor air models (the review of step 1 plus resolved, i.e. not existing gaps)
  - gaps (that remain) from an indoor air perspective
  - recommendations and strategies to deal with these gaps

## Summary of selected studies in the field

The sources identified (AQ-MDS, FAIRMODE, Defra UK-reviews) are quite authoritative and comprehensive summaries of the state of outdoor modelling in Europe, far more detailed than what we aimed to do. Considering indoor air pollution, and potential area of interest from outdoor air pollution models, we created a **spreadsheet** that included the following characteristics:

- A. Model Name
- B. Field of application
- C. Model limitation
- D. Chemical transformation model
- E. Resolution
- F. User interface
- G. User community
- H. Validation & evaluation
- I. Previous application
- J. Source of information

For the *Field of application* we considered the following options (i) regulatory purposes, (ii) policy support, (iii) emergency, (iv) research and (v) other. The models that had no application in any of these fields were included in another category called “others” and a short description was provided.

*Model limitation* described any model restriction regarding type of grids used, special meteorological conditions, dependency on other models, etc.

The use of a *chemical transformation model* is marked, and the type of chemical transformation described.

The *resolution of models* includes the description of temporal, horizontal and vertical resolution. For the purposes of this task information regarding the user interface is useful, if a community of users for a certain model exists and if the models have been validated and evaluated internationally (e.g. in inter-comparison studies).

The *previous application* of the models was included in the analysis in order to provide information about the type of area/environment (urban, rural), where the models were used and about the type of pollution simulation (episodes or other specified by the users).

The outdoor air dispersion models analysed in the Air Quality Model Documentation System ([AG-MDS, 1997](#)) are at different stages of development (from first versions to mature and commercial models) and present a great variation regarding field of application. The models have a wide range of resolution:

- time step varies from seconds to days;
- receptor networks could be set-up with a resolution from 1 m to km. The most frequent value is 100 m;
- area covered varies from few m<sup>2</sup> up to thousands of km<sup>2</sup>;
- vertical dimension is between ground level (0 m) and up to 5 000 m.

Chemical transformation modules are not included in every model. The most used chemical transformations are of nitrogen oxides, sulphur oxides and ozone. The CHIMERE model offers the option to include different gas phase chemical mechanisms. The original, complete scheme describes more than 300 reactions of 80 gaseous species ([AQ-MDS 1997](#), [Bessagnet, 2012](#)).

Almost all the models have user communities but the extent of this presents large variations. The most common tools used are mailing lists, websites and emails addresses for Q&A.

The most common approach for validation and evaluation are model inter-comparisons in various field tests and applications (i.e. City-Delta, Euro-Delta). Source of information are indicated for each model.

## **1) Use of outdoor models for indoor-air applications**

Here we consider the potential use cases listed at the beginning of this chapter where a direct application of the outdoor model is relevant. Examples of the most suitable types of models follow each use case:

1. Inform the planning of indoor air pollution studies about pollution levels to be expected in European regions and cities
2. In urban/local studies, prognostics of meteorological variables, including data from at the least the meso-meteorological scale, wind velocity and direction, temperature and relative humidity fields;

Numerous Eulerian models are available, many of them operating on multiscale domains. These are either on-line coupled with meteorological models (ALLADIN-CAMx, MM5-CAMx, WRF-Chem, ADMS-Urban, TAPM) or use prescribed meteorological fields – the Chemistry Transport Models (CTM) – e.g. CHIMAIR, EMEP, LOTUS-EUROS, SILAM, MATCH, CMAQ, EPISODE. The maximum grid resolution of these models vary, typically from a few km to tenths of meters (see the table in the appendix). For Europe re-analyses and short-term forecasts employing assimilation of measurements produced by a model ensemble are available on c.a. 10-km resolution from CAMS. A large number of Gaussian models is used for regulatory purposes, these models, however, do not involved secondary chemistry other than a simple decay which makes their suitability for detailed studies of interactions of outdoor air with indoor air pollutants somewhat limited.

The meteorological data on an urban scale can be obtained from the meteorological models, with or without coupling to the atmospheric chemistry module, e.g. ALLADIN, MM5, WRF or TAPM. The data can also be obtained from national weather services or from ECMWF, these are, however, often on coarser grid resolution.

3. In microscale studies, 3D wind, temperature and pressure fields, namely around buildings;
4. Provide data input for indoor air modelling that includes outdoor pollution as a source;

On the microscale, several types of models are used for modelling of urban meteorology and air pollution: Computational Fluid Dynamics (CFD) models and Large Eddy Simulation (LES) models are the most complex models concerning the dynamics, which can simulate complex transport of air pollutants in street canyons, around buildings or in the urban vegetation canopy. Their high complexity in the dynamics however sets a strong limitation on the atmospheric chemistry representation. Such models have been used offline to drive, for example, aerosol particle and cloud processes in trajectory ensemble mode (Feingold et al., 1998; Romakkaniemi et al., 2009) demonstrating the ability to represent a high degree of process detail at high spatial resolution as may be needed for indoor studies. CFD models have been coupled to representations of particle dynamics in commercial packages enabling extremely high resolution simulation of the transport and growth of fine particles (e.g. the FLUENT fine particle model, FPM) and in non-commercial packages to describe particle transport in street canyons (e.g. Tay et al., 2010). The most recent generation of LES models have also been coupled to complex representations of aerosol (and cloud) dynamics (Tonttila et al., 2017). Other type of models used are Gaussian plume dispersion models, sometimes combined with a box-model chemistry part limited to e.g. NO to NO<sub>2</sub> oxidation by ozone available in the system. An example of a Gaussian street-scale model is the Operational Street Pollution Model-OSPM.

## 2) Modular assessment of the outdoor models

A number of the models listed in the supplementary table have a modular approach, i.e. the model setup for a task in question is assembled from interchangeable modules treating the meteorological fields, dispersion of pollutants, gas-phase chemistry processes, aerosol chemistry processes and surface reactions, photochemical processes, aerosol physics, anthropogenic, biogenic and fire emissions and others. The treatment of the atmospheric chemistry and physics employed in outdoor air models can be directly or with some modifications also employed in the indoor models. Special care needs to be paid to the treatment of the photolytic rates which are different in the indoor environment, also processes that are not described explicitly (e.g. heterogeneous reactions) often involve parameterization that is developed for outdoor conditions and would need modifications for indoor air applications. Here we consider the potential use cases listed at the beginning of this chapter where application of these modules is relevant:

5. Assess the chemistry models and schemes used to inspire indoor air modelling;

**The model treatment of atmospheric chemistry processes** used in the outdoor models range from extremely complex automatically-generated explicit mechanisms coupling gaseous photochemistry to simplified aerosol treatments such as GECKO-A (e.g. Aumont et al., 2005; Lee-Taylor, et al.; 2011; Aumont et al., 2016), through to simplified, but still near explicit schemes such as the Master Chemical Mechanism (MCM; <http://mcm.york.ac.uk>; Saunders et al., 2003; Jenkin et al., 2003 ). The MCM describes the detailed gas-phase chemical processes involved in the tropospheric degradation of a series of primary emitted volatile organic compounds (VOCs), developed to provide accurate, robust and up-to-date information concerning the role of specific organic compounds in ground-level ozone formation in relation to air quality policy development in Europe. The MCM is extensively used in support of field measurements and in the development and evaluation of reduced or lumped mechanisms that are required for inclusion into more complex chemistry-transport and chemistry-climate models. Of all the chemical models used outside, this is the most useful for indoor applications (e.g. Carslaw, 2007). Currently, the degradation of methane and 142 non-methane VOCs is represented. There are ongoing efforts to couple the automated generation GECKO-A and MCM approaches (Jenkin et al., 2019). Simple generic or reduced mechanisms describing the main photochemical processes of NO<sub>x</sub>, SO<sub>x</sub>, ozone and hydrocarbons also exist, often including simple equations for formation of sulphate, nitrate and organic particulate matter, as e.g. chemistry scheme employed in TAPM.

Several chemical mechanisms, although going back 30 years, are commonly used in chemistry transport models, and adopt the latest findings from atmospheric chemistry research. Examples are Carbon Bond IV and V (CBM-IV, V ([Sarwar et al., 2008](#))), SAPRC 99 ([Carter 2000a](#); [Carter 2010b](#)) and RADM-2 ([Stockwell et al., 1990](#)) and RACM ([Stockwell et al., 1997](#)) and the mechanism used in the EMEP model. A more recent reduced scheme, traceable to the MCM and aiming to reproduce its ability to predict VOC degradation and O<sub>3</sub> production, is the Common Reactive Intermediates mechanism (CRIMEch; [Jenkin et al., 2008](#)). Five further reductions of the CRIMEch version 2 were developed and reported by [Watson et al. \(2008\)](#) and its use in large-scale models first reported by [Utembe et al. \(2010\)](#). Its first use in an Eulerian model was reported in [Archer-Nicholls et al. \(2014\)](#), where it was compared with the CBM-Z carbon bond based mechanism ([Zaveri and Peters, 1999](#)). All these mechanisms include basic atmospheric chemistry of SO<sub>x</sub>, NO<sub>x</sub>, NO<sub>y</sub>, CO and the later versions often also halogens. The organic reactions are treated in different ways, the later developments often include biogenic VOCs and more complex mechanisms for formation of secondary organic nitrates and SOA.

CBM IV and V is a condensed reaction mechanism that is currently used in many photochemical smog or air quality models as e.g. CMAQ and WRF-Chem. In CBM-IV, VOCs are classified based on their molecular structure. In CBM-IV, carbon bonds are divided into different functional groups such as paraffin carbon bond (PAR), olefinic carbon bond (OLE) and toluene (TOL). The mechanism includes chemistry of SO<sub>x</sub>, NO<sub>x</sub> and ozone. The later developments of CBM (V, VI and Z) also includes the chemistry of isoprene. The SAPRC, RADM, RACM and EMEP mechanisms use lumped species to represent the complex VOC mixture, although the lumping differs among the mechanisms. Both the recent EMEP and SAPRC mechanisms include SOA formation.

#### **Aerosol modules for outdoor applications:**

The Modal Aerosol Dynamics for Europe module (MADE; [Ackermann et al., 1998](#)) is a well-established modal aerosol representation and has been coupled with the Secondary Organic Aerosol Model (SORGAM; [Schell et al., 2001](#)) in various applications. M7 is an efficient size-resolved aerosol microphysics module for large-scale aerosol transport models ([Vignati et al., 2004](#)), representing aerosol in 7 modes, thereby enabling representation of quite complex compositional distributions. GLOMAP-mode ([Mann et al., 2010](#)) was an efficient modal aerosol scheme developed for online coupled global climate simulations and followed the original development of the binned GLOMAP-bin aerosol scheme ([Spracklen et al., 2005](#)) which uses a 2-moment representation of aerosol dynamics for use in offline simulations of detailed aerosol processes. The Model for Simulating Aerosol Interactions and Chemistry (MOSAIC; [Zaveri et al., 2008](#)), is a sectional aerosol representation using an internally-mixed assumption that has been adopted as one of the aerosol options in WRF-Chem and has been updated ([Archer-Nicholls et al., 2014](#)), to incorporate N<sub>2</sub>O<sub>5</sub> heterogeneous chemistry (coupled both to CRIMEch and CBM-Z). A comparison of the various chemistry and aerosol model treatments in WRF-Chem in simulations of chemistry of the Eastern Mediterranean has been reported in [Georgiou et al. \(2018\)](#).

The Sectional Aerosol module for Large-Scale Applications (SALSA; [Kokkola et al., 2008](#)) is a variable resolution binned microphysics model that has been adopted in a range of models from the ECHAM Earth system model to the UCLALES Large Eddy framework. There has simultaneously been much active development of highly-detailed representations of aerosol processes used successfully for outdoor simulation of specific processes, all of which may have relevance for indoor air pollution. Detailed simulations of aerosol particle mixing state have been conducted using the PartMC and PartMC-MOSAIC model in box and 1-D configurations in various environments, from e.g. urban outflow to ship plumes (<http://lagrange.mechse.illinois.edu/partmc/>; [Riemer et al., 2009; 2010](#); [Zaveri et al., 2010](#); [Tian et al., 2014](#); [Curtis et al., 2017](#)). Thermodynamics of outdoor aerosol particles have been investigated thoroughly using a range of numerical descriptions at various levels of complexity (<http://www.aim.env.uea.ac.uk/>; [Wexler and Clegg, 2002](#); [Topping et al., 2005a,b](#); <https://isorropia.epfl.ch/>; [Fountoukis and Nenes, 2007](#); [Zuend et al., 2011](#)) and these models have been variously incorporated into large scale models. They have also been

included in relatively simple frameworks to predict partitioning of gases and aerosols (e.g. [Barley et al., 2009](#); <http://umansysprop.seaes.manchester.ac.uk/>; [Topping et al., 2016](#)).

Dynamical interactions between gases and aerosol particles are explicitly treated in the Model of Aerosol Numerics including Chemistry (MANIC) model of photochemistry and binned microphysics ([Lowe et al., 2009; 2011; Topping et al., 2009; 2012](#)). Treatments of the effect of SOA viscosity in affecting particle evolution through diffusional limitation in the condensed phase has been explored by [Shiraiwa et al. \(2012\)](#), [Zaveri et al. \(2014\)](#) and [O'Meara et al., \(2017\)](#). There have been significant recent advances attempting to describe formation of heavily oxygenated molecules (HOM) formed from auto-oxidation of VOC and subsequent SOA and new particle formation (e.g. [Pye et al., 2019](#); [Roldin et al., 2019](#)). Finally, coupled models of aqueous and gas phase chemistry that have been used for simulating the outdoor atmosphere, may also find direct application for indoor air pollution problems ([https://capram.tropos.de/capram\\_intro.html](https://capram.tropos.de/capram_intro.html); [Herrmann et al., 2005](#)). This section illustrates the rich variety of model types that may be of use for indoor air pollution; it is not exhaustive, but should serve as a starting point for the availability of relevant resources.

6. Coupling of indoor and outdoor air pollution to assess the (short- or long-term) health effects in cohorts;

#### **European Air pollution health effects research and links to the indoor pollution community:**

For several decades already, European experts have collaborated to describe the consequences of outdoor air pollution on human health. This research requires harmonised approaches to assess both estimates of exposure and health endpoints. Early projects looked mostly at measured data, but soon air pollution models became popular because they proved useful to address the variability within cities related to microenvironments ([Schweizer et al. 2007](#)) and spatial distribution ([Auchincloss et al. 2012](#); [Beelen et al. 2013](#)). In European regulations, outdoor pollutants are regulated by limiting the concentration that is present in the outdoor environments, not the amount of pollutants that infiltrate indoors or the actual personal exposure levels. Also, most outdoor pollution projects provide only health effect estimates for outdoor pollutants and treat indoor sources and infiltration differences mostly as confounding factors. It is likely that the outdoor pollution community will benefit from collaborating with indoor pollution specialists to address indoor-related questions, namely to switch to an estimation of individual (personal) pollutant exposure levels (rather than the levels outside the buildings) and – more importantly – better information about indoor sources, which will allow also for clearer insight into how much of the exposure comes from outdoors and indoors (which is important to distinguish from a regulatory perspective).

7. Development and evaluation of indoor air intervention strategies that consider outdoor pollution as an important health impact.

#### **Indoor intervention studies and the link to outdoor pollution:**

Interventions in indoor environments may be aimed at reducing air pollutants exposure but they may also have other main goals, for example improved energy efficiency. In any case, when an intervention is planned in an indoor environment, the consequences for human health should be assessed. Outdoor air pollution was recognized as one of the important burdens of disease also in the indoor air context ([Hänninen et al. 2013](#)). Namely aerosols are an important field where outdoor pollution plays an important role and where the complex interactions with the indoor environment are not yet well understood ([Koivisto et al. 2019](#)). Even in the presence of strong indoor sources such as smokers in restaurants, outdoor particles still provide a clear modulation of the indoor levels ([Daly et al. 2010](#)). Understanding outdoor pollutant concentrations will be helpful to design intervention studies in a way that either ambient pollution is similar for different intervention objectives, or that there is a balanced number of intervention and control objectives for high and low outdoor pollutant concentrations.

## List of top research questions, hypotheses, recommended future steps in the field

For the indoor air pollution modelers, the **main questions** are related to:

- How to develop common instruments to assess performance, validate results, ensure transparency, evaluate accuracy and offer proper documentation for each model;
- How to couple indoor and outdoor air pollutant models;
- How to design indoor measurement campaigns aimed at a better understanding of indoor-outdoor relationships (i.e., data from outdoor pollution modelling would help to identify the most informative seasons for these studies as well as locations with high or low levels of outdoor pollution);
- Plan indoor health campaigns that also consider the effect of outdoor air pollutant concentrations on health, for which more refined temporal and spatial data are needed (estimate better the outdoor exposure for the participants included in the indoor studies and in this way increase the trust in data for indoor effects);
- Identify existing outdoor air models and their modules that can be coupled with indoor models.

### Future steps

- create initiative similar to HARMO and FAIRMODE for indoor air pollution community (modelers, researchers, health and environmental experts, legislative experts);
- create links between indoor and outdoor air pollution modelling community (common workshops, working groups, research networks). We have started this by including representatives of outdoor model communities in our INDAIRPOLLNET-meetings.
- Include information on how those outdoor studies can address indoor-relevant questions such as cooking (indoor sources) or indoor-outdoor ratio variability
- include indoor aspects into outdoor exposure models if they are being used to attribute exposure levels to individuals spending time in those indoor environments (currently a gap).

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<http://envs.au.dk/en/knowledge/air/models/ospm/>

<https://www3.epa.gov/scram001/7thconf/information/adms.pdf>

## 3. Simulation chamber studies

Sarka Langer, Peter Wiesen

### Introduction to the subtask

The subtask “Simulation chamber studies” summarizes the experience from studies performed in large European chambers for investigating atmospheric processes, which may be relevant for indoor air chemistry. This report is not intended to be an exhaustive state-of-the-art review but to present examples of how the chamber studies may help to carry out indoor air chemistry studies.

For this purpose, we have used published studies from the chambers within the EU project EUROCHAMP-2020 that aims at integrating the most advanced European atmospheric simulation chambers. We have selected the chambers with a volume larger than 30 m<sup>3</sup> to be of comparable size with the so-called Reference room used in normalizing VOC emissions from construction products. In the next stage, we have contacted the principal investigators for the individual chambers with a request of providing articles with results of their chamber studies published during 2009 – 2018. The selected chambers were: SAPHIR (Jülich, Germany), EUPHORE (Valencia, Spain), HELIOS (Orléans, France), PACS-C3 (Villigen, Switzerland), and AIDA (Karlsruhe, Germany). We have identified the articles relevant for this subtask from the lists or files provided by the chambers’ principal investigators. We have added articles from another chamber and a flow tube study in order to cover other important atmospheric chemical issues not treated in the primarily selected chambers.

### Brief summary of the state-of-the-art

The advantage of the simulation chamber studies is that they enable studying isolated/separated processes under well controlled, defined and stable conditions regarding temperature, relative humidity, pressure, light and (low) concentrations of the species. The chambers resemble indoor environments in a much closer way than outdoor field campaigns and as such, obtained results are directly transferable.

This report provides an overview of how the experience of the chamber community within the atmospheric chemistry may help the indoor community to study and understand indoor air chemistry. The major aspects are fundamental atmospheric chemistry (reaction rates and products) in the gas-phase as well as SOA formation, reaction on particles, yields and properties, intercomparison of available instruments for measurements of selected species and testing of novel instruments.

### Summary of selected studies

In total, 63 articles were revised, and the results are summarized in this report. An additional output is a table (in excel format) with details about the species, concentrations and instrumentation, not provided here. The areas/issues addressed in the recent studies from the chamber studies with potential knowledge exchange for the indoor chemistry community are summarized in Table 3.1.

Table 3.1. Overview of processes studied in chambers relevant for indoor air chemistry.

Area	Parameters
Atmospheric chemistry – gas-phase	<ul style="list-style-type: none"> <li>• Rate coefficients for reactions with OH and NO<sub>3</sub> radicals, Cl atoms, ozone and NO<sub>2</sub></li> <li>• Identification of reaction products and quantification of the product yields</li> <li>• OH radical budget, reactivity and recycling</li> </ul>
Atmospheric chemistry – SOA	<ul style="list-style-type: none"> <li>• SOA formation from OH- and ozone-initiated reactions of model anthropogenic (aromatics) and biogenic (isoprene, terpenes) compounds</li> <li>• Particle formation, growth and aging</li> <li>• SOA yields</li> </ul>
Intercomparison of instruments	<ul style="list-style-type: none"> <li>• Selected organic compounds</li> <li>• OH and NO<sub>3</sub> radicals and peroxy radicals</li> <li>• Radical precursors HONO, N<sub>2</sub>O<sub>5</sub></li> <li>• Regulated air pollutants (NO<sub>2</sub>)</li> </ul>
Development and testing of new instruments/chambers	<ul style="list-style-type: none"> <li>• Organic chemical composition of particles</li> <li>• Black carbon in single particles</li> <li>• Reactive oxygen species (ROS)</li> <li>• Peroxides in particles</li> </ul>

## 1) Atmospheric chemistry – gas-phase

The first group of studies presents results of fundamental gas-phase kinetics, i.e. determination of reaction rate coefficients for various organic compounds with the atmospheric oxidants ozone, hydroxyl (OH) and nitrate (NO<sub>3</sub>) radicals and chlorine (Cl) atoms. The focus of our selection was on articles dealing with organic compounds with relevance for indoor environments.

*Rate coefficients* have been determined for saturated esters reacting with OH radicals and Cl-atoms (Cometto et al., 2009; Liang et al., 2010; Zhang et al., 2014), and for unsaturated esters, mostly acrylates and methacrylates, with ozone (Bernard et al., 2010), with NO<sub>3</sub> radicals (Zhou et al., 2017) and with ozone and OH radicals (Ren et al., 2019). Rate coefficients have been determined for reactions of Cl atoms with butenols (unsaturated alcohols) (Liang et al., 2011) and methylpentanones (Ren et al., 2018) and for the reaction of Cl atoms and OH radicals with pentanols (Lendar et al., 2013) and hydroxyketones (Messaadia et al., 2013).

In addition, the reaction rates have been published for the reaction of ozone with 3-carene and 2-carene (Chen et al., 2015), OH radicals and ozone with pyridine (Errami et al., 2016) and NO<sub>3</sub> radicals with C<sub>1</sub> – C<sub>6</sub> alkanes (Zhou et al., 2019).

The chamber studies provide results of both the kinetic data and the *reaction products*, sometimes complemented with *modelling*. The reaction of an allyl alcohol (2-propen-1-ol) with OH radicals and ozone was studied, producing formaldehyde and glycolaldehyde (Le Person et al., 2009). The OH-initiated oxidation of methyl vinyl ketone, the major reaction product of the oxidation of isoprene, was studied in a comprehensive experiment, which focused on yields of the major products methylglyoxal and glycolaldehyde combined with modelling the reaction using a model based on the Master Chemical Mechanism (MCM). Regarding model calculations, chamber specific properties were added to the model (Fuchs et al., 2018). Reactions of unsaturated compounds with NO<sub>2</sub> may be considered negligible as atmospheric removal processes. However, reactions of isoprene, 1,3-cyclohexadiene, myrcene and ocimene with NO<sub>2</sub> can under certain conditions produce organic nitrates, organic peroxy nitrates and HONO (Bernard et al., 2013). Kinetic data, gas-phase products and SOA yields are provided for the reaction of furan and methylfurans with OH radicals (Gómez Alvarez et al., 2009), and for isoprene, methacrolein and methyl vinyl ketone with ozone (Ren et al., 2017).

Simulation chamber experiments were performed to study *OH radical budgets* using aromatic hydrocarbons (benzene, toluene, p-xylene and 1,3,5-trimethylbenzene) (Nehr et al., 2014), β-pinene (Kaminski et al., 2017)

and 2-methyl-3-butene-2-ol (MBO) (Novelli et al., 2018). Chamber experiments were used to study *OH* reactivity of isorene and its reaction products, coupled to MCM modelling (Nölscher et al., 2014). *OH* radical recycling was observed and modeled (MCM) using isoprene (Fuchs et al., 2013) and methacrolein (Fuchs et al., 2014).

Of particular interest for the indoor community may be studies focusing on one or several substances, frequently found in the indoor environment, and providing a complete characterization of the oxidative fate of the(se) compound(s). The kinetic data, gaseous reaction product (carbonyls) yields and the SOA yields are presented for the reaction of linalool and 6-methyl-5-hepten-2-ol (6-MHO) with ozone and OH radicals (Bernard et al., 2012) as shown in Table 3.2.

Table 3.2 Example of the comprehensive assessment atmospheric transformation of the VOC. The rate coefficients are in unit of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Source: Bernard et al., 2012.

Compound	$k_{\text{OH}}$	$k_{\text{O}_3}$	Reaction products	SOA yield (20 -1000 nm)
Linalool	$(1.7 \pm 0.3) \times 10^{-10}$	$(4.1 \pm 1.0) \times 10^{-16}$	acetone, formaldehyde, hydroxyacetone, glycol aldehyde, 6-MHO, formic acid	14 – 52 %
6-Methyl-5-hepten-2-ol	$(1.0 \pm 0.3) \times 10^{-10}$	$(3.8 \pm 1.2) \times 10^{-16}$	acetone, formaldehyde, hydroxyacetone, formic acid, methylglyoxal, 4-hydroxypentanal	0.2 – 08 %

Ozonolysis and the subsequent autooxidation of terpenes ( $\alpha$ -pinene) and aromatics (benzene, toluene, ethylbenzene, xylenes, naphthalene and biphenyl) with respect to the formation of *highly oxygenated molecules* (HOM) was studied in chamber or flow-tube experiments (Molteni et al., 2018, 2019). The gas phase HOMs from the  $\alpha$ -pinene ozonolysis were measured with a nitrate chemical ionization atmospheric pressure interface time of flight mass spectrometer (CI-API-TOF). The potential pathways of formation and the chemical composition of the HOMs were presented (see Figure 3.1). The trends in the HOMs from  $\alpha$ -pinene oxidation were successfully simulated using the Master Chemical Mechanism (MCM) with an added pseudo-mechanism for HOM formation. Another study presents the formation of highly oxidized products from the OH radical reaction with 1,3,5-trimethylbenzene (TMB), another specie frequently found indoors. The experimentally identified products were compared with model simulations (MCM) and the SOA yield were estimated (Muller et.al 2012).

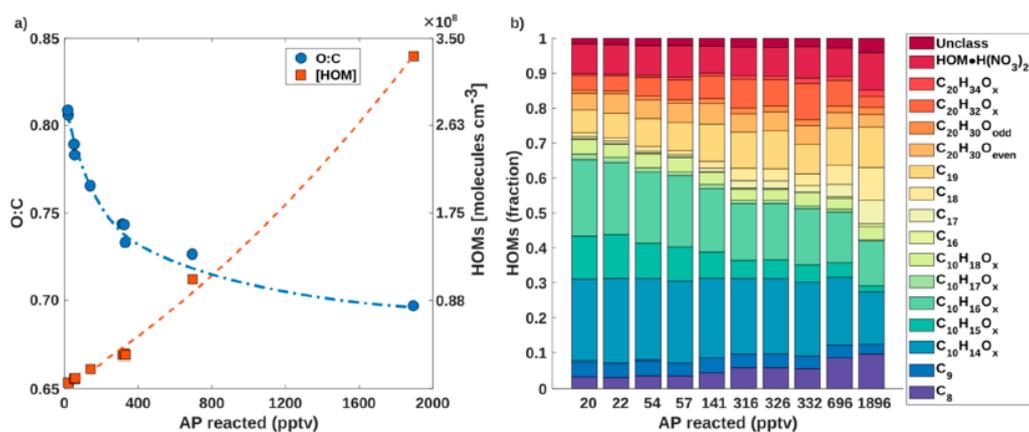


Figure 1. (a) HOM concentration and average O/C as a function of reacted AP. The HOM concentration (in orange) is corrected for wall loss and the condensational sink on particles. In blue, the average O/C of all HOMs is displayed. The curves are to guide the eye. An increase in reacted AP leads to less oxygenated HOMs. (b) Relative contributions of HOM classes at different amounts of AP<sub>react</sub>. HOMs with 11–15 carbon atoms are grouped as unclassified (Unclass).

Figure 3.1. Example of the formation of HOM through ozonolysis of  $\alpha$ -pinene. Source: Molteni et al., 2019.

## 2) Atmospheric chemistry – SOA

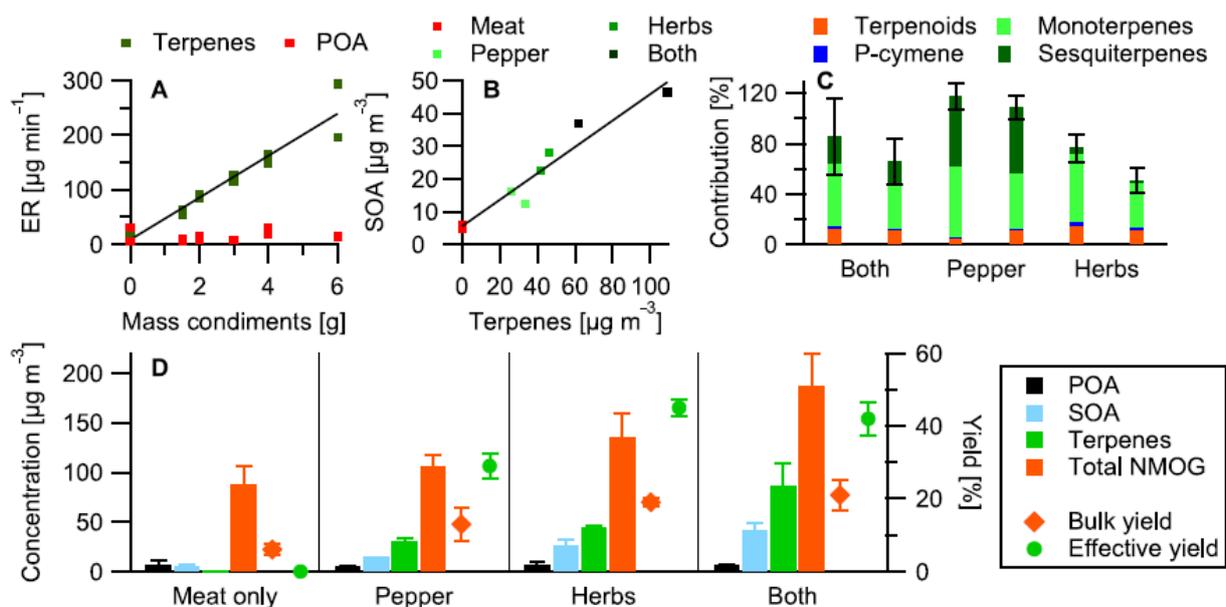
The experiments to simulate SOA formation in the chambers focus on model compounds for biogenic and anthropogenic precursors. The *biogenics* are most often monoterpenes and isoprene, the *anthropogenics* are aromatics.

SOA formation from the reactions of  $\alpha$ -pinene is reported for OH radicals (Tillman et al., 2010) and ozone (Krapf et al., 2016). First generation of SOA from the reaction of  $\alpha$ -pinene and OH radicals and its aging were studied by both experimental methods and modeling using the 2D volatility basis set (Donahue et al., 2012) and Monte Carlo simulations (Stirnweis et al., 2017). New particle formation, particle growth, aerosol yields and chemical composition of SOA from the reaction of the terpenes  $\alpha$ -pinene,  $\beta$ -pinene and limonene with ozone and OH radicals were presented by Zhao et al., 2015; formation of cloud condensation nuclei (CCN) from the ozonolysis and OH reaction of  $\beta$ -caryophyllene by Frosch et al., 2013, and multi oxygenated products and SOA aging from the OH reaction with isoprene in the aqueous phase by Liu et al., 2012.

Both, anthropogenic (1,3,5-trimethylbenzene, o-xylene, octane, toluene) and biogenic (isoprene,  $\alpha$ -pinene, limonene) precursors were used to study the yields of SOA from OH radicals-reaction (Vivanco et al., 2011). Another study presents single particle functional group composition of SOA produced from OH reactions with glyoxal,  $\alpha$ -pinene, isoprene and 1,2,4-trimethylbenzene (Shakya et al., 2013). Newland et al. (2018) present experimental, theoretical (quantum chemical) and modelling studies of the impacts of the ozonolysis of monoterpenes ( $\alpha$ -pinene,  $\beta$ -pinene and limonene) on the formation of stabilized Criegee intermediates (SCI) and the subsequent oxidation of SO<sub>2</sub> by SCIs. SOA yields were studied for the OH reaction with toluene (Leskinen et al., 2015) and with benzene (Borras et al., 2012).

The chambers were used to study how different *indoor activities* affect primary and secondary organic aerosols (POA and SOA). Emissions (POA) from wood burning were characterized and aged by ozone, OH and NO<sub>3</sub> radicals and SOA formation was observed (Tiitta et al., 2016).

Emissions from cooking (frying meat with herbs and pepper) were characterized in real time in a chamber experiment with respect to aerosol and gas phase composition (Klein et al. 2016). The article presents an example of the fate of emissions from human activities indoors. Emissions of fried meat itself or spiced with two different seasonings were injected into a simulation chamber and then aged by OH radicals generated by photolysis of HONO (figure 3.2).



**Figure 3.** (A) Terpene emissions per gram seasoning (Table S3), (B) Secondary organic aerosol (SOA) formed from different amounts of terpenes in the chamber and (C) contribution of different terpene species to SOA (double columns represent experiment repeats). (D) Gives an overview of primary organic aerosol (POA), SOA, and terpene concentrations in the chamber for all experiment conditions and calculated bulk and effective yields (mass SOA formed divided by mass terpenes reacted). Every experiment was repeated once. Error bars in (C) represent the measurement error and the uncertainties resulting from the literature yields. Error bars in (D) represent the range of results.

Figure 3.2. Example of the composition of the primary and aged emission from the frying meat experiments. Source: Klein et al., 2016.

### 3) Intercomparison of instruments

Several chambers studies were dealing with the intercomparison of instruments for measuring organic (mainly oxygenated) species, radicals, radical reactivity (OH) and radical precursors or properties of particles (water uptake).

Intercomparison campaigns were performed to compare instruments for the measurement of formaldehyde (Wisthaler et al., 2008; Catoire et al., 2012), glyoxal and methyl glyoxal (Pang et al., 2014; Thalman et al., 2015) and a series of oxygenated volatile organic compounds (OVOC) (Apel et al., 2008).

Campaigns to compare instrumentation present measurements of OH radicals (Schlosser et al., 2009; Fuchs et al., 2012a), OH radical reactivity (Fuchs et al., 2017) and potential interferences in the detection of OH radicals (Fuchs et al., 2016); nitrate radicals  $\text{NO}_3$  (Dorn et al., 2013),  $\text{NO}_2$  (Fuchs et al., 2010) and peroxyradicals  $\text{HO}_2$  and  $\text{RO}_2$  (Fuchs et al., 2009). Instrumentation has been compared for measuring the radical precursors HONO (Ródenas et al. 2013) and  $\text{N}_2\text{O}_5$  (Fuchs et al., 2012b).

Hygroscopicity tandem differential mobility analyzers (HTDMAs) were intercompared to harmonize the design and the quality assurance protocols of HTDMAs in order to improve and ensure comparability of field measurements taken by different research groups (Duplissy et al., 2009).

Black Carbon (BC) in particles can be measured by the Single Particle Soot Photometer (SP2). The parameters determined by SP2 are BC mass concentration, number size distribution, mass size distribution and optical number size distribution (Laborde et al., 2012). In this work, 6 partners calibrated and tested the same, commercially available instrument using calibration aerosol (aqueous suspensions of fullerene soot), SOA from ozonolysis of  $\alpha$ -pinene, combustion aerosol standard (CAST soot), diesel car exhaust and an ambient sample.

#### 4) Development and testing of new instruments/chambers

Chambers have also been used for testing newly developed or otherwise unconventional instruments.

A novel off-line analytical technique for the characterization of the organic composition of primary and secondary aerosols has been developed and tested. The technique consists of stepwise heated conventional thermal-optical EC/OC analyzer coupled to Photo-Ionization Time-of-Flight Mass Spectrometer (PI-TOFMS), which provides MS fingerprints of the samples with the possibility to assign the mass signals to individual chemical compounds (Diab et al., 2015).

Butanol- $d_9$  has been shown to be a very promising universal OH tracer, which reacts only with OH and reveals no interferences with other compounds in the Proton transfer reaction mass spectrometry (PTR-MS)  $m/z$  signal (Barnett et al., 2012).

An analyzer for reactive oxygen species (ROS) was developed for both on-line and off-line ROS analyses, with a detection limit of  $1.3 \text{ nmol L}^{-1}$  and a response time of approximately 8 min (Zhou et al., 2018). A very specific and sensitive instrument based on a colorimetric reaction for measurements of ammonia was developed and tested. Detection in the liquid phase is about  $10 \text{ nmol}^{-1}$ . In the gas phase, this concentration means a detection limit of about 35 pptv (Bianchi et al., 2012).

A new off-line instrument to quantify peroxides in aerosol particles using iodometry in long path absorption spectroscopy was developed and was called peroxide long path absorption photometer (Peroxide-LOPAP). The Peroxide-LOPAP was sensitive enough to quantify peroxide concentrations in smog chamber experiments at typical atmospheric concentrations of VOC and aerosols (Mertes et al., 2012). A system consisting of a sampling device and ion chromatography (IC) with a high-resolution mass spectrometer (HR-MS) selectively separates and detects on-line several organic acids from both gas and aerosol phases (Praplan et al., 2014).

A new chamber facility ChAMBRé was designed for the research on atmospheric bio-aerosols as well as the protocols to produce, inject, expose and collect bio-aerosols (Massabò et al., 2018).

#### List of top research questions, hypotheses, recommended future steps in the field

What can the chamber community do for the needs of the indoor community?

- The chamber community can help the indoor community to understand and quantify the **atmospheric transformations** of the compounds present indoors for which the kinetic and reaction product information as well as degradation schemes is still missing. These data serve as inputs for and refinement of models.
- The chambers can be operated under conditions resembling those of indoor environments with respect to the stability and controllability of the conditions relevant for indoor environments (temperature, relative humidity) to **study separate processes** through e.g. aging. The chamber owners/operators are in possession of advanced instrumentation and know how to use it. There may be issues with the usability and movability of the instruments; some may not be suitable for typical indoor environments.
- The findings from the chamber studies are most usable as an input to *WG3: How to measure*. **Intercomparison of instruments** for various species can provide guidance for the selection of instrumentation during indoor campaigns. Chambers can be used for **calibration and intercalibration** of instruments.

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## 4. Linkage between WG2 and WG1

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### Introduction to the subtask

This subtask is dedicated to identify cross sections between scientific interests and top research questions reported by WG1 and WG2 for indoor and outdoor air chemistry, respectively. The objectives are to (i) highlight areas of research where both communities could learn from each other, (ii) identify what knowledge and expertise could be transferred, and (iii) pinpoint potential gaps in the WG reports which should be further investigated.

The main advances in outdoor atmospheric chemistry that the indoor community could benefit from have already been highlighted in the 3 previous sections and will only be briefly summarized below. In addition, a few gaps identified in these sections, which could be of interest for indoor scientists, are also highlighted and may deserve additional thoughts.

Since the field of indoor air chemistry is still at an earlier stage of development than its outdoor counterpart, it was not straightforward to identify what knowledge and expertise could be transferred to outdoor scientists and only a few suggestions are discussed below.

### Brief summary of the state-of-the-art

The idea that indoor and outdoor scientists could learn from each other has been floating around for more than a decade now. Examples of a few selected workshops, whose goals were to initiate discussions and collaborations between the two communities, are reported below:

- American Chemical Society symposium “Bringing Outdoor Chemistry Indoors” (Science & Technology, C.H. Arnaud, 88, 34-36, 2010) held in San-Francisco in 2010
- IBIAC (Interactions Between Indoor and Ambient Chemistry) workshops held in Lille in 2015 (online report, <http://www.ibiac.fr/ibiac2015>).
- Workshop held during the Indoor air conference in Ghent in 2016 (J.R. Wells et al., International Journal of Hygiene and Environmental Health, 220, 1222-1229, 2017)

These workshops highlighted that the higher level of funding provided to outdoor pollution research, approximately 100 times higher than for indoor research (IBIAC 2015), led to a rapid development of knowledge for the former. Opportunities and challenges to advance our understanding of indoor air chemistry through a transfer of knowledge and expertise from the outdoor community were identified for different topics related to the characterization of the indoor composition, gas-phase and heterogeneous chemical processes, aerosol composition and aging, and occupant exposure to indoor pollutants and health effects. A common perception in these workshops was that using the advanced instrumentation developed by the outdoor community indoors would yield important new discoveries for this environment. These tools allow, but are not restricted to, the rapid measurements of free radical species in the gas-phase, radical precursors such as HONO and ClNO<sub>2</sub>, oxidation products of complex organics such as human lipids, aerosol composition and size, new integrated metrics such as the total OH reactivity, and the composition of organic surfaces. For the latter, challenges remain for investigating the surface reactivity including the generation of

oxidants at the surface, the collection of emitted gaseous products and SOA, the characterization of oxidation products adsorbed at the surface, etc.

These workshops emphasized that while field campaigns in representative buildings would be of particular interest to advance our understanding of reactive chemical processes taking place indoors, it is not straightforward to design such campaigns due to the heterogeneity observed between buildings (nature of the building materials, light irradiation, HVAC systems, occupant related emissions, etc.). In addition, bringing the advanced outdoor instrumentation indoors requires adapting these instruments to the presence of occupants. It was recommended to (1) establish the characteristics of the “ideal” building where highly instrumented field measurements could be performed and (2) identify the species that need to be monitored based on the objectives of the study. The complementarity between field measurements and laboratory experiments was also stressed to better understand the underlying chemical processes occurring indoors. In addition, these workshops highlighted that assessing health effects based on IAQ was still challenging and requires assessment of (1) the impact of aerosol particles and radicals on the function of airway cells and (2) the impact of surfaces on indoor exposure.

## Summary of selected studies

The main documents used for this subtask are the **summary** reports provided by WG1 & 2 under this COST action, reports on the IBIAC 2015 and 2016 workshops summarized above and a few recent publications reported in Table 4.1.

Table 4.1 Recent publications cited below to highlight additional topics of interest which should be further investigated.

Topics	Titles	References
<b>Instrumentation</b>	Analytical challenges and opportunities for indoor air chemistry field studies	D. Farmer Anal. Chem. (2019) DOI:10.1021/acs.analchem.9b00277
	Autoxidation of limonene emitted in a university art museum	D. Pagonis et al. Environ. Sci. Technol. Lett. (2019) DOI:10.1021/acs.estlett.9b00425
<b>Emissions, chemical and biological processes</b>	Volatile chemical products emerging as largest petrochemical source of urban organic emissions	B.C. McDonald et al. Science (2018) Vol. 359, p 760-764
	Atmospheric chemistry of bioaerosols: heterogeneous and multiphase reactions with atmospheric oxidants and other trace gases	Estillore et al. Chem. Sci. (2016) Vol. 7, p 6604–6616 DOI: 10.1039/c6sc02353c

The following is divided in 3 sections to highlight 1) how the indoor community could benefit from the outdoor community, 2) the reverse, 3) topics that are not discussed in the WG1 & 2 reports and which may deserve to be addressed. In order to display the full picture of benefits for both communities, potential transfers of knowledge and expertise are summarized in Figure 4.1.

### 1) Transfer of knowledge, expertise and tools from the outdoor field to the indoor community

- Online instrumentation used in field studies and coupled to atmospheric chambers allowing measurements of
  - Oxidants (OH, NO<sub>3</sub>, O<sub>3</sub>) and integrated parameters of reactivity (total loss rates of OH and NO<sub>3</sub>),

- Organic compounds of various volatility (VVOC to SVOC), including highly oxidized organic matter (HOM),
- Inorganic species acting as radical precursors (HONO, ClNO<sub>2</sub>, etc.) and important for the formation of aerosols (NH<sub>3</sub>, amines, etc.).
- Simulation chambers
  - Available kinetic data on gas-phase reactions of atmospheric interest and SOA formation such as IUPAC (International Union of Pure and Applied Chemistry) or JPL (Jet Propulsion Laboratory) compilations dedicated to atmospheric studies,
  - Procedures and infrastructures for intercomparison exercises of instruments under indoor conditions to ensure that measurements are free from artefacts,
  - Conduct kinetic studies of interest for the indoor environment. For instance, a need to study the Cl-initiated oxidation of VOCs specific of the indoor environment has been identified in WG1.1 and WG1.2c,
  - Investigate changes in gas and aerosol composition of emissions from indoor activities such as wood burning and cooking.
- Field measurements & modelling
  - Knowledge related to the volatility of organic compounds and its partitioning between the gas and condensed phases,
  - Chemical processes related to the formation of HOM,
  - Large panel of chemical mechanisms: from explicit/near-explicit (GECKO-A, MCM) to reduced/condensed (Carbon bond, RACM, etc.) mechanisms,
  - Computational fluid dynamic models used to simulate air pollution on a microscale with high spatial resolution.

## 2) Transfer of knowledge and expertise from the indoor community to outdoor scientists

- Since surfaces are more prevalent indoors compared to outdoors, a significant body of literature has emerged on gas-surface interactions. For instance, studies investigating O<sub>3</sub>-surface chemistry or surface aging in the indoor environment may be of interest to assess the impact of outdoor urban surfaces (concrete, asphalt, painted surfaces, etc.) on atmospheric composition. Such surfaces could act as both sinks and sources of trace gases and aerosols and could serve as a media for chemical transformations (conversion of NO<sub>2</sub> into HONO, N<sub>2</sub>O<sub>5</sub> into ClNO<sub>2</sub>, etc.). It is still unclear whether urban surfaces could significantly impact the composition of urban air,
- Indoor emissions of volatile chemical products and their release outdoor may explain a significant fraction of the gap in emission inventories for urban VOC sources ([McDonald et al., 2018](#)). A more exhaustive characterization of indoor emissions is therefore of interest for outdoor scientists to better assess this unaccounted urban emission source,
- Biological processes leading to the consumption or the release of trace gases and bioaerosols at the surface of materials are occurring indoors (WG1.2d). The knowledge developed in this field for the indoor environment may be of interest for outdoor scientists since investigations on sources of biological aerosols and their chemical transformations in the outdoor atmosphere remains limited ([Estillore et al., 2016](#)). This topic is also of interest to better understand the PM<sub>2.5</sub> effects on human health,
- An improved knowledge on personal exposure to indoor pollutants will help the outdoor community to better assess the effect of outdoor pollutants on human health.

## List of top research questions, hypotheses, recommended future steps in the field

- Both WG1 and WG2 identified that outdoor instrumentation is more advanced and its recent use in the indoor environment already provided new insights in our understanding of indoor air chemistry. However, this instrumentation was developed for an air matrix that was less complex (number and nature of compounds, ranges of concentration and reactivity) than indoor air since the latter results from the enrichment of outdoor air with additional indoor emissions. It is therefore important to assess whether outdoor instruments are free of measurement artefacts in the indoor environment (Farmer, 2019).
- The autoxidation of organic peroxy radicals leading to HOM formation has been observed in indoor environments under suitable conditions (Pagonis et al., 2019). This chemical process is missing in WG1.1 and should be considered for the indoor environment.
- Homogeneous chemistry in liquid phase and heterogeneous chemistry (gas-surface) are not covered in WG2 while WG1 identified these processes as important for the indoor environment. Of particular interest, the chlorine chemistry in liquid phase may be important for the indoor environment (WG1.2c). It is advised to assess whether the research field focusing on liquid phase chemistry in outdoor air could be of interest for indoor scientists.
- Test chambers or test houses designed to investigate material emissions and indoor chemical processes are not covered in WG1. These are the equivalent of simulation chambers for the indoor community. It is advised to investigate the complementarity of these 2 approaches and to highlight which tool better suits particular studies.
- Molecular dynamics and ab-initio calculations have reached a degree of maturity which allows investigating gas-phase chemical reactions but also gas-surface interactions. This topic is not addressed in WG2 and only briefly mentioned in WG1. It is recommended to further investigate whether modeling studies performed at the molecular level could provide useful information for modeling indoor processes at a larger scale.
- Statistical tools such as source-receptor models (CMB, PMF) are discussed in both workgroups for source apportionment of pollutants. It is advised to assess whether exchanges of methodologies between the indoor and outdoor communities could be beneficial for both communities.

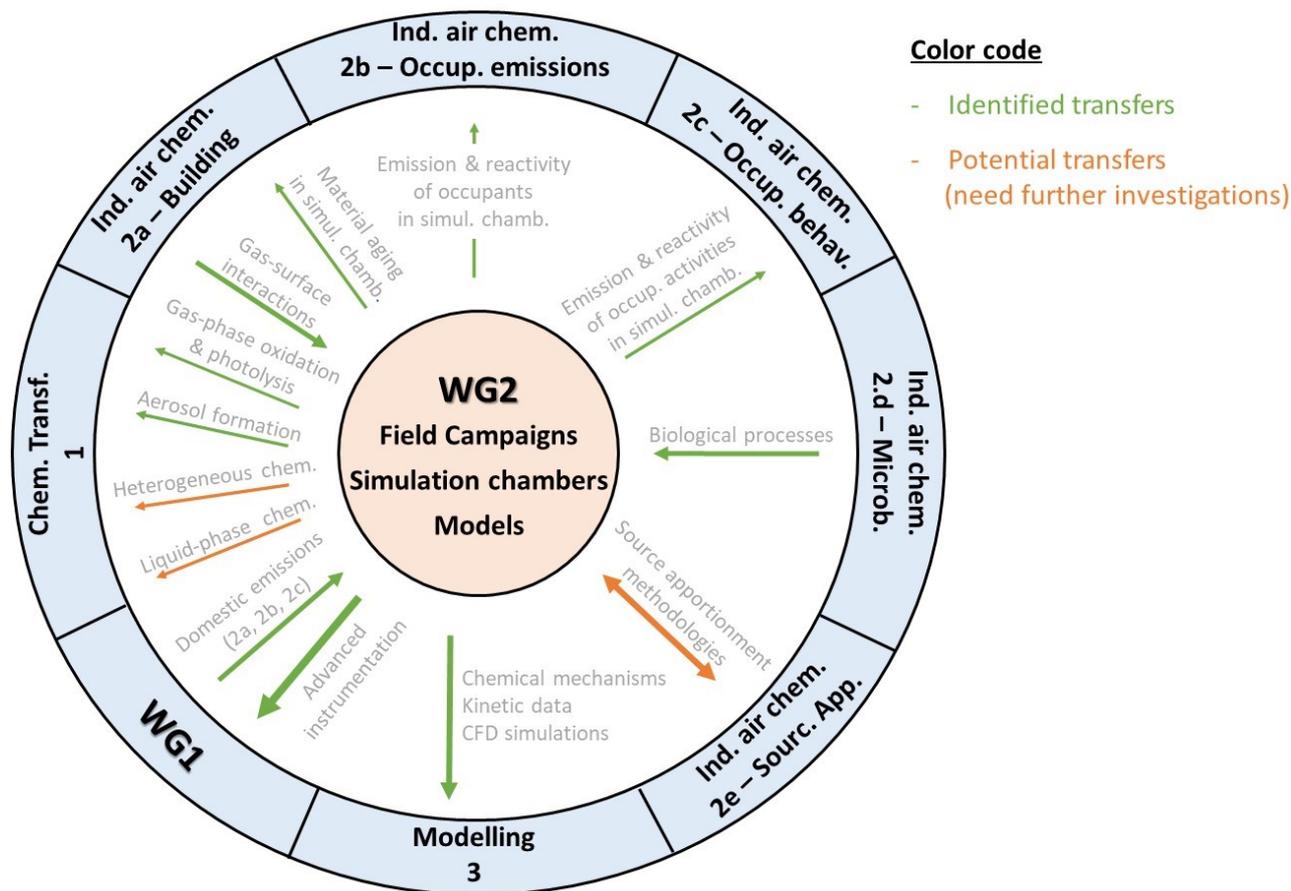


Figure 4.1 Potential transfers of knowledge, expertise and tools between the indoor and outdoor air communities.

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