

WORKING GROUP 1

**What do existing measurement
and model results reveal about
indoor air chemistry?**

Final Summary 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 summary report of INDAIRPOLLNET COST Action 17136 Working Group 1, based on review of recent literature to provide source apportionment of indoor pollutants, identify key indoor species and parameters causing uncertainties in models as well as list recommendations for other working groups.

Acknowledgements

The report was **prepared by** Gabriel Bekö, Nicola Carslaw, Patrik Fauser, Violeta Kauneliene, Sascha Nehr, Gavin Phillips, Dikaia Saraga, Coralie Schoemaeker, Aneta Wierzbicka and Xavier Querol. We would also like to **acknowledge the work** of Elena Gomez Alvarez, Noel J. Aquilina, Steigvile Bycenkiene, Nuno Canha, Regina Duarte, Emer Duffy, Sebastien Dusanter, Renata Kovacevic, Mila Ródenas García, Pawel Misztal, Aleksandar Petrovski, Ana Maria Scutaru, Milena Jovasevic-Stojanovic, Kristina Plauškaitė-Šukienė, Teresa Vera, Lenka Wimmerová, Tareq Hussein, Dunja Sokolovic and Joonas Koivisto.

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Suggested citation: INDAIRPOLLNET (2020) *Final summary report of INDAIRPOLLNET Working Group 1: What do existing measurement and model results reveal about indoor air chemistry? Deliverables of COST Action 17136 Indoor Air Pollution Network INDAIRPOLLNET.*

An editorial based on this work has been published in *Indoor Air: Bekö G, Carslaw N, Fauser P, Kauneliene V, Nehr S, Phillips G, Saraga D, Schoemaeker C, Wierzbicka A, Querol X (2020) The Past, Present, and Future of Indoor Air Chemistry. Indoor Air 30(3):373-376. doi: 10.1111/ina.12634.*

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

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Final summary report of INDAIRPOLLNET Working Group 1

Introduction

Measurements of indoor air pollutants to date have focused on schools and offices, with fewer in homes, hospitals and leisure settings and consist mostly of regulated outdoor pollutants (e.g. PM, O₃ and nitrogen oxides). Further measurements of these species are unlikely to yield major new insights. More recently, outdoor techniques have been used to measure more exotic species indoors, OH radicals initialising oxidation processes, a large range of VOCs and to detail aerosol composition. Such measurements have provided us with insight into chemical behaviour indoors and this WG attempts to review where future measurement efforts should focus. Indoor air chemistry models also exist, though validation of their results has been limited owing to the absence of the relevant measurements. Indoor models have highlighted the importance of OH and other radicals indoors, even in the absence of source activities, with predicted concentrations at the low end of those observed outdoors. We discuss how future studies can be designed to reduce model uncertainties, so major sources, transformations and losses of pollutants indoors can be better understood and appropriate mitigation strategies developed.

Key objectives

To identify species to measure indoors based on existing indoor results.

In order to achieve this objective, the following tasks were carried out through reviews of existing literature and current projects:

1. Identify key indoor gas- and particle-phase species based on existing measurements and model results. This includes measurements in buildings, but also relevant measurements from chamber or laboratory studies.
2. Provide source apportionment of indoor pollutants, both in the gas- and particulate-phases (e.g. indoor vs outdoor; human vs natural, primary vs secondary).
3. Identify parameters that cause major uncertainties in indoor air models.
4. Provide a list of recommendations for WGs3-6.

Approach

WG1 provides the background for the future work that aims towards a better understanding of indoor air chemistry and improve its representation within modelling. We summarize the relatively recent literature in order to be able to define chemical species (emissions and their transformations) that require or deserve attention in future measurements and modelling of indoor air chemistry. The aim was to build on the most recent knowledge about what occurs in indoor air and help to advance that knowledge.

The task was divided into the following subtasks/topics:

1. Chemical transformations (gas phase, surface chemistry, secondary organic aerosols, impact of moisture - hydrolysis, oxidation, role of ventilation, ...)

2. Indoor air chemistry related to the following sources:
 - a. Buildings (building materials, HVAC system...)
 - b. Occupants (human emissions, bioeffluents, clothes and their chemical transformations)
 - c. Occupant behaviour/household products (cleaning agents, electronic equipment, cooking, smoking, appliances, furnishing...)
 - d. Microbial activity
 - e. Role of particles
 - f. Source apportionment of select chemical and particulate compounds
3. Modelling indoor air chemistry (identify existing models, compare their complexity, usefulness, weaknesses, experimental validations...)

In our literature search we focused on peer-reviewed literature, primarily review articles and original papers published in the past 10 years (January 2009 – December 2018). Non-peer-reviewed literature was excluded, except government and reports published by authoritative organisations such as WHO, EPA, UN. Older landmark studies were included, especially when a particular field is not well covered in recent literature. We focused on indoor air chemistry, not necessarily indoor air chemicals alone. Purely exposure studies (studies reporting air and dust concentrations, exposure pathways, intake, metabolism, elimination and health effects) were only included to a limited extent. The literature on particulate pollution is overwhelming. We focused on the aspects most relevant for indoor chemistry and included this information in the respective sub-sections with the focus on the chemical mechanisms for indoor particulate formation.

WG1 contains several distinct scientific areas, each possibly requiring a somewhat different approach. The leaders of each subtask had the freedom to define the scope and the relevant search terms. However, for relative consistency, the following thread was proposed for the literature search:

- Use Web of Science, Scopus or Google Scholar platforms.
- Include common search terms as relevant: “indoor air”, “chemistry”, “gaseous pollutants”, “organic compounds”, “chemical transformation”
- Add specific search terms relevant for the subtask (e.g. emission, particle/aerosol, source apportionment, microbial...)
- Begin with the most recent review articles. Several reviews may be of interest, as they tend to approach a topic from various angles and have different scopes. Since WG1 needs to identify compounds, looking into specific articles cited in the reviews may have been necessary.
- Look for articles published after the reviews
- Add articles not found by the search engine, if relevant
- Focus only on non-occupational environments

Output

The following deliverables have been produced by WG1:

- Partial full report (incomplete draft from March 2019)
- Summary report including list of top research questions, hypotheses, recommended future work for each subtask/topic
- Excel file listing the most important chemical species and compounds (input to WG3), along with information on measurement location and methodologies (input to WG4 & WG5). A list of priority compounds based on the EU-LCI list (Lowest Concentration of Interest) is also included.

1. Chemical transformations

Coralie Schoemaeker

Introduction to the subtask

The subtask is dedicated to the description of chemical processes which can occur indoors. These processes have been identified by laboratory studies, indoor field measurements or modeling. Processes suspected to occur indoors from the knowledge acquired through atmospheric chemistry understanding are also considered. However, the physico-chemical boundary conditions indoors are quite different compared to that encountered outdoors. Therefore, the relative importance of the chemical processes might be different indoors compared to outdoors, due to the specific indoor environment characteristics such as high surface/volume ratio, different sources of pollutants, different temperature ranges, different light characteristics and different pollutant dispersion characteristics. The processes such as oxidation in the gas phase (from oxidants such as ozone, OH, NO₃, Cl radicals), surface processes (on or in solid materials, in the liquid phase, photocatalytic processes), a general description of the reactant sources and the products formed are described. The competition between different processes is also discussed.

Brief summary of the state-of-the-art

The chemical transformation processes of indoor gaseous trace constituents may arise from hydroxyl (OH), chlorine (Cl) and nitrate (NO₃) radical-initiated oxidation processes or from the ozonolysis of unsaturated VOCs. The main source of ozone indoors in the absence of specific equipment (e.g. photocopiers and laser printers) is from outdoors through ventilation/infiltration (Fadeyi, 2015). Ozone is known to react with a variety of unsaturated VOC to produce stable products, mainly carbonyl compounds, and are also a direct source of OH, HO₂, RO₂ and Criegees (Johnson et al., 2008). The peroxy radicals (HO₂ and RO₂) can then propagate to OH through their reaction with nitric oxide (NO). Criegees can also decompose to produce OH and more peroxy radicals.

Photolysis from natural light can also take place indoors (the impact of artificial light seems limited with our current knowledge), but at longer wavelengths compared to outdoor conditions due to the presence of windows, to produce oxidants such as OH and Cl (Gandolfo et al., 2016; Kowal et al., 2017; Wong et al., 2017; Blocquet et al., 2018). Photochemical precursors include HONO from heterogeneous reactions or combustion sources (Zhou et al., 2018; Zhang et al., 2019) or HOCl from bleach (Wong, Carslaw et al., 2017). Peroxy nitrates such as peroxyacetyl nitrates (PAN : RCOONO₂), produced outdoors can be thermally decomposed (Singh et al., 2015) and could generate RO₂ radicals when transferred into warmer indoor environments. The presence of photocatalysers or air cleaners can generate high level of HOx radicals indoors (Carslaw et al., 2017). The reaction of NO₂ with O₃ is a source of NO₃ in specific conditions (Nojgaard, 2010; Arata et al., 2018).

When oxidants are present indoors, they can react with VOCs, which have numerous sources (furniture emission, see 2a; human emission, see 2b; human activities, see 2c; microbial volatile organic compounds (MVOCs) formed by molds or bacteria, see 2d; outdoor input, see WG2 for more details). However, only unsaturated species react fast enough with OH, O₃ and NO₃ to undergo significant chemical processing (competition with air exchange). This allows us to rank the importance of species in terms of indoor reactivity with these oxidants as following: alkanes<alkenes<di-alkenes<terpenes, etc. Gas phase reactions of SVOC

may have an impact but their pseudo-first order rate constants are in the range of hours for those which have been identified and considered (Wei et al., 2017) whereas those with some terpenes are in the range of 0.1-1/h with ozone, OH and NO₃ considering respective concentration in the range of few tens of ppb, 5x10⁻⁵ ppb and few ppt. On the contrary, reactions with Cl radical are fast for most of the VOCs and can compete with air exchange.

Heterogeneous processes taking place indoors are numerous and involve interaction between the gas phase and solid or liquid phases; surfaces of indoor walls or furniture which can be covered by a water layer or soiled by organic films, human skin. As the moisture can be high indoors, it will produce water film on indoor surfaces or indoor aerosols when RH >65% (Weschler et al., 2018). The measured indoor HONO mixing ratios may vary between 2 and 25 parts per billion (ppb) (Pitts et al., 1989; Febo and Perrino, 1991; Spengler et al., 1993; Vecera and Dasgupta, 1994; Febo and Perrino, 1995; Leaderer et al., 1999; Lee et al., 2002) and are much higher than those observed in the troposphere (Febo and Perrino, 1995; Finlayson-Pitts and Pitts, 2000) due to infiltration from outdoors and several indoor sources (combustion processes). High concentrations have been measured in field campaigns (Gomez Alvarez et al., 2013; Mendez et al., 2017) and in laboratory studies on different surfaces (Gómez Alvarez et al., 2014). Interactions between aqueous aerosol and gas pollutants dissolved in it can take place in the presence of oxidant species (e.g. the chemistry of glyoxal (Lim et al., 2010)). Few studies deal with liquid-phase oxidation processes in the indoor environment. Measurements of WSOGs (water soluble organic gases, governed by Henry's law) in homes were reported by Duncan et al. (2017 and 2019), where strong variations in the carboxylic acid concentrations were observed as a function of the RH and the running of air conditioning (AC). It is not clear whether absorbed species can react in the liquid films and be oxidized by OH for instance or the impact of these reactions on indoor air. Hence, studies aimed at elucidating and quantifying this chemistry are necessary. A laboratory study focused on the role of adsorbed water on surfaces on heterogeneous reactions involving nitrogen oxides, sulfur dioxide, carbon dioxide, ozone and organic acids (Rubasinghege et al., 2013). Some products will stay in the condensed phase (oxalic acid produced by oxidation of glyoxal or acetic acid, low volatility oligomers, imidazoles,...) but VOCs can be released in the gas phase (formic acids by OH oxidation of phenols or formaldehyde). Other processes observed outdoors, such as the photochemistry at fatty acid-coated air-water interface may also occur indoors (Rossignol et al., 2016) as well as photosensitized reactions (Gomez Alvarez et al., 2012). Photo-sensitization processes have a proven role in enhancing halogen chemistry (Coral-Arroyo et al., 2019) and the generation of HONO (Monge et al., 2010; Gómez Alvarez et al., 2012; Gómez Alvarez et al., 2014; George et al., 2015; Teich et al., 2016; Cheng et al., 2016).

Oxidation on indoor surfaces can take place on clean and new surfaces or soiled ones (presence of organic films) through reactions with oxidants present in the gas phase, such as ozone or OH (Alwarda, 2018). Reaction between ozone and occupant skin involving in particular squalene (Fu et al., 2013; Heine et al., 2017), cleaning products (Nazaroff et al., 2004; Ham et al., 2011; Shu et al., 2011; Shu et al., 2012), products of combustion activities like benzo[a]pyrene (BaP) sorbed to glass producing epoxides (Zhou et al., 2017) or tobacco smoke (Petrick et al., 2011) have been identified. It has been shown that the heterogeneous reactions of ozone is strongly influenced by the material type, the environmental conditions, the soiling (Rim et al., 2009; Weschler et al., 2017; Gall et al., 2018; Shen et al., 2018; Weschler and Carslaw, 2018) and the reactive compounds involved. Secondary products of chlorine bleach mopping (HOCl) on organic films of squalene and oleic acid have been recently studied (Schwartz-Narbonne et al., 2019). It leads to the production of di- or trimeric chlorinated acids with oleic acid. The photocatalytic properties of TiO₂ containing paints used as remediation processes for NO₂ or some VOCs, such as formaldehyde, can lead to the formation of other undesirable species such as HONO, HNO₃ or other VOCs (Gandolfo et al., 2018; Mamaghani et al., 2018; Shayegan et al., 2019).

Summary of selected studies

The recent studies concerning the indoor air chemistry processes studied in real indoor environments are summarized in Table 1.

Table 1. Recent studies on indoor air chemistry processes studied in real indoor environments

Process	Conditions of field measurement	Reference
Photolysis (light characterization)	Office	Gandolfo et al., 2016
	Offices	Kowal et al., 2017
	Offices, classrooms	Blocquet et al., 2018
	Lab room	Liu et al., 2019
Gas phase oxidant measurement or oxidants precursors	Chemistry laboratory, bleach mopping, presence of HOCl	Wong et al., 2017 Gómez Alvarez et al., 2013
	Classroom, HONO and HOx formation	Mendez et al., 2017
	Classroom, impact of cleaning and air cleaner on HOx formation	Carslaw et al., 2017
	Lab room, HONO formation NO ₃ formation	Liu et al., 2019 Arata et al., 2018
Gas phase secondary products (from gas phase or heterogeneous reaction)	Dwelling, secondary species formed from cleaning	Rossignol et al., 2013
	Aircraft cabin, secondary species formed from reaction of human skin with ozone	Weschler et al., 2007
	Dwellings, ozone + carpets source of aldehydes	Morrison et al., 2002
Liquid phase/WSOG	Dwellings	Duncan et al., 2017
	Dwelling with AC	Duncan et al., 2019
	Dwellings	Duncan et al., 2019b

List of top research questions, hypotheses, recommended future steps

- **Assessing the potential for the formation of radicals and the oxidation processes in the gas phase depending on the prevailing boundary conditions in indoor environments**

The presence of short-lived indoor oxidants and their effect on the abundance of oxidation products that building occupants inhale, ingest or dermally absorb requires systematic research in the following areas:

Role of photolysis processes. Few characterizations concerning light distribution indoors and artificial light are available. For comprehensive studies on indoor air chemistry, measurements of the transmission of solar light through windows and the integration within the whole volume of a room are needed. Furthermore, the role of artificial light sources needs to be assessed. These measurements need to be coupled with radical measurements too.

Systematic studies on the Cl-initiated photochemistry are needed. The formation of Cl₂ and HOCl after bleach washing has been reported in the literature (Wong et al., 2017). Nitryl Chloride (ClNO₂) has been shown to be an important source of chlorine radicals (and NO₂) in ambient air in high polluted environments (where the concentrations of NO₂ are quite high) (Mielke et al., 2011). This species is mainly produced by heterogeneous reaction occurring on surfaces (including aerosol surfaces) and may be of importance in the indoor environment where surfaces are more important and NO₂ concentrations can be higher than outdoors due to combustion sources.

Evaluation of chemical transformations under different indoor conditions. The dominant trace gases result from infiltration of outdoor air (e.g. NO_x (sum of NO and NO₂), O₃, VOCs from outdoor sources) and indoor emission. Systematic investigations are required to assess the chemical conversion of VOCs by reactions involving gas phase oxidants (ozone, OH, Cl, NO₃) for the VOCs depending on the conditions (oxidant level, ventilation rate, representative outdoor conditions). Studies that compare the relative importance of OH, Cl, NO₃ and O₃ as oxidants and the conditions under which each of them dominates are needed. The contribution of the different reaction pathways to the formation of secondary oxidation products needs further attention in the assessment of indoor air quality (respective role of the oxidants, different NO_x regimes). For that, broader application of measurement techniques for short-lived oxidants like OH, HO₂, RO₂, NO₃, and Reactive Oxygenated Species (ROS) is needed to determine realistic and representative indoor conditions.

- **Completing the knowledge of the abundance and the concentrations of organic trace constituents in indoor air**

The incomplete knowledge of the abundance and the concentrations of atmospheric trace gases remains a major uncertainty in atmospheric chemistry and indoor air chemistry alike. The direct measurement of the OH reactivity provides the chemical reactivity that would be expected by calculation from individual trace gas measurements. This approach allows for the quantification of the chemical reactivity due to unmeasured or unidentified trace constituents. The identification of tracers of oxidation species should be considered to better quantify the role of these processes.

- **Investigating the impact of solid and liquid phase processes indoors**

Few studies are dedicated to reactivity in the liquid phase indoors and the impact of this type of reaction on IAQ has to be established (species formed, level reached indoors). Acid-base chemistry is still not well understood or studied indoors.

- **Parameterization of heterogeneous processes**

Production yields of secondary species from heterogeneous reactions are needed to better determine their role on indoor air quality. For that, we need more data on deposition rates (and for more species than just ozone) and the subsequent yield of e.g. aldehydes and HONO, for representative indoor surfaces and in real environments.

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2a. Buildings

Violeta Kauneliene

Rationale for selecting the most relevant building material related VOCs for further research

Buildings are diverse, and it is important to understand the impacts that variations in building construction, location and operation can have on indoor air chemistry (Weschler & Carslaw, 2018). The current labelling schemes have a range of requirements with respect to the number of chemicals to be quantified. A comparison of 13 schemes worldwide has identified 15 lists of target compounds, comprising a total of 611 different chemicals (Brown et al., 2013)

We suggest using the EU-LCI list (LCI: Lowest Concentration of Interest) as a background for selecting the most relevant building material related VOCs for further research. The EU-LCI values are health-based reference concentrations of chemical substances for inhalation exposure used to assess emissions after 28 days from a single construction product during a laboratory test chamber procedure as defined in the EN 16516. EN 16516 describes a European harmonized reference method for the determination of emissions of volatile organic compounds (VOC; boiling point BP 50-100 to 240-260; WHO 1989), semi-volatile organic compounds (SVOC; BP 240-260 to 380-400) and very volatile aldehydes (VVOC in general; BP <0 to 50-100) into indoor air from construction products. According to the EN 16516 the construction product is placed into the chamber under defined test conditions for temperature, air change rate (rate of ventilation with fresh air), relative humidity, air velocity in the test chamber and the amount or surface area of the material in the chamber. The specific emission rates determined using this standard are associated with application of the product in a defined reference room. The reference room has a base area of 3 m x 4 m and a height of 2.5 m. To ensure that the measurement results obtained in a test chamber are transferable to the reference room, a loading factor is set for the test chamber measurement that takes the product's intended use into account. Standardized loading factors are defined in the EN 16516. EU-LCI values apply only for VOCs originating from building products.

EU-LCI values are derived using a compilation of epidemiological and toxicological data from risk assessments published by established international and national committees and/or other relevant studies. EU-LCI are thus based on reported scientific data and expert judgment and represent concentration levels that are considered likely not to cause adverse effects over the longer term by use of the model room as a reference. The derivation of EU-LCI values is a continuous process as more data becomes available, with new compounds constantly added on the list. The EU-LCI values are currently updated annually (https://ec.europa.eu/growth/sectors/construction/eu-lci/values_en).

There are several categories of EU-LCI values:

- **Derived** (*The EU-LCI value of a compound derived de novo using the EU-LCI protocol.*) This new protocol is a health-protective, science-based and transparent procedure for assessing chemical emissions from construction products. The key study and the lowest reasonable point of departure (POD) is chosen (NOAEL/LOAEL/BMD/PBPK)¹ after thorough evaluation by the experts of the EU-LCI Working Group (WG)

¹ NOAEL: No Observed Adverse Effect Level - An exposure level at which there are no statistically or biologically significant increases in the frequency or severity of adverse effects compared to those observed in the control group
LOAEL: Lowest Observed Adverse Effect Level - The lowest dose or exposure level at which there is a statistically or biologically significant increase in the frequency or severity of an adverse effect compared with the unexposed control group.

by expert judgement. “Chronic” studies are generally preferred, except where a “short-term” study provides valuable information about an important endpoint. Human studies are preferred to animal studies, provided the study design is robust. Inhalation studies are preferred to oral studies, although the latter can be used with an appropriate route-to-route extrapolation factor applied to the derived critical dose value. NOAELs are normally preferred over LOAELs. The use of assessment factors is in accordance with ECHA² guidance for REACH³ (adjustment for exposure duration, study length, route-to-route extrapolation factor, dose-response, severity of effect, interspecies differences, intraspecies differences, sensitive population, quality of database).

The first EU-LCI list was published in 1997 in the ECA Report No. 18, so many compounds have been on the list since 1997. Some of the substances on the list may no longer be relevant as building products emissions anymore, given changes in product formulations over recent years. There is no information in Europe regarding relevance of substances emitted from building products. It should also be noted that some substances present in building products do not necessarily have to be found indoors (they may be bound in the product or reactions take place producing new compounds that may then be emitted).

- **Ascribed** (*The EU-LCI value given to a compound that has identical or very similar (differing by 20% or less) LCI values in the French ANSES and German AgBB lists (these two lists were the basis for the substances in the current EU-LCI list)*). The ‘ascribed’ values are older and based on a quite different procedure to the *de novo* protocol of the EU-LCI WG. The ascribed values will be re-evaluated in the coming years.
- **Derivation pending** are substances not yet officially incorporated into the EU-LCI due to insufficient data available (substances still to be harmonised).

Substances with derived values have summary fact sheets, providing toxicology oriented data and references. Some of substances have more comprehensive reports where information on likely concentrations indoors can also be found.

Based on the EU-LCI procedure and the needs identified in the COST INDAIRPOLLNET, suggestion for prioritising the substances are:

1. To use three main criteria: toxicity, levels indoors and reactivity.
2. Substances with lower LCI values would be more toxic. There is a suggestion to take substances with LCI values up to 300 µg/m³ for further investigation. There is no scientific justification for this limit, which was chosen as a starting point to reduce the substances for further focus to a reasonable number. The list also contains substances that are derivation pending, presuming that some are likely to be “emerging” substances.
3. Toxicity information was retrieved from the ECHA website. Special attention has been given to carcinogenic, mutagenic and reprotoxic (CMR) substances. CM substances of category 1A and 1B are not in the list since there is a prohibition to use/commercialize building products that emit above 1 µg/m³ (after 28 days). Substances classified as carcinogenic of cat. 2 and reprotoxic are evaluated on a case-by-case basis and the derivation of a LCI value is usually possible. Relevant R substances usually have LCI values (in many cases the effects are reversible). C of cat 2 usually also get a LCI value.

BMD: Benchmark Dose – The dose or exposure of a compound associated with a specified low incidence of risk, generally in the range of 1% to 10%, of a health effect, or the dose associated with a specified measure or change of a biological effect.

PBPK: Physiologically based pharmacokinetic [modelling] - Mathematical modeling of the kinetic behavior of a substance in the body, based on measured physiological parameters (Also known as physiologically based toxicokinetic modelling).

² ECHA: European Chemicals Agency

³ REACH: Registration, Evaluation, Authorization and Restriction of Chemical Substances (EU)

Only toxicity codes relevant to indoor air have been recorded (e.g., aquatic toxicity or toxic if swallowed were excluded). CLP codes indicating certain degree of CMR properties are highlighted in red in the sublist provided as part of subtask 2a.

Note: The notification obligation under CLP requires manufacturers and importers to submit classification and labelling information for the substances they are placing on the market to the C&L Inventory held by ECHA.

4. Substance reactivity has not been given special attention at this stage. It could be taken into consideration in the subsequent steps of prioritisation, especially taking into account suggestions from subtask 2a on chemical transformations.
5. Following the criteria set in the Memorandum of Understanding of the COST INDAIRPOLLNET Action (MoU), the priority should be given to novel substances over others that are quite well characterised, e.g., formaldehyde.
6. The Excel file provided as part of this subtask contains the following sheets:
 - a. The original EU-LCI list.
 - b. The sorted list with the increasing LCI values. Substances with no LCI values available yet are provided at the bottom of each chemical class.
 - c. List of substances with LCI values up to 300 $\mu\text{g}/\text{m}^3$ plus substances with no LCI values. This has been a working list and contains all additional information.
 - d. Suggested list for WG3 is largely based on previous work. Substances not available at ECHA (most likely, not on the market anymore) or not classified as toxic have been eliminated. Substances with CMR toxicity as well as substances with indoor levels typically exceeding LCI values are highlighted. Compounds for which comprehensive dossiers/reports are available are marked yellow.
 - e. CLP hazard codes are provided.

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2b. Occupants

Gabriel Bekö

Introduction to the subtask

It has been reported that the compounds associated with the presence of humans contribute up to 40% of the measured daytime VOC concentration in indoor spaces (Liu et al., 2016). In another study, human-emitted VOCs were the dominant source during occupied periods in a well-ventilated classroom (57%) together with ventilation supply air, which was the second most important source of pollution (35%) (Tang et al. 2016). Indoor non-occupant emissions constituted 8% of the pollutant mass. The total occupant-associated VOC emission factor was 6.3 mg h^{-1} per person. This report summarizes the contribution of building occupants to indoor air chemistry, via primary emissions and their chemical transformations.

Brief summary of the state-of-the-art & summary of selected studies

Primary emissions from humans: Humans emit many different organic compounds originating from sweat and sebaceous secretions from skin, breath, and intestinal gases (flatulence). Some studies measured whole-body bioeffluents, others analyzed bioeffluents emitted when breathing (exhaled bioeffluents) and through skin (dermally emitted bioeffluents) or bioeffluents from a particular part of the body, for example the oral cavity, axillae, scalp, hand, feet, and intestines. Hundreds of compounds have been identified in breath and skin emissions, some at volume fractions in the low parts per billion range (Ruzsanyi et al., 2012). Emission rates of some VOC can be higher from skin than from breath (Zou et al., 2018). The composition of exhaled breath can be considerably influenced by exposure to pollution, indoor-air contaminants and particularly by smoking (Filipiak et al., 2012). Changes in metabolism affect VOC breath and sweat composition (Pereira et al., 2015; Shirasu and Touhara, 2011). Diet is another influencing factor (Havlicek and Saxton, 2009). Dermal emissions can vary with age and sex (Gallagher et al., 2008; Haze et al., 2001; Sun et al., 2017b). The types of pollutants and their emissions also vary with differences in health condition, menstrual cycle, hygienic standards, environmental exposure or addiction to alcohol and cigarette smoking (Curran et al., 2005; Penn et al., 2007; Havlicek and Saxton, 2009), among other factors.

Ammonia is emitted from occupants' skin as well as breath (Schmidt et al., 2013). The average whole-body dermal emission fluxes of ammonia was measured to range from 2.9 to 12 mg h^{-1} with an average of $5.9 \pm 3.2 \text{ mg h}^{-1}$ per person (Furukawa et al., 2017). Ammonia emissions from humans, their variability and the underlying factors (e.g. age, diet, oral hygiene, smoking habit, health status) remain insufficiently studied.

Skin oils contain pyroglutamic acid, a natural moisturizing substance present at 1% in the human epidermis. Pyroglutamic acid does not react with gas-phase ozone, since it does not contain a carbon-carbon double bond. This chemical may be a convenient tracer of human skin oil contamination in indoor environments (Zhou et al., 2016b).

The external environment contributes significantly to the skin's chemical composition. Molecular features of skin can be matched with hygiene, diet, clothing, use of cosmetics, exposure to plasticizers or food constituents. Molecular families including constituents of personal care products (PCPs) were found on skin (Bouslimani et al., 2015). Constituents of personal care products used by occupants can contribute to occupant-related gaseous indoor pollutants. Cyclic volatile methylsiloxanes (especially

decamethylcyclopentasiloxane - D5), are abundant in PCPs (such as antiperspirants), and have been reported as dominating VOC emissions in an occupied classroom, but the emission rate declined over the course of the day as the products off-gassed (Tang et al., 2015). Emissions of exogenous compounds like terpenes or siloxanes from personal care products were indeed shown to depend on the time since their application (Stöner et al. 2018a).

Human skin and breath emissions strongly vary over the course of a day. Emotional state can also influence emissions. Small scale variances in emission rates were found to occur reproducibly over multiple screenings of the same film in a cinema. The peaks occurring in the time series of a compound during the screening of the film were induced by the physiological response of the audience to audio-visual stimuli (Stöner et al., 2018b; Williams et al., 2016). It has even been reported that crowd-based breath analyses may in the future help to assess group-based behaviour, exposure and perhaps even opinions and changes in mood (Williams and Pleil, 2016).

Occupant-related chemical transformations and their products: Human emissions can undergo chemical transformation and result in a suite of new compounds in indoor air (Weschler, 2016). These reactions occur in the presence of humans and in previously occupied spaces, as skin flakes and their constituents shed by people soil indoor surfaces. Approximately 80–90% (by weight) of skin oils contain long-chain acyl groups as free fatty acids, glycerides, wax esters, cholesterol esters, ceramides, and other species. Squalene is responsible for most of the remaining fraction (~10%) of skin surface lipids. The primary reaction is that between squalene and ozone. Ozonolysis of skin lipids is an important source of indoor VOCs and a sink for indoor ozone. Acetone, geranyl acetone, 6-methyl-5-hepten-2-one (6-MHO) (all from squalene), aldehydes, especially decanal, undecanal, dodecanal, nonanal, hexanal, octanal (from unsaturated fatty acids) are the major products (Weschler et al., 2007; Pandrangi and Morrison, 2008; Wisthaler and Weschler, 2010, Fischer et al., 2013). Additional less volatile products of ozonation of squalene include a number of long-chained polyunsaturated aldehydes and carboxylic acids, that remain bound to the surfaces of skin, hair, clothing, particles. Some products (e.g. acetone, geranyl acetone, 6-MHO, 4-oxopentanal (4-OPA)) are produced through secondary surface reactions between ozone and some of the primary squalene reaction products.

First- and second-generation skin lipid ozonolysis products were found to correlate with CO₂ and anticorrelate with O₃ (Liu et al., 2016; Veres et al., 2013). Thus, the surface reactions of aged skin lipids (during unoccupied periods) transferred to indoor surfaces may be minor compared to the surface reactions on humans and on other indoor surfaces that contain freshly transferred skin oils during occupied periods.

Human skin lipids contain long-chain unsaturated fatty acids. Ozonolysis of skin lipids via the Criegee mechanism can produce hydrogen peroxide, organic peroxides and short-lived highly reactive products including hydroxyl, hydroperoxyl and alkyl peroxy radicals. These radicals will themselves react with squalene and primary and secondary products. Dicarboxylic acids including adipic acid and suberic acid, arising from oxidation of the most common unsaturated acids, cis-hexadec-6-enoic acid and cis-octadec-8-enoic acid, respectively, were observed after exposing skin oil to ozone (Zhou et al., 2016b).

Levulinic acid, succinic acid, adipic acid, suberic acid and 4-oxobutanoic acid are the major condensed phase products remaining on the skin, clothes and other surfaces from heterogeneous ozonolysis of squalene (Zhou et al., 2016a,b). Some of these acids can partition into the gas phase. They were identified in the gas phase with their indoor concentration substantially higher than outdoors (Liu et al., 2017). 6-oxohexanoic acid and levulinic acid were observed to correlate with CO₂.

Tsushima et al. (2018b) measured the ozone-initiated transformation of organic compounds emitted from the human body in a unique stainless-steel twin-chamber that enabled the separation of dermal and exhaled emissions. The difference in product concentrations between the two chambers was smaller when no ozone was present in the chamber. More squalene and geranyl acetone was present in the chamber with dermal

emissions. With ozone, higher levels of reaction products were seen in this chamber. Acetic acid was identified in the chamber with exhaled breath in the presence of ozone.

In addition to ozone, other major indoor oxidants include hydroxyl radicals (OH) and nitrate radicals. Occupants affect the indoor air's oxidative capacity. They reduce oxidant concentrations and affect the formation of new products, including radicals (hydroxyl radicals (OH), hydroperoxy radicals (HO₂), and peroxy radicals (RO₂)) and nitrated organic compounds (Kruza and Carslaw, 2019). The reaction of ozone with 6-MHO produces hydroxyl radicals (OH), but 6-MHO rapidly consumes OH. It also reacts at a fast rate with nitrate radicals (produced by ozone reaction with nitrogen dioxide (NO₂)). However, if humans are present in an indoor setting, ozone levels are lower, resulting in lower NO₃ levels. Geranyl acetone is expected to react rapidly with OH and NO₃, producing additional 6-MHO. 4-OPA reacts with both OH and NO₃ radicals, but it is only a moderate sink for OH and a negligible sink for NO₃. Exhaled isoprene reacts slowly with ozone, but reacts more quickly with hydroxyl and nitrate radicals, forming methacrolein and methyl vinyl ketone among other products (Weschler, 2016). Moreover, when isoprene reacts with OH, alkyl peroxy radicals are formed, which can then react with nitric oxide (NO) to form organic nitrates. NO reacts rapidly with ozone, generating NO₂, but its contribution to indoor NO₂ levels is small. NO also reacts rapidly with NO₃.

Modifying factors: Changes in environmental conditions such as temperature and relative humidity (RH) can affect the types of bioeffluents emitted as well as their emission rates (Tsushima et al., 2018b). Metabolic rate and clothing changes with temperature and this can consequently affect human emissions. Moreover, at higher temperature sebum becomes soft and secretion increases, increasing volatilization and consequently the emission and reaction rate of squalene. Analogously, ozone consumption and byproduct formation on clothes are affected by various environmental factors (ozone level, RH, air change rate). The number of resident skin flora also increases with higher temperatures, RH and nutritional status of the skin.

Licina et al. (2019) review the state of knowledge regarding how clothing influences exposure to chemicals, abiotic and biotic particles, including microbes and allergens. The underlying processes that govern the acquisition, retention, and transmission of clothing-associated contaminants and the consequences of these for subsequent exposure are explored. Chemicals of concern have been identified in clothing, including byproducts of their manufacture and chemicals that adsorb to clothing during use and care. The reaction products can desorb into indoor air. Clothing acquires skin oils, which can be altered via microbial activity or react with ozone. Squalene reacts with ozone on T-shirts producing the above mentioned products (Wisthaler et al. 2005, Coleman et al., 2008; Rai et al. 2014).

List of top research questions, hypotheses, recommended future steps

- Future studies should more closely investigate the personal and environmental factors that may influence human emission, such as diet, stress level, hygiene habits, age, sex, health condition, activity level, personal care products, types of clothing worn and their laundering.
- The inter- and intrapersonal variability needs to be taken into account together with the influence of prior exposure on human emissions deserves attention. It is currently unclear how indoor air quality affects the dermal and oral emissions.
- Real-time measurements of OH, NO₃, Criegee intermediates and other short-lived, highly reactive species in occupied and unoccupied indoor environments can significantly advance our understanding of indoor air chemistry (Gligorovski and Weschler, 2013; Weschler 2016).
- Occupants remove chemicals from air via inhalation, dust ingestion and dermal absorption. Occupant presence can thus significantly reduce the concentrations of volatile chemicals and compete with other removal mechanisms, reducing the reactive capacity and decreasing the concentrations of reaction

products. It is unclear whether this removal can outweigh the production of new species caused by the presence of occupants.

- The quantification of how indoor environments change with occupancy is not well established. Occupancy leads to changes occurring on indoor surfaces. Little is known about the accumulation of the less volatile products of ozone/skin oil chemistry on indoor surfaces.
- Measurements probing the impact of occupancy on indoor air chemistry should be performed in parallel under occupied and unoccupied conditions in order to reveal potential connections between the various species of interest indoors. These should be coupled to modelling studies for further insight (e.g. Kruza and Carslaw, 2019).
- Aerosol mass spectrometry can be used to investigate the influence of occupancy on the composition of airborne particles.

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2c. Occupant behaviour, household products

Patrik Fauser

Introduction to the subtask

The overall scope of this sub-task is to advance our understanding of indoor air chemistry. Limited focus is therefore on primary emissions, with the major focus on chemical transformations, reactive compounds and reaction products.

This subtask focuses on emissions from occupant behaviour (e.g. smoking, cooking) and from household products (e.g. cleaning agents, electronic equipment, appliances, furniture, carpets, toys, paints, adhesives). Focus is on residential-, public buildings, schools and offices, not on occupational environment.

We conducted a Web of Science search from 2009 to present with the search items:

TOPIC: ("indoor air" and chemistry and (VOC or semi-VOC or organic or particle)) AND TOPIC: (emission or product or activity or cleaning or electronic or cooking or smoking or furnishing or dusting or appliances).

This gave 136 results. Some were however not relevant. In the excel sheet we have reviewed a number of these and compiled the results, with one row for each chemical and a reference, in terms of:

- Chemical/group, with CAS No., including reactants, their reaction products and the oxidants involved, such as O₃, OH, NO₃ or HO₂. Only papers describing reactions of chemicals are considered.
- Indoor use: product, activity or sink.
- Reaction type: ozonolysis, photolysis, hydrolysis, microbial degradation.
- Measurement method: Where and how was it measured (chamber, field, building)?
- Health effects, References, Comments.

Brief summary of the state-of-the-art

There are many sources of reactive species indoors including the infiltration of pollutants from outdoor air (oxidants, particulate matter, reactive volatile organic compounds) and those emitted as primary or secondary products of occupants, their activities and furnishings/building materials. Occupant behaviour (e.g. cooking, cleaning, smoking) and household products (e.g. paints, varnishes, cleaning and other fragranced products) can contribute significantly to indoor air pollution. Indoor air quality is also affected by indoor materials (e.g. carpets, soft furnishings, painted walls) that may act as sources and/or sinks of gas-phase air pollutants. Primary pollutants are emitted directly from surfaces and these pollutants can undergo gas-phase transformations or interactions at surfaces to produce secondary pollutants.

Primary sources of reactive chemicals indoors include cleaning agents and air fresheners (e.g. terpenes, sodium hypochlorite, ammonia, acetic acid), electronic equipment such as photocopiers and laser printers that can be a source of ozone (O₃), smoking, combustion appliances, cooking, and heating (e.g. nitrogen dioxide (NO₂), nitric oxide (NO), nitrous acid (HONO) and acrolein). Reactions at building and occupant surfaces indoors consume ozone resulting in the emission of volatile carbonyls, carboxylic acids and other oxidised species (Wisthaler and Weschler, 2010., Lamble et al. 2011), many of which can have adverse effects on human health or on perceived air quality. As a result there is increasing interest in secondary pollutant emissions following surface interactions indoors including materials such as carpets, furniture and painted walls (Weschler and Carslaw, 2018; Kruza et al., 2017).

Summary of selected studies

Very volatile organic compounds, V-VOCs, as categorized by the WHO (1989), are an important subgroup of indoor pollutants that cover a wide spectrum of chemicals. Some V-VOCs are components of common indoor products and activities, such as cleaning products, air fresheners and cooking, frying, and baking. Some are reactive precursors of secondary products which can be V-VOCs themselves (Salthammer, 2016).

Terpenes and terpenoids, e.g. in personal care products, air fresheners and cleaning agents are some of the most important precursors of V-VOCs. They react rapidly with ozone, producing a number of compounds as well as ultrafine particles (Yang and Waring 2016). V-VOCs such as methanol, formaldehyde, formic acid, ethanol, acetaldehyde, and acetone are products of the terpene–ozone chemistry and/or direct biogenic emissions (Salthammer, 2016; Weschler & Carslaw, 2018; Odabasi, 2008).

Acrolein is a particularly undesirable V-VOC due to its hazardous properties. It is formed by the intensive heating of food which contains glycerin. Cooking with vegetable oils generates considerable amounts of acrolein and other carbonyls leading to temporarily high concentrations of these potentially toxic chemicals indoors (Seaman et al., 2009). Cooking led to NO, NO₂, and HONO levels 20–100 times greater than background levels (Zhou et al., 2018). Furan is also formed through heating food. Furthermore, 2,3-butanedione (diacetyl) is formed from microwave popcorn (Zhang et al., 2014).

Open burning processes are among the strongest sources of emissions for V-VOCs in indoor areas (Manoukian et al., 2013). During test chamber investigations on the behaviour of burning incense sticks, Lee and Wang (2004) were able to prove the presence of V-VOCs such as formaldehyde, acetaldehyde, acetone, acrolein, propanal, methacrolein, butanal, methyl chloride, dimethyl chloride, 1,2-dichloroethene, and chloroform.

A large number of V-VOCs cannot be attributed to a particular source. This applies to typical solvents such as dichloromethane, 1- and 2-propanol, methyl acetate, 1- and 2-butanol, 2-butanone, tetrahydrofuran, 2 and 3-methyl pentane, acetonitrile, and dimethylformamide. The substances can be found in diverse chemical products used indoors such as paints, waxes, adhesives, sprays, and cleaning materials (Ayoko, 2009).

Formaldehyde is one of the most common toxic pollutants found in indoor air. Its main sources are anthropogenic. Small amounts are produced naturally by plants, animal and humans. It is formed from combustion processes or as a component of the resins used in furniture and building materials. Common sources are pressed woods and particle boards. Other significant sources include upholstery, carpeting and various plastic products. Consumer products containing formaldehyde are antiseptic and cleaning agents, cigarettes, combustion processes, cosmetics, fertilizers, electrical insulation, paints and varnishes, preserved food or from chemical reaction between ozone and VOCs released during the use of personal computers, laser printers and photocopiers. In recent years, due to health and environmental awareness and regulations, industries have significantly decreased the formaldehyde level. In homes, there are also re-emitters, which are porous products such as carpets or gypsum boards, which could adsorb formaldehyde and release it with time (Suresh et al., 2018).

Indoor materials high in organic content such as wood, carpet, fabric and paint can off-gas VOCs. These primary emissions may subsequently interact with ozone to generate secondary emissions. Household furnishings have been demonstrated to be important materials contributing to indoor air pollution with respect to ozone removal. Significant increases in carbonyl emissions (including formaldehyde, acetaldehyde, acetone, heptanal, octanal, decanal and particularly nonanal) have been reported for different carpet materials (Abbass et al. 2017), soft furnishings and painted walls (Kruza et al. 2017). Indoor surfaces can exhibit varying reactivity depending on their age or level of soiling (Wang and Morrison, 2010).

S-VOCs are important as they partition between the gas phase and indoor surfaces and form organic films. Partitioning to indoor surfaces, especially for SVOCs with log K_{oa} (octanol-air partition coefficient) between 10 and 13, provides a large reservoir of S-VOCs for both surface and gas-phase chemistry. When the original source is removed, this reservoir persists for days, months, or even years (Weschler, 2018). Lucattini et al. (2018) and Yang et al. (2017) list the main classes of S-VOCs used in consumer products: Polychlorinated biphenyls (PCBs), Polycyclic and nitro-polycyclic aromatic hydrocarbons (PAHs and NPAHs), Polyfluorinated alkyl substances (PFASs), Polybrominated diphenyl ethers (PBDEs), Brominated flame retardants (BFRs), Emerging brominated flame retardants (EBFRs), Organophosphate flame retardants (OPFRs), phthalate esters, musks/fragrances, organochlorine pesticides and pyrethroids.

Many S-VOCs have harmful effects. The reactivity of S-VOCs in the indoor environment has not been investigated in-depth here. A well-known example is the atmospheric oxidation of fluorotelomer alcohols (FTOH) resulting in perfluorinated carboxylic acids (PFCA). Both groups are found as impurities in polymer products and are used as water repellents in textiles, leather, paper, boards, lubricants, paints, lacquers and polishing materials (Liu et al., 2015; Ellis et al., 2004). FTOHs and PFCAs show estrogenic activity (Rosenmai et al., 2016).

Gaseous chlorine (Cl₂) and hypochlorous acid (HOCl) arise after floor washing with a commercial bleach solution, along with nitryl chloride (ClNO₂), dichlorine monoxide (Cl₂O), and chloramines (NHCl₂, NCl₃). The elevated Cl₂ and HOCl levels lead to enhanced concentrations of reactive free radicals, OH, Cl, and ClO that will shorten the lifetimes of gas-phase organics with subsequent enhanced rates of secondary organic aerosol formation. Bleach washing leads to enhanced oxidation rates on both applied surfaces and in the gas-phase. In addition, the uptake of HOCl onto other room surfaces has the potential to react with organics and amines present on these (Wong et al., 2017).

Commonly studied traditional water disinfection byproducts (DBP), trihalomethanes and haloacetic acids, can enter indoor air via washing machines, showers, dishwashers, and taps. Emissions are dependent on the concentration of chlorine and DBPs present in municipal drinking water (Dawe et al., 2018).

The current literature states that gas phase nicotine is expected to be rapidly removed by sorption to indoor surfaces and re-emitted during ventilation, leading to third-hand smoke exposure and to concentrations that are up to ~10% of those observed during the smoking phase indoors. Residual nicotine from tobacco smoke sorbed to indoor surfaces was shown to react with ambient nitrous acid (HONO) to form carcinogenic tobacco-specific nitrosamines (Sleiman et al., 2010). Borduas et al. (2016) suggest that the atmospheric removal of nicotine by OH radicals may compete with surface deposition and air exchange and may be a source of isocyanic acid (HNCO) in indoor air.

List of top research questions, hypotheses, recommended future steps

- Continue characterisation of pollutant deposition and reactive products generated on various indoor surfaces (e.g. carpets and furniture) will be important towards identifying or developing the most promising building and furnishing materials for improving indoor air quality. These could be zero/low emitting materials or materials that actively remove pollutants.
- Conduct field studies with a particular focus on surface reactivity and the importance of S-VOC enhanced surface films. What is the importance of S-VOCs with respect to indoor reactivity and the health implications of primary S-VOCs and their reaction products?
- Continue investigation into common occupant activities as a source of reactive species (e.g. cooking) that can generate extremely high levels of many air pollutants including VOCs (acrolein and formaldehyde

among many others), PM_{2.5} and ultrafine particles <0.1µm, in addition to cleaning activities and associated reaction products due to their potential hazardous nature.

- Move beyond ozone to investigate surface reactivity in the presence of other indoor air pollutants such as RH (and potential impact on aqueous chemistry), chlorine (e.g. from chlorinated water, cleaning) and other reactive species (e.g. free radicals, terpenes) in both unoccupied and occupied environments is recommended.
- Continue research to study the impacts of NO_x and O₃ concentrations and RH and temperature over the different reactions that can occur indoors, not only in the gas phase but also in the SOA formation. This includes understanding the interaction between different pollutants that can generate opposite effects, and where the reduction of one pollutant can increase the presence of another.

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2d. Microbial activity

Gavin Phillips

Introduction to the subtask

Microbial life is ubiquitous within buildings and is frequently the cause of indoor air quality issues and has been linked to human health effects. Microbial colonies such as moulds produce a wide variety of volatile compounds in the course of their metabolism. A range of functional moieties have been identified as being produced by microbes and a wide range of these compounds has been detected in air indoors.

Whilst there is significant evidence of biological effects of microbes on human health within buildings, the evidence of large effects on the chemistry indoors and on health of occupants is less strong with the majority of studies focused on the qualitative and quantitative analysis of emissions from microbes and not the holistic study of the effects of such emissions in an indoor chemical context.

This subtask is concerned with assessing the current state of knowledge on MVOCs (microbial volatile organic compounds) and work needed to answer questions regarding the importance of MVOCs in the chemistry of indoor atmospheres.

Brief summary of the state-of-the-art

The most recent published studies have begun to deploy real time mass spectrometric methods to the identification and quantification of MVOCs both indoors and directly from microbes in controlled conditions. These studies build on the literature, which has used off-line sampling methodologies coupled with hyphenated mass spectrometric methods indicating the huge variety of individual compounds produced by microbes. The variety of volatile compounds, coupled with the variety of building environments presents a challenge when considering the most important biological and chemical species indoors.

However, these studies still have not answered the more fundamental question “does it matter that microbes produce volatile compounds in indoor environments?” and “what is their effect on the chemistry of indoor environments?” The main functional groups reported from microbial activity are the organic acids, carbonyls, alcohols and terpenoid molecules and broadly the reported molecular families overlap substantially with those sampled in natural ambient environments. Analogous behaviour in the ambient atmosphere suggests that these compounds are chemically and photochemically active and are likely to affect chemistries both in the gas phase and on stationary and dispersed surfaces (i.e. the building itself and on the aerosol phase). We suggest that a set of well constrained experiments within realistic environments can begin to answer whether MVOCs are of significant import in general for the indoor environment.

Summary of selected studies

Microbial activity emits bioaerosols (Aleksic et al., 2017) and a wide variety of VOCs arising from primary and secondary metabolic activity of fungi and bacteria e.g. (Garcia-Alcega et al., 2017; Anne Korpi, Järnberg, & Pasanen, 2009). The importance of these emissions indoors is uncertain for reasons which include the variability of microbial colonization e.g. , species variability, e.g. (Adams et al., 2015), the extreme variety of emitted molecules (Misztal et al., 2018), the difficulty in assigning the source of volatile emissions in an

environmental context (Garcia-Alcega et al., 2017; Schleibinger et al., 2008) and the uncertain linkages between microbial metabolites and human health (Gilbert & Stephens, 2018).

A wide range of microbial species have been detected in homes globally with associated MVOCs, e.g. (Adams et al., 2015; Anne Korpi et al., 2009; Ryan & Beaucham, 2013). The commonest fungi genera *Cladosporium*, *Penicillium*, *Aspergillus* and *Stachybotrys*, and Gram negative bacteria and mycobacteria (Kelley & Gilbert, 2013; Verdier et al., 2014) with the composition of communities of fungi and bacteria being determined indoor by separate factors (Adams et al., 2013; Weigl et al., 2016). Some of the most abundant chemical species observed are the C8, C5 and C4 alcohols and the bicyclic C12 compound geosmin, such as so-called mushroom alcohol (1-octene-3-ol), 3-methyl-2-butanol and 2-methyl-1-propanol (Anne Korpi et al., 2009). Other oxygenated chemical species are commonly detected including ketones such as 2-heptanone and 3-octanone (Anne Korpi et al., 2009; Misztal et al., 2018). Pyrazines and other nitrogen-containing compounds have also been detected as MVOCs (Korpi et al., 2009).

The MVOCs emitted by microbes vary with growth substrate, i.e. building material (e.g. Ezeonu & State, 1994). Halogenated aromatics have been reported in indoor air arising from the metabolism of preserved wood, (e.g. Gunschera et al., 2004; Lorentzen et al., 2016); 2,3,4,6-tetrachloroanisole and chloroanisole congeners were detected in buildings constructed from wood preserved using pentachlorophenol. The decomposition of wood and wood products can result in the emission of organic acids: acetic acid, propionic acid, isobutyric acid, butyric acid and valeric acid have been detected in addition to ethanol, ethyl acetate and hexanal (e.g. Claeson et al., 2009; Ewen et al., 2004; Gutarowska et al., 2015; Hübert et al., 2011). MVOCs are frequently associated with “problem buildings” with monitoring following reports of odours or complaints of health issues (Ghaffarianhoseini et al., 2018). Fungal communities in damp or historical buildings with moisture problems are likely to be distinct from those found in non-damp buildings and consequently the MVOC composition will also differ in composition and quantity (Gilbert & Stephens, 2018; Wessén & Schoeps, 1996).

The human (and animal) microbiome is a major contributor to the indoor environment (Gilbert & Stephens, 2018) with recent work distinguishing the contribution to the indoor microbiome of specific sources (Wilkins et al., 2016). *Staphylococcus epidermidis* and lipophilic corynebacteria that dominate bacterial community in the axillary region of the skin produce malodorous volatile products (Kuhn & Natsch, 2009; Natsch et al., 2006; Natsch et al., 2004; Fredrich et al., 2013; Grice & Segre, 2011). Molecular signatures can be correlated with local microbial community, indicating molecular interrelations among the microbiota, human skin, and environment. Bouslimani et al. (2015) visualized the chemical composition and microbiological community composition of human skin surface.

The further chemistry of MVOCs indoors is likely to occur both in the gas phase and through reaction occurring on surfaces. Bioaerosols alone and in association with household dust (Korpi et al., 1997), in the form of viral particles, bacteria, and fungal fragments provide surface area for further chemistry in addition to possible risks of infection.

MVOCs have been studied in cultural institutions such as museums, libraries and archives as one of the major reasons of deterioration of cultural assets (e.g. Skóra et al., 2015). It has been confirmed that the presence of microbial species and their population structure is influenced by the building microclimate. A correlation between microclimatic conditions and numbers of microorganisms in the air as well as the correlation between ergosterol (ergosta-5,7,22-trien-3 β -ol) concentration and the number of fungi in the air was found. The presence of various bacteria, fungi and yeast was observed (e.g. *Bacillus* sp., *Pseudomonas* sp., *Alternaria alternaria*, *Aspergillus* sp., *Cladosporium* sp., *Mucor* sp., *Penicillium* sp., *Rhizopus oryzae* and *Cryptococcus laurentii*).

The presence of microbes is related to the concentration of respirable and suspended dusts. It was found that the concentration of respirable and suspended dusts is 2-4 times higher than the WHO-recommended

limit (Air Quality Guideline (AQG) for PM_{2.5} = 25 µg/m³) in museum storerooms. The particles within the dominant fractions of culturable fungal aerosols had aerodynamic diameters between 1.1-2.1 microns (Skóra et al., 2015). This information is important from the point of the targeted application of preservative agents and cleaning chemicals (not in a surplus dosage) as the application of biocides leads to a conflict of interests – the protection of cultural assets versus healthy conditions for museum staff and visitors (Schieweck et al., 2006).

List of top research questions, hypotheses, recommended future steps

- What is the relative VOC load from microbial activity in a “normal dwelling” during “normal occupancy”?
- What is the relative VOC load from microbial activity in a “problem dwelling” during “normal occupancy”?
- Do these levels of MVOC have a significant impact on the chemistry (and health of occupants) in dwellings?
- Beyond the fundamental question of the chemical significance of MVOCs indoors the following questions should be answered:
 - Does the variety of species indoors affect the indoor air chemistry?
 - Does the microbial processing of widely-used building materials result in significant levels of toxic volatile emissions? Therefore should materials used in buildings use components which do not result in toxic microbial metabolites?
 - What is the balance between the building biome versus the occupant biome on the chemistry of indoor environments?
- Due to the variety of emissions factors, species factors, and indoor environments globally the questions above are likely not to have definitive answers. However, a good start could be made by coordinating a network of well characterised test facilities (c.f. EUROCHAMP) with a minimum set of controlled variables in conjunction with a coupled indoor chemistry/dynamics model framework, for studying the above questions with respect to all activity types and not just the action of microbes indoors.
- Microbial activity may be individually studied by the use of standardized coupons whereby known quantities of microbes are introduced into well characterised realistic environments and the marginal effects of the microbial activity can be measured and the effects scaled beyond the particular case.

Table 2. Reported functional groups from microbial activity indoors.

Function group (example)	
Organic acids	Terpenoids
Carbonyls	Lactones
Alcohols (1-octen-3-ol)	Furans and furanones
Amines	Sulfur-containing
Esters	Amino acids
Ethers	Halogen compounds

Table 3. Example of the variety of MVOCs associated with or emitted from one species of microbe (*A. versicolor*)

Molecules Detected	Method of Detection	Reference
heptane, <i>N,N</i> -Dimethyl-heptadecylamine, phenol, 2-methyl-5-(1-methylethyl), 1-octen-3-ol, 3-octanol, 3-octanone and 2-methyl-5,12-dithianaphtho{2,3- <i>b</i> }quinoxaline.	SPME and GCMS	Bingley et al., 2012
2-ethyl-1-hexanol, 1-octanol, 1-octen-3-ol, 2-pentanone, 2-hexanone, 2-heptanone, 3-octanone, alpha-pinene, beta-pinene, camphene, limonene.	GCMS	Pasanen et al., 1997
3-methylfuran, 2-methylfuran, 2-pentanol, 3-methyl-2-butanol, 3-methyl-1-butanol, Pyrazine, 2-methyl-1-butanol, 2-butanone oxime, 1-octen-3-ol, 3-octanone, 3-octen-2-ol, 3-octanol, 2-octanol, 2-n-pentylfuran, 2-ethyl-1-hexanol.	GCMS with selected ion monitoring	Schleibinger et al., 2008
1-Octen-3-ol, 3-octanone, α -pinene, β -pinene, camphene, terpinolene, 1,3-dimethoxybenzene, 4-Methoxystyrene, δ -deca-2,4-diene-lactone, 1,6,7-trimethylnaphthalene (identified by MS only), ethylbenzene, <i>m</i> -xylene, 2-methylisoborneol and derivatives, 1-heptanol, 4-methylanisole, (<i>Z</i>)- β -ocimene, terpinolene, daucene, α -chamipinene, cyperene, β -cedrene, isobazzanene, (<i>E</i>)- β -farnesene, β -acordiene, γ -curcumene, α -zingiberene, α -himachalene, β -himachalene, isodaucene, α -chamigrene, cuparene, α -cuprenene, β -bisabolene, β -sesquiphellandrene; dauca-4,8-diene, <i>trans</i> - α -bisabolene.	GCMS	Polizzi et al., 2012
pentane; 2-methylpentane; heptane; octane.	GCMS	Wilkins et al., 2000
3-Methyl-1-butanol, 2-methyl-1-propanol, 2-heptanone, 2-hexanone, terpineol.	GCMS	Gao et al., 2002
2-Ethylhexanol, Isoprene, Limonene, Camphor. 1,3-Octadiene, 1-Octen-3-ol, 2-Methyl-1-Butanol, 2-Methylfuran, 3-Methylfuran, 3-Methyl-Butanol, 4-Heptanone, 2-Methylisoborneol, 2(5H)-furanone, 2-Heptene, 3,5-Dimethyl-2-Cyclohexen-1-one, 3-Ethyl-3-hexene, Diisobutyl phthalate, Dimethyldisulfide, Isobornyl acetate, Methoxy-benzene, O-Hydroxyphenyl, Trans 2-octene	GCMS	Moularat et al., 2008
2-Pentanol, 1-Octen-3-ol, 3-Octanol, 2-Ethyl-1-hexanol, 1,3-Octadiene, 2-Pentanone, 3-Octanone, 5-Ethyl-4-methyl-3-heptanone, 1,3-Dimethoxybenzene, Trimethylnonanoic acid methylester, 2-Heptanone, 2-Nonanone, 2,6-di-tert-Butyl-p-benzoquinone and sesquiterpenes.	SPME and GCMS	Matysik et al., 2008
Methoxybenzene, 1,2-Dimethoxybenzene, 1-(3-Methylphenyl)-ethanone, 6-Methyl-2-heptanone, α -Curcumene, α -Humulene-like, α -Muurolene, Myrcene, 3-Methyl-1-butanol (isopentanol), 2-Methyl-1-butanol, 1-Octen-3-ol.	GCMS	Fischer et al., 1999

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2e. Role of particles

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Introduction to the subtask

Airborne particles form an integral part of an indoor air chemistry, and a large proportion of them have to be viewed as a system where dynamic changes between gas and particle phase chemicals take place continuously (Salthammer et al., 2018; Morawska et al., 2013; Lucattini et al., 2018). Airborne particles in indoor environments originate from 1) infiltration of outdoor pollution particles with a wide range of origins; 2) emissions from indoor sources (e.g. combustion sources such as cooking, tobacco smoking, candles burning; resuspension of settled particles), 3) new particle formation from the interaction of gas phase precursors of both indoor and outdoor origin. Regarding the dynamic gas/particle phase interactions indoors, airborne particles can form 1) a sink for gas phase compounds in indoor air, when they adsorb on existing particles (e.g. SVOCs, H₂O) or when new particles, i.e. secondary organic aerosols (SOA), are formed due to reaction of two gas phase compounds (e.g. terpenes and O₃); or 2) a source for gas phase compounds (when compounds desorb from particles' surface (e.g. SVOCs, ammonium nitrate); 3) a substrate for heterogeneous chemistry processes, sometimes leading to degassing of resulting reaction products. Partitioning between particle and gas phase is influenced by ambient conditions (e.g. T, RH, air concentration gradient) (Nazaroff 2004; Lunden et al., 2003; Benning et al., 2013; Wu et al., 2017; Lazarov et al., 2016).

Particles in indoor air are strongly influenced by both physical and chemical processes which change their chemical composition, physical characteristics and concentration in the air (Morawska and Salthammer 2003; Morawska et al., 2013; Thatcher et al., 2003; Nazaroff, 2004). Some of the processes that affect particles concentration and characteristics are 1) presence of active indoor sources (cooking, candles, cleaning), 2) size dependent infiltration of outdoor particles indoors, 3) deposition of particles on indoor surfaces and their subsequent contribution to reactions taking place on indoor surfaces, 4) resuspension of particles deposited on surfaces, 5) removal by ventilation, 6) airing and cleaning practices. Infiltration, deposition, resuspension and exfiltration are strongly size dependent. For example, deposition of particles smaller than 100 nm increases with decreasing size due to diffusion, for those larger than 500 nm deposition increases with increasing particle size due to gravitational sedimentation; while those between 100 and 500 nm display lower deposition i.e. they remain airborne longer (He et al., 2005; Howard-Reed et al., 2003). Below we supply a short review of how particles are measured and analysed, from the most classical offline to the modern online chemical speciation tools.

Brief summary of the state-of-the-art & summary of selected studies

Offline measurements of aerosol levels and composition are usually done using conventional samplers fitted with different size cut off inlets and with impactors and subsequent analysis (Morawska et al., 2013; Turner and Colbeck, 2008; Weisel et al., 2005; Turpin et al., 2007, Amato et al., 2016, among many others). These measurement techniques provide mass concentration values. Additionally, online measurements of PM levels is carried out indoor by using a large variety of optical methods that indirectly calculate the mass concentrations of different PM size fractions. Other methods such as beta-attenuation, or tapered element oscillating microbalance (TEOM) are also used but are more common outdoors than indoors. The size

detection limit of the optical measurements for particulate matter (PM) is usually 300 nm. To measure levels of ultrafine particles (UFP) or total particle number concentration (PNC, dominated by UFP according to Wichmann et al., 2000 and Kumar et al., 2010, among others) other instruments have been used in indoor measurements. Examples are the Condensation Particle Counters (CPCs) (Afshari et al., 2005) to characterise UFP indoor sources in chamber studies, Nanotracer (Bekö et al., 2013) to identify major indoor sources of UFP; P-Trak (Kearney et al., 2014) to measure indoor infiltration; and Disc-mini (Reche et al., 2015) to evaluate levels and sources of UFP in schools; among others. To measure size segregated levels of PNC, Scan Mobility Particle Sizer (SMPS) or Fast Mobility Particle Sizers (FMPS) have been used (see Wierzbicka et al., 2015 and Talbot et al., 2017; and Soppa et al., 2014, respectively, among others). It is important to note that several of the above studies find nucleation of particles (new particle formation, NPF) to be a relevant indoor process affecting level and composition of particles. Although SMPS and FMPS might be able to provide evidence of the occurrence of these nucleation episodes-and, if it is the case, growing of newly formed particles, or shrinking of coarser particles- it is important to note that many of these instruments have a lower and upper size detection limit close to 10 and 500 nm, respectively. Thus, in order to measure finer particles (1-5 nm) generated from NPF, the Particle Size Magnifier (PSM) is used (Vanhanen et al., 2016). Accordingly, in order to appropriately monitor the whole range of particle sizes, simultaneous measurement with PSM/AIRMODUS, SMPS/FMPS and APS/OPC should be performed.

A number of studies have been carried out to characterise mass concentration and chemistry of quasi-UFP (with a coarser size limit from 250 to 500 nm) using Berner, Nano-Moudi or Sioutas impactors (Arhami et al., 2010, Li et al., 2018, among others). These are adequate for metals, elemental carbon (EC), and a number of organic and inorganic species, but significant sampling artefacts might take place for the semi-volatile ones.

For chemical characterisation of particles, while informative and needed, the above offline methods do not allow insight into time-resolved changes in chemical composition or differentiation between the composition of the core of the particles and their coating. Modern online X-Ray Fluorescence (XRF) instrumentation allows the determination of elemental composition of PM_x with less than 1 h resolution, but these instruments are not usually used in indoor air, being more common in outdoor studies (see e.g. Furge et al. 2017). Multi-Angle Absorption Photometers (MAAP) and Aethalometers have been used to measure black carbon (BC) indoors as an indicator of road traffic infiltrated pollution, and combined with UFP to distinguish primary UFP from road traffic and secondary ones (Rivas et al., 2014; Reche et al., 2014 and 2015). Semi-real time aerosol analysers have been used to determine concentrations of some inorganic gaseous pollutants and soluble aerosol ions (Particle into Liquid Sampler (PILS) and Monitor for AeRosols and GAses in ambient air (MARGA), for example) but these are also used only in outdoor air studies (see Twigg et al., 2015).

In the last fifteen years great developments have taken place on new instrumentation capable of yielding online information on chemical composition of the inorganic and organic fractions of particles. Thus, real time aerosol mass spectrometry (AMS) currently allows determination of time and size resolved chemical composition of non-refractory components airborne particles. Thanks to the Aerosol Mass Spectrometry (AMS) technique substantial advances in understanding the aerosol transformations and atmospheric processes have been achieved, although indoor studies are still scarce. Examples are the use of High Resolution Time of Flight Aerosol Mass Spectrometry (HR-ToF-AMS) to characterise the chemical profiles and SOA formation of different types of cooking (He et al., 2010.; Klein et al., 2016, Liu et al., 2017), in some cases comparing results from the AMS with Proton Transfer Time of Flight Mass Spectrometry (PTR-ToF-MS) or vacuum ultraviolet single photon ionization ToF-MS (VUV-SPI-TOF-MS). These studies measured mass spectra profiles, which were dominated by ions from alkanes, alkenes, and long-chain fatty acids. They evidenced, when cooking with herbs, large emissions of mono-, sesqui- and diterpenes, various terpenoids and p-cymene, which are very reactive and upon aging can lead to SOA formation; and a high SOA formation rate after monoterpene and terpenoid emissions from frying with spices under excess O₃. However, emissions rates of primary organic aerosols (POA) were higher than their production rates of SOA. Stir-frying spices increased emissions of aldehydes. AMS has been also used to study transformation of outdoor particle

components upon transport indoors in non-occupied residences (Johnson et al., 2016; Talbot et al., 2016, 2017; Avery et al., 2019). Similar proportions of chemical species indoors and outdoors during non-occupancy time was observed (important to note, no indoor active sources were present at the time of the measurements). Seasonal differences i.e. winter and summer in I/O ratio of chemical species was observed. The use of AMS coupled with PTR-MS technique(s), provides a powerful tool to determine gas-particle partitioning and fate and behavior of different species both in gas and particle phase in indoor air.

Use of positive matrix factorization (PMF) on real time characteristics of particle chemical composition determined by AMS has proven to be successful for source apportionment of outdoor particles. So far, knowledge about mass spectra signatures for specific indoor sources is very limited. Creating a library of mass spectra of different indoor sources (on the basis of experimental studies) can open up new possibilities for source apportionment especially in typical situations in indoor environments when several sources co-occur and are difficult to discriminate. Lately, the Aerosol Chemical Speciation Monitor (ACSM) (a simplified version of AMS) also allows performing interesting studies without size resolved analysis of the non-refractory aerosols at lower cost and enables operation during long time periods. The combined use of AMS or ACSM in combination with offline organic speciation can be quite useful for source apportionment studies when there is no information about indoor or outdoor sources and hence a library of m/z profiles is not available. However, AMS and ACSM only measure non-refractory PM and cannot provide information about the chemical composition of the nucleation mode particles. They are more appropriate for the aiten and accumulation mode aerosols. Thus, it is always convenient to have simultaneous measurements of PM mass and BC.

Chemical Ionization Atmospheric Pressure Interface Time-of-Flight Mass Spectrometry (CI-API-ToF-AMS) is a valuable technique to obtain information of the composition of the ion clusters leading to NPF events, but until now these studies have only been done outdoors (Riva et al., 2019 and references therein).

Theoretical and modeling of Semi-Volatile Organic Compounds (SVOCs) partitioning between gas and particle phase has been described by Pankow (1987, 1994), Weschler (2003), Weschler and Nazaroff (2008, 2010), Liu et al. (2012, 2013), Cao et al. (2017), Salthammer and Goss (2019). The particle/gas partition coefficient, K_p , plays an important role and affects the fate and transport of SVOCs. Studies that experimentally determine K_p are very limited especially for SVOCs, which are of interest in indoor environments. More information is available on K_p for compounds important for atmospheric processes and modelling. The few studies that address experimental determination of SVOCs emissions (phthalates esters examples), uptake on particles and K_p determination are Benning et al. (2013), Wu et al. (2017), Lazarov et al. (2016). It has been confirmed that the presence of particles affects gas/particle equilibrium of SVOC in the air and increase their emissions from building materials (shown on examples of di-2-ethyl-hexyl-phthalate (DEHP) emissions from vinyl flooring, (Benning et al., 2013; Wu et al., 2017), and Tris (1-chloroisopropyl) phosphate (TCIPP) from polyisocyanurate insulation boards (Lazarov et al., 2016)). Several parameters influencing SVOCs uptake on particles remains unclear, namely how uptake is influenced by number concentration and size of particles, their chemical composition and surface area.

To study the gas/particle partitioning, some studies have used PTRMS and AMS with online derivatization simultaneously, thermal desorption aerosol gas chromatography (SV-TAG), and Filter Inlet for Gases and Aerosol - Chemical-Ionization-Mass Spectrometry (FIGAERO-CIMS), the latter allowing to obtain real-time measurements of speciation of the volatile and particle phases (see the project HOMEChem: House Observations of Microbial and Environmental Chemistry, Farmer et al., 2019). Furthermore, to study the source (indoor or outdoor) of the volatile and particulate species, a number of studies used automated inlet switches allowing the air to be alternatively sampled from outdoors and indoors (e.g. Talbot et al., 2017).

Towards understanding health effects due to exposure to particles. Oxidative reactivity measured as reactive oxygen species (ROS) is used as a marker of particle toxicity. Several studies have shown that ROS can lead to oxidative stress, which may lead to adverse health effects (Bates et al., 2015). Numerous studies on ROS

production from ambient aerosols exists, and some have shown that organic aerosol (OA) contributed to the majority of the ROS production (Lin et al., 2011; Verma et al., 2015; Bae et al., 2017; Dou et al., 2015). Organic aerosols (OA) are abundant in indoor environments, but studies on ROS from indoor aerosols are not available. Additionally, coating of particles with low volatile organic compounds seem to change their oxidative reactivity (Zhao et al., 2018), which again seem to be an important aspect to address processes occurring in indoor environments. Epidemiological studies could help to understand the problem of exposure to indoor aerosol components especially those increasing the OA concentration. To this end, ACSM instruments are very useful since they can work on a continuous basis for up to a year.

List of top research questions, hypotheses, recommended future steps

- Study of the factors influencing SVOC uptake on particles, e.g. influence of number size distribution, chemical composition of particles, environmental parameters, experimentally determined Kp for SVOCs
- Source apportionment results of size-resolved particle concentrations.
- Characterization of indoor processes and sources yielding to new particle formation, and growth and decrease of particle size.
- Determination of particle and gas phase chemical composition, as well as size resolved particulate emission factors for specific indoor sources on the basis of laboratory studies using PTRMS and AMS in parallel
- Determination of mass spectra/signatures for individual indoor sources and creation of open access mass spectra library to enable source apportionment studies
- Study of the physicochemical characteristics (chemical and size resolved parametrisation) of particles upon infiltration
- Determination of chemical transformations/aging/formation of secondary pollutants in indoor air when outdoor and indoor air pollutants in gas- and particle phase mix
- Assessment of the oxidative reactivity of particles from specific sources and their mixtures under laboratory conditions and comparison with measurements in occupied real indoor environments; assessment of the effect of particle coating

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2f. Source apportionment

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Introduction to the subtask

Source Apportionment (SA) is the practice of *deriving information about pollution sources and the amount they contribute to the air pollution concentrations*. Receptor models apportion the measured mass of an atmospheric pollutant at a given site (receptor), to its emission sources by using multivariate analysis to solve a mass balance equation (Belis et al., 2014). Nowadays, tools have been developed with improved capabilities in terms of source resolution and the accuracy of source contribution quantification. Positive Matrix Factorization (PMF), Chemical Mass Balance (CMB) and Principal Component Analysis (PCA) are among the receptor models most frequently used.

Although the number of applications of SA for the outdoor air has been increasing steadily, comparatively few studies have attempted to estimate the contribution of specific sources of indoor pollutants using SA techniques. While the major indoor sources have been identified, comparatively little is known about the chemical nature of associated airborne emissions, especially particle-phase and vapor-phase organic compounds. Furthermore, indoor pollutant concentrations can be further affected by outdoor-generated pollutants penetrating indoors. *Thus, source apportionment of indoor air pollution is challenging because indoor air pollution is controlled by both indoor and outdoor sources, ventilation, outdoor meteorology and long-range transport of pollutants* (Uhde and Salthammer, 2007).

Brief summary of the state-of-the-art

Literature indicates that more than 70% of the indoor SA studies have been performed and published during the last ten years. 45% of them were conducted in Europe, 37% in Asiatic countries, 12% in USA, Canada and S. America while 6% in Africa and New Zealand. Regarding the examined indoor environment, 51% of them have been conducted in residential buildings, 24% in schools and university buildings and 10% in office buildings. In addition, 4% of the studies refer to elderly care home, 2% to hospitals and 2% to restaurants and bars. A limited number (<8%) of indoor SA studies have examined microenvironments of special characteristics, including aircraft cabins, plant facilities, churches, and subway stations.

A literature review on the indoor air pollution source apportionment studies has been performed. In particular, from the 72 publications found through Scopus, Web of Science and Google Scholar platforms, 57 were relevant to our review criteria: (a) residential, school and office environment-targeted studies (b) studies of the last decade (1/2009-12/2018).

Based on our review, the ratio of studies having coupled indoor and outdoor measurements to those having only indoor measurements was 50%-50%. A part (13.8%) of the experimental campaigns included also air pollutants monitoring at the breathing height (personal exposure). 38.4% of the studies included sampling during two or more seasons.

The majority of the studies (69%) have used *particulate matter (PM) chemical composition or size distribution* as tracers to apportion PM concentrations to their potential sources. The chemical species used as tracers for the PM source apportionment are ions (in 19% of the studies), metals (35%), organic/elemental/black carbon (24%), PAHs (12%), water-soluble organic compounds (WSOC) (6%), levoglucosan (3%), organic acids

(1%). The rest of the studies (31%) have performed source apportionment on volatile organic compounds, carbonyls and aldehydes.

Regarding the SA method used, the majority of studies have used PCA (32%), PMF (28%) and CMB (12 %). Absolute Principal Component Scores (APCS), Multilinear Regression and Factor Analysis have been used in 5%, 4% and 3% of the studies, respectively. Finally, a non-negligible percentage of the publications, have reported that Enrichment Factors (EF) have been used for source apportionment purposes, usually combined with the application of a receptor model. Studies that have used CMB models for indoor source apportionment were based on the a priori knowledge of the source profiles (Lai et al. 2019; Arhami et al., 2010; Kopperud et al. 2004). The overwhelming majority of them focus on PM. The main strength of the CMB model is that, unlike other statistical receptor models, it does not require a large input dataset. Moreover, unlike factor analysis techniques, the CMB output does not require additional identification of the contributing sources/factors, as the profiles are selected *a priori* for well-defined sources. It is not necessary to perform repeated measurements at a sampling location. The model solves for the source contributions while explicitly accounting for simultaneous indoor and outdoor sources of each species. On the other side, the lack of composition data as well as the local (outdoor) or specific (indoor) source profiles is a significant limitation for this approach selection. Due to CMB limitations, studies using PMF and PCA methods for indoor SA are more numerous, while being targeted to both PM and VOC apportionment. Another advantage of MPF and PCA models is that by combining several microenvironments, all observations can be put into one large model. This can be important in studies involving time-consuming sampling strategies (e.g., parallel outdoor, indoor, and personal exposure sampling), where the number of sampling days is a limiting factor or in large scale studies where a large number of similar indoor environments (e.g. offices, schools) is targeted (Molnár et al., 2014; Campagnolo et al. 2017). However, there is a principal limitation with regard to the application of PMF and PCA on indoor data as indoor activities vary between different buildings. Thus, the actual composition profile of indoor-generated pollutants is strongly variable from building to building, and even from day to day within one building. *This variation violates the basic assumption of PMF modeling that source profiles are stable over time*, and such variation cannot be correctly modeled by two or three factors. For this reason, the modeling of indoor as well as personal data must be regarded with caution.

The number of sources identified in each SA study ranged between 2 and 13. It is remarkable that the overwhelming majority of the studies reveal the presence of the outdoor environment within the identified sources indoors. To be more specific, the outdoor environment is represented by 1-7 distinguished outdoor sources (e.g. vehicle emission, combustion-related sources, crustal sources, secondary aerosol, industrial emissions, sea salt) which contribute with $51\pm 27\%$ in total to the measured pollutant (e.g. PM or VOC) indoors. The absolute (or relative) contribution of the *outdoor sources*, may differ between the studies due to local and regional conditions, e.g. vehicle fleet composition, building types and ventilation, climate, season, and industries nearby the sampling stations. It is therefore hard to make quantitative comparisons between studies from different locations, but qualitative comparisons can be helpful especially during the factor identification process.

The type of indoor sources identified is certainly dependent on the selection of the chemical species to be used as tracers for the SA methods. As a general picture, 35% are grouped as *building materials and furniture emissions* (including paints, adhesives, floor/wall/ceiling coverings, insulation foam), 22% as *combustion-related sources* (including smoking, fireplace/wood/charcoal burning, incense/candle burning, diesel/kerosene stoves emissions), 13% as *cooking-related sources* (including cooking in general, frying and toasting), 13% as *resuspension sources*, 11% as *cleaning and consumer products emissions* (household cleaning products, fresheners) and <6% as other products and activities emissions. It is noticeable that in 25 out of 57 publications, two or more sources were presented as combined or mixed sources, as their distinction was not possible from the models. This happens when the component used as a tracer corresponds to more than one group of sources.

Although nowadays, UFP or total particle number concentrations (PNC) are very often measured in indoor studies because of the high health impact potential of the UFP, and the fact that indoor emissions and aerosol processes might have a larger impact on PNC than in PM mass concentrations, the number of studies on source apportionment of size-resolved UFP is very scarce in indoor environments. These have been done based on chemical databases obtained from impactor-sampling and off-line analysis (Arhami et al., 2010), and measurement of total PNC and with activity reporting being able to apportion contributions of specific processes (Bekö et al., 2013), among others. However, receptor modelling of UFP or particle size distributions is commonly applied in outdoor environments by using, in addition to the above methods, three additional approaches. The first is based on the use of BC and PNC data to apportion the primary contributions to total PNC by primary traffic emissions versus (Rodriguez and Cuevas, 2007); the second is the use of cluster analysis to apportion the contributions to ambient size segregated PNC (Beddows et al., 2009); and the third the use of PMF and PCA for the same purpose as the latter (Harrison et al., 2011; Pey et al., 2009). There is a need to implement such studies indoors.

Summary of selected studies

The literature review resulted in a number of outcomes that future source apportionment studies should take under consideration. The type of indoor source identified is certainly dependent on the selection of the chemical species to be used as tracers for the SA methods. Indicatively, for the resuspension related sources, metals of crustal origin (Mg, Cr, Cu, Ba, Ni, Ca, S, Al, Fe, Mn) were used as tracers (Suryawanshi et al. 2016; Tunno et al. 2016; Taner et al., 2013). The combination of specific VOCs, PAHs, ions and metals (e.g. acenaphthene, phenanthrene, benzo(a)anthracene, chrysene, hexane, benzene, cyclohexane, heptane, toluene, nonane, 1,3,5-trimethylbenzene, decane, Fe, K, Mg, Na, sulphate, Mn, Ni, Cd, Sn, Ce, Ba) have been used for identifying combustion related sources, including smoking (Chen et al. 2017; Suryawanshi et al. 2016; Romagnoli et al. 2016; Tunno et al. 2016; Clougherty et al., 2011). VOCs and aldehydes (e.g. toluene, trimethylbenzenes, n-octane and n-nonane, 4-methyl-2-pentanone, n-butyl acetate, tetra-chloroethylene) have been mainly used for assigning the resolved sources to building materials and consumer products emissions (Huang et al. 2018; Suryawanshi et al. 2016; Poulhet et al. 2014; Shin and Jo 2012).

Indoor air chemistry is expected to be reflected in source apportionment approaches. Several monitoring studies have already shown that ozone-initiated reactions with emissions from consumer products (Sarwar et al., 2004), building materials (Aoki and Tanabe, 2007), and cleaning products lead to SOA formation in indoor environments. Moreover, indoor WSOC is also impacted by primary sources such as organic acids from cleaning and other consumer products. Through a SA approach, Campagnolo et al. (2017) have recognized as indoor sources of ozone-reactive compounds in an office environment, the occupants themselves, soft wooden-based materials (e.g., flooring and oriented strand boards), carpets (with latex backing), cleaning products and air fresheners, natural rubber adhesives, photocopier toner, printed paper, soiled fabrics, soiled ventilation filters, personal care products. This source had significantly higher contribution during summer campaigns as the greater ultraviolet radiation in summer caused higher ozone concentrations that led to ozone-initiated reactions involving ozone-reactive compounds and the formation of oxidation products. The formation of secondary particles in indoor environments from reactions of household products with ozone and hydroxyl radicals was also reported by Zhu et al. (2012), who remarked that there was a higher contribution of secondary aerosol indoors than outdoors in summer.

Of the few studies done on source apportionment of UFP it is relevant to highlight the high contributions from candles to total PNC in 56 Danish homes (Bekö et al., 2013) and the high contribution to indoor PM_{0.25} from road dust emissions (Ahmri et al., 2010).

List of top research questions, hypotheses, recommended future steps

The literature review revealed a number of research questions regarding indoor air pollution source apportionment to be answered by future studies:

- How can indoor air chemistry influence SA model applications? Which assumptions should be taken? How can the constraints of indoor measurement datasets be overcome (e.g. unstable source profiles over time)?
- Is receptor modeling application independent of derived or measured values of decay rate, air-exchange rate and penetration factor? What is the role of ventilation?
- How important are the simultaneous outdoor measurements for an indoor source apportionment study? Can we distinguish the outdoor source of certain VOCs with confidence?
- What are source contributions to indoor UFP or PNC?
- What are the sources contributing to indoor NPF bursts?
- How important is the unapportioned fraction of pollutants?
- How reliable is the on-line source apportionment based on low-cost sensor networks?
- Do we need to define basic guidelines for SA in indoor environments and how should this be approached?

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3. Modelling indoor air chemistry

Nicola Carslaw

Introduction to the subtask

The previous sub-sections have demonstrated that an increasing number of indoor air pollutant measurement techniques are becoming available. However, they are still unable to measure indoor air pollutants at sufficient temporal frequency, with the required specificity, or in a wide enough range of buildings, to provide a broad and representative understanding of chemistry indoors. The development and use of indoor air models is, therefore, a substantial requirement for understanding indoor air chemistry and to allow us to evaluate the impacts of indoor air pollution on human exposure.

Indoor air chemistry models need to include the important sources and sinks of pollutants within a building envelope, such as chemical reactions, material emissions and surface interactions, human emission and activity (e.g. cleaning, cooking), exchange of pollutants with outdoors, or transport of pollutants within/between different zones of a building. Field and laboratory measurements help to develop model frameworks to improve chemical mechanisms or provide more accurate input parameters for models. In turn, modellers can help to design future experiments that are needed to further improve understanding. This chapter will identify existing models and briefly discuss their main features, comment on their complexity, usefulness and limitations and the potential for undertaking evaluation by comparing to experiments.

Brief summary of the state-of-the-art

Carslaw (2007) developed a detailed chemical box model, which included near-explicit chemical degradation schemes for the VOCs and inorganic species responsible for driving the indoor air chemistry. The INdoor air Detailed Chemical Model (*INDCM*) model was constructed based on the master chemical mechanism (MCM v3.1) (Jenkin et al., 1997, 2003; Saunders et al., 2003). This comprehensive mechanism was modified for use indoors (e.g. by adding in basic schemes for limonene, camphene, terpinene and carene) and included ~15,400 degradation reactions and ~ 4700 species. The model considers a single well-mixed environment and includes irreversible deposition to surfaces, photolysis from both attenuated sunlight through windows and artificial lighting, exchange with outdoors and internal emissions. The model was later updated to include partitioning reactions for limonene oxidation products (Carslaw et al., 2012), surface interactions of ozone with materials (Kruza et al., 2017) and people (Kruza and Carslaw, 2019). It is currently being extended to consider partitioning of α - and β -pinene and to improve its representation of photolysis reactions.

Mendez et al. (2015) presented a time-resolved model called the *INCA-Indoor* model, which was developed from the INteraction with Chemistry and Aerosols (INCA) model for outdoors (Hauglustaine et al., 2004; Folberth et al., 2006). The INCA-Indoor model made the well-mixed assumption and included photochemistry, deposition and emissions processes, as well as surface processes indoors. The surface interactions were determined by the ozone that ingress from outdoors, emissions from building materials, sorption processes and heterogeneous chemistry reactions at surfaces. The INCA-Indoor model included a chemical mechanism based on an updated but simplified version of the SAPRC-07 mechanism (Carter, 2010), which consisted of 1400 oxidation reactions of 640 VOCs. For VOCs, the model considered three regimes: the

bulk air, a boundary layer adjacent to a surface and the surface itself. VOC species were assumed to adsorb reversibly on the material surface. Gases could also diffuse from the bulk air through the boundary layer to undergo direct uptake to the surface, as well as diffuse out of the boundary layer and back into the bulk air. The model also included irreversible deposition for inorganic species.

So far we have described detailed, largely explicit models, but reduced-order, inexplicit models are also used. One advantage of reduced order models is that they are less computationally intensive than detailed models, so they are useful in large modeling efforts such as Monte Carlo (MC) frameworks, which use probability distributions as inputs in mechanistic models to bound uncertainty and/or understand stochastic influence (Saltelli et al., 2006). For instance, Waring (2014) used a variant of the modelling framework first set forth in Youssefi and Waring (2012) in a MC framework to determine SOA formation in residences and the fraction of fine particle mass in the SOA (Youssefi et al., 2012). The MC framework allowed this application to be carried out over a wide range of building parameters. Ito and Harashima 2010 used coupled Computational Fluid Dynamic analysis of particle size distribution on indoor SOA derived from ozone/limonene reactions. This modelling suite provides comprehensive prediction incorporating a bi-molecular chemical reaction model, SOA generation, and collision/coagulation and deposition models.

A major area of model development in recent years have been to investigate the ozonolysis of skin oil and the impact of the subsequent chemistry on indoor air quality. Ozonolysis reactions with skin lipids can decrease ozone concentration indoors and increase the potential for secondary pollutant formation (e.g. Wisthaler and Weschler, 2010). A new model by Lakey et al. (2016) aimed to evaluate and quantify ozone–skin lipid reaction products, especially monocarbonyls and dicarbonyls which might cause skin or respiratory irritation, but could also be absorbed to the bloodstream over time. The Kinetic Multilayer model of SURface and Bulk chemistry of the skin (KM-SUB-Skin), includes mass transport and chemical reactions at the skin-surface, in the near-surface gas phase and in the bulk gas-phase. The surface layers include a sorption layer, a skin oil layer, bulk layers and a layer of blood vessels. This model has also been recently adapted to include the effect of clothing in KM-SUB-Skin-Clothing, which explicitly resolves mass transport and chemical reactions in the gas phase, in clothing, in the gap between clothing and skin and in skin (Lakey et al., 2019).

Finally, it is worth mentioning the MOCCIE (MOdeling Consortium for Chemistry of Indoor Environments) Consortium here (Shiraiwa et al., 2019). MOCCIE aims to bring together state-of-the-art models to produce a modelling framework for indoor air chemistry. The project started in 2017 with early steps to integrate models going from the molecular level all the way up to CFD scale. The eventual aim is to work towards an integrated indoor air chemistry model/model framework.

Summary of selected studies

The INDCM has been used in numerous studies to gain insight around the chemical detail that is not yet possible from measurements alone. In particular, it has yielded information around indoor air chemistry following cleaning, such as the SOA composition following cleaning with a limonene-based cleaner (Carslaw et al., 2012, Carslaw, 2013) and the impact of cleaning with bleach on radical formation under different indoor lighting conditions (Wong et al., 2017). It was also used to investigate the impact of outdoor biogenics on indoor SOA formation (Carslaw et al., 2015) and the use of air cleaning devices indoors, which were shown to produce very high radical concentrations (Carslaw et al., 2017). The INDCM has been particularly useful to explore the chemistry of the more 'exotic' species such as radicals and secondary VOCs formed through the chemical reactions that occur indoors, but that are currently very challenging to measure. For instance, occupancy was predicted to reduce oxidant concentrations, enhance the formation of nitrated organic compounds and change the peroxy radical composition (Kruza et al., 2017; Kruza and Carslaw, 2019).

INCA-Indoors was used to simulate various indoor conditions including cooking and cleaning, and to assess the impact of indoor chemistry, focusing on the production and loss pathways of formaldehyde and

acetaldehyde (as potentially harmful species). Formaldehyde was shown to derive largely from building materials and chemical production only became important when indoor OH concentrations were high (Mendez et al., 2015). INCA-Indoors was also used to predict OH and HO₂ concentrations and compare to those measured during the SURFin campaign (Gómez Alvarez et al., 2013; Mendez et al., 2017). Although the model reproduced variations in concentrations, the modelled OH concentrations were 20% lower than measured, whilst modelled HO₂ concentrations were 58% lower than those measured. The authors noted the strong influence of HONO on OH concentrations and also that the mechanisms for HONO formation indoors are currently unclear.

Waring and Wells (2015) used a MC framework to investigate the relative importance of the OH, ozone (O₃) and nitrate radical (NO₃) reaction with terpene species. Input parameters were varied probabilistically, to evaluate VOC gas-phase oxidation rates with the three oxidants across a range of typical residences. The model was also able to evaluate the importance of sources of these oxidants indoors, such as the photolysis of nitrous acid (HONO) to generate OH radicals versus ozone-terpene reactions and the reactions of NO₂ with stabilized Criegee intermediates to form NO₃. Reactions with O₃ and OH were found to dominate VOC oxidation over NO₃ for the conditions studied. Mohan et al. (2017) developed chemical reaction kinetics of VOC (toluene, benzene, isobutylene and formaldehyde) ozonation and tested them in Ansys Fluent CFD to predict VOCs ozonation.

KM-SUB-Skin was used to show that two people in a 28.5 m³ volume could reduce the ozone concentration from ~33 ppb to ~16 ppb over 4 hours. In addition, as the ozone concentration decreased, the gas-phase concentrations of skin-oil oxidation products increased: 6-MHO increased to 2.5 ppb and 4-OPA up to 2 ppb both from a concentration close to zero. By increasing the number of people in the room (20 occupants, 28.5 m³), the concentrations of ozone and the reaction products decreased, since each occupant was exposed to a lower concentration of ozone. An increase in the ventilation rate (higher than 1 h⁻¹) caused higher ozone concentrations indoors (~14 ppb), but a lower total concentration of carbonyl products (0.1-0.8 ppb) in the gas-phase and blood as they were flushed out more rapidly once formed. A similar study by Rim et al. (2009), using Fluent 6.3 model studied the influence of chemical reactions at the human surface on breathing zone levels of reactants and products. Russo and Khalia et al. (2010) studied wall adsorption of ozone and d-limonene and the resulting volumetric reaction. Corresponding 2D computational concentration profiles were compared to the experimental results from Ito (2007) with reasonable agreement. The validated model was then implemented in a 3D simulation of a typical office space. Additionally, Morrison et al. (2019) modelled reactions taking place within the boundary layer over indoor surfaces, which resulted in greater than anticipated deposition rates and possibly higher oxidation rates for highly reactive species like OH radicals. The authors concluded that OH may be an important oxidizer of surfaces coated with organic films, especially if those films exhibit low ozone reactivity.

List of top research questions, hypotheses, recommended future steps

The recent review of Morrison et al. (2017) provided a comprehensive summary of the major indoor air modelling needs, split into broad categories of (i) processes (divided into gas-phase, aerosol-phase and interfacial mechanistic phase), (ii) model evaluation and (iii) building data and simulation. The reader is referred to this review for more information, but the key findings are summarized in this section.

Indoor air chemistry is a complex subject which provides many challenges for modelling studies. One of the main issues is that many measurements within indoor environments (for model evaluation) are very challenging (e.g. of radical species). It is often difficult to measure in real buildings and to do so in a meaningful way that encapsulates the wide variety between different buildings. Therefore, models often lack the required measurements for full validation/evaluation. In addition, a limitation of many models is that they assume well-mixed air in buildings, when spatial variation within zones should ideally be considered.

Indoor air chemistry models typically use chemical mechanisms, which were originally constructed for modelling outdoor chemistry. Consequently, they lack appropriate degradation schemes, e.g. for terpenes, which are emitted during cleaning and air freshener use and some of the organics emitted from indoor surfaces such as human skin. Likewise, current models include estimated photolysis rates indoors, since there are few measurements, though some have become available recently (Gandolfo et al., 2016; Kowal et al., 2017; Bloquet et al., 2018). This is particularly a problem when considering the propagation of light indoors, such as the variation between the air close to a window and in the shadow on the far side of the room from the window.

We also need to understand more about gas-to-particle partitioning and SOA aging indoors. Most of the focus to date has been terpene species: less is known about aromatics and longer-chain alkanes for instance. There are also very few measurements of deposition rates of gas-phase species indoors. Those that exist are mainly for ozone, nitrogen dioxide and sulphur dioxide (Grontoft and Raychaudhuri, 2004) and are limited to relatively few surfaces. Measurements for gases such as formaldehyde and HONO are absent for indoors, but based on outdoor deposition rates, could potentially play a role indoors. There are few existing surface-phase models and these typically focus on one type of surface, such as human skin. There is still a need to develop models, which include surface interactions in more realistic indoor environments.

Finally, field experiments in real (preferably occupied) buildings are necessary, since in controlled experiments there are limited opportunities for discovery of new phenomena or species. For example, real and simulated human activities may have different impacts on indoor environments as revealed by detailed chemical speciation over time. Morrison et al. (2017) also stress the need for modelers and experimentalists to work together more often: models help design experiments and the experimental results can be used to improve models.

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