INDAIRPOLLNET

IMPROVING INDOOR AIR QUALITY

WORKING GROUP 1

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

Recommendations

COST Action 17136 Indoor Air Pollution Network

COST EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

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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 report constitutes the recommendations of INDAIRPOLLNET COST Action 17136 Working Group 1 to Working Groups 3-6, based on review of recent literature to gather the existing information and expertise in outdoor air studies to be used in the development of planning indoor air campaigns.

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Recommendations drawn from the literature review on indoor air chemistry

With regard to indoor air chemistry, three types of chemical transformations are of interest: i) oxidation processes in the gas phase; ii) heterogeneous processes (gas-liquid, gas-solid); and iii) oxidation processes in the liquid phase. These transformations involve **oxidants** (which are linked to their **precursors**), **primary generated species** reacting with the oxidants and **secondary generated species**. These four families of compounds and their **relevant parameters** to identify the potential importance of these processes indoors are of interest for WGs 3-6 of INDOORAIRPOLLNET.

Recommendations for deciding key species and relevant parameters (WG3)

- Real-time measurements of OH, Cl, HO_2, RO_2, NO_3, Criegee intermediates, ion clusters and other short-lived, highly reactive species as well as their precursors in occupied and unoccupied indoor environments can significantly advance our understanding of indoor air chemistry. Measurements of RO_2 composition would also be beneficial for detailed chemical models.
- Real-time measurements of key secondary species (gas-phase and aerosol-phase) as tracers for indoor air chemistry (e.g. peroxides, organic nitrates, carbonyls etc.), is recommended.
- Source of oxidants involve precursors and photolysis processes. Real-time measurements of parameters such as the transmission of solar light through windows and the integration within the whole volume of a room are needed. Characterization of artificial light sources is needed.
- The infiltration of outdoor precursors and oxidants might play a key role in driving chemical and phase transformations. The input and levels derived from this source should be monitored.
- Future campaigns on indoor air chemistry should recognize the increasingly clear and important role of occupant emissions. An extensive list of compounds has been identified as primary human emissions. Of these, measurements are recommended to focus on those, which i) have a relevance for human health; ii) are relatively poorly understood in terms of sources and driving factors of exposure; and iii) are known or suspected to significantly contribute to chemical transformations in indoor air.
- A number of occupant-related reaction products have been identified. These mostly originate from reactions of O_3 with squalene or fatty acids (skin lipid ozonolysis). Some are increasingly well understood, others need more attention. The health effects of most are relatively poorly understood.
- The impact of humans on levels of oxidants (OH, nitrate-, hydroperoxy-, peroxy-) and related chemistry requires further studies.
- The contribution of personal care products to indoor air chemistry seems to be substantial. Identification of sources and measurements of associated chemistry warrant attention.
- The contribution of clothing (e.g. detergent residues, anti-crease agents) should be isolated.
- An extensive list of compounds has been identified as primary emissions from indoor activities and building and consumer products. Of these, measurements are recommended to focus on those, which i) have a relevance for human health; ii) have important sources, i.e. have high abundance, or are suspected to have high abundance, indoors; iii) are known or suspected to significantly contribute to chemical transformations in indoor air and/or indoor surfaces. A prioritized list based on ranking of these three parameters should be made.
- The chemical species can benefit from a categorisation according to the three source cases outlined above. The volatility, solubility and hydrophobicity are relevant parameters for determining the susceptibility towards air vs. particles/dust/surfaces.

- Real-time measurement of OH radicals indoors may help determining the OH-reactivity (according to the reactivity of the species in the gas phase with OH). This is of interested for gas phase chemistry.
- Kinetic data would be of use, e.g. chemical mechanisms for some indoor species such as terpenes, terpene alcohols, skin oxidation products. Models would also benefit from more data around gas-to-particle partitioning, such as vapor pressure measurements and the rates of auto-oxidation.
- Parameters relevant for heterogeneous reactions and reactions in the liquid phase are needed (production yield of secondary species, deposition rate of oxidants for representative indoor conditions).
- Real-time measurements of identified secondary species from heterogeneous reactions and those released in indoor environments due to reactions in the liquid phase are needed.
- More information on surface interactions such as deposition velocities and yields of formation, in addition to surface emission and reactivity, adapted to indoor surfaces would be beneficial.
- Studied should be the processes leading to generation of nitrous acid (HONO) indoors. It is of special relevance to the indoor environment due to the abundance of surfaces, high surface to volume ratios, high concentrations of NO_2 and high relative humidity levels. Photo-sensitized processes leading to the enhanced formation of HONO warrant attention.
- Reactions leading to the heterogeneous release of halogen radicals (and in particular Cl and Cl oxides) should receive a closer look. In particular, measurement of $ClNO_2$ is advised as a Cl radical reservoir and the possibility that it photolyzes indoors. This is formed by heterogeneous reaction of Cl-containing particles with N_2O_5, which is expected to be high indoors.
- For source apportionment/receptor modelling application, chemical specification, detailed information about PM fractions/VOCs/aldehydes is needed. New key-species should be examined for optimizing the source identification. Ultrafine particles (UFPs) should be also approached in source apportionment studies. If data on chemistry is not available, clustering of size distribution measurements and activity questionnaires might help to obtain this information.
- Airborne particles deserve attention due to their confirmed adverse health effect. Their chemical composition, physical characteristic (number, mass, surface area concentrations, size distribution), toxicity, oxidative reactivity, are of interest.
- UFPs gain increasing interest from health perspective (translocation, neurodegenerative diseases, cognitive performance). Considering that particle number concentrations indoors in private homes are dominated by UFPs from active indoor sources or the interaction of infiltrated outdoor species and oxidants, this should put UFPs on a list of key species, by measuring not only particle number concentrations, but also their size distribution.
- Concerning combustion-derived particles, there is ongoing debate if toxicity of the particles is driven by their core component or coating, here elemental carbon EC (black carbon BC, soot) or organic coating are in focus. Thus measuring EC and organic coating of particles would be beneficial.
- Toxicological studies link the surface area of particles with their toxicity, therefore surface area of the particles may be of interest.
- Measurements of the oxidative reactivity/potential of particles in occupied indoor environments and the effect of particle coating might yield relevant information.
- Characterise indoor processes and sources yielding to new particle formation, their growth and shrinkage. Measurements of ion clusters (CI-API-TOF) produce key data to understand the specific processes resulting in nucleation of new particles.
- Determine chemical transformations/aging/formation of secondary pollutants in indoor air when outdoor and indoor air pollutants in gas- and particle phase mix.
- Study SVOCs uptake on particles and factors influencing it. In this way the simultaneous measurements of the VOCs and organic PM fractions might give very relevant information.

- In relation to microbial activity, measurements should include all physical environmental parameters and heterogeneous chemistry such as relative humidity and surface moisture and surface chemistry.
- Identification of model microbial species is needed and marker compounds possibly by chemical functional group to allow implementation into chemistry models.
- Modelled sensitivity studies using measured data should study the effect of microbial volatile organic compounds (MVOCs) on the chemistry indoors an also the lifetimes of MVOCs in different indoor composition scenarios. Do MVOCs contribute to chemistry in "normal" situations?
- Test mechanisms in conditions representative of the indoor environment, i.e, extremely high concentrations of oxidants, such as NO, NO_2 or HONO since the mechanisms could proceed through different routes.

Recommendations for considering how to measure (WG4)

- Measurement techniques used indoors should be adapted to the environment: small enough to be installed in the room (for reactive species) or if possible in an adjacent room (stable species), it should not influence the conditions in the room.
- The indoor concentrations of volatile compounds, oxidants, and PM components should be monitored with a holistic approach with real-time measurements of organic and inorganic precursors and products, oxidants, and key photochemical parameters, and the below mentioned aerosol science tools.
- Knowledge about occupant-related indoor chemistry is advancing primarily thanks to new rapid online monitoring equipment with high sensitivity for a large range of chemicals (originally used for atmospheric chemistry). The success of any future indoor air chemistry campaign in occupied spaces will be unlikely without some of these latest instruments available. See Farmer et al., 2019 (HOMEChem study) for a list of currently believed to be top instruments.
- Measurements in the gas phase should be done on varying timescales depending on the type of emission, the processes to study, the variation of the conditions in the indoor environment (ventilation, activities): i) Short: Emission peaks of minutes to a few hours, reactive in the gas phase, linked to a fast change in the conditions; ii) Medium: Emission peaks of hours to less than a week, produced by heterogeneous reactions or in the liquid phase (without fast changes in the conditions); iii) Longer: Emissions up to months and years. This should be reflected in the measurement techniques, e.g. on-line monitoring for i) and ii), passive sampling for ii) and iii), medium-volume sampler for ii) and iii), dust and surface sampling for all three.
- Measurements should be done on a varying spatial scale for the air and particle phase, which typically corresponds to the characteristics of the emission source. During emissions: i) Highest concentrations are in the immediate vicinity (within one meter) of the source; ii) There can be a concentration gradient from the source to the surrounding room air; iii) There can be less pronounced concentration gradient from the source to the surrounding room air, and to adjacent rooms, i.e. more well mixed in room air during the life time of the source. In all cases dust and surface measurements are relevant both close to the sources and further away in the space.
- Taking into account that information about the levels of some VOCs originating from building materials and possibly consumer products is limited if at all available, qualitative screening study would be recommended followed by quantification of the most prominent species.
- Measurements of surface emission and reactivity adapted to indoor surfaces, as well as measurements of surface interactions such as deposition velocities and yields of formation should be proposed.
- Particle measurements and characterization using similarly advanced instruments (in addition to the often used Condensation Particle Counters (CPC), Scanning Mobility Particle Spectrometers (SMPS), Fast Mobility Particle Spectrometers (FMPS) should accompany the chemical measurements of the impact of

occupants on indoor chemistry (Aerosol Mass Spectrometry (e.g. HR-TOF-AMS) coupled with PTR-ToF-MS or VUV-SPI-TOF-MS (vacuum ultraviolet single photon ionization ToF-MS), Chemical Ionization-Atmospheric Pressure Interface-Time Of Flight Mass Spectrometers (CI-API-TOF-MS) to analyse ion clusters giving rise to nucleation, Particle Size Magnifier (PSM) for measurements of particle sizes down to 1 nm, FIGAERO-CIMS (Filter Inlet or Gases and Aerosol - Chemical-Ionization-Mass Spectrometry), SV-TAG or alike, to measure VOCs and PM components). Support such measurements with off-line sample collection to quantify findings.

- For source apportionment/receptor modelling application, an adequate number of samples is needed (practically >50-100). Measurement time interval should be selected in accordance to the source characteristics: 24-h sampling does not allow for an instant (sharp emission peak) source identification. On the other hand, short-time samples cannot identify permanent sources, e.g. building material emissions. The above mentioned online measurement tools allow obtaining large datasets that are appropriate for receptor modelling tools for source apportionment.
- Simultaneous outdoor measurements are needed to estimate the contribution and impact from outdoor environment (including traditional pollutants, oxidants and chemical precursors). Outdoor reference measurements are also needed for a better understanding of indoor air pollution, as the physico-chemical characteristics of outdoor pollution change during infiltration.
- Microbial emissions are very variable and experimental controls will be vital. Measurement of marker compound emission factors in model species followed by scaling up by production of standardised coupons or larger moveable colonies in controlled realistic environments is recommended.
- The detection, quantification and identification of microbial emissions can be achieved using analytical techniques such as PTRMS and selected ion flow tube (SIFT) mass spectrometry in real-time. Integrated samples are obtained by using canister and hyphenated chromatography. Aqueous denuder measurements using either integrated offline analysis or continuous denuders using online LC could be used for water-soluble organic gases.
- Identification of microbial species is needed in “problem” buildings.

Recommendations for choosing which buildings to measure (WG5)

- Different types of buildings should be examined in order to establish the type of buildings of particular relevance for their indoor air quality/chemistry or impact on exposure. Different building types have different specific requirements. WG5 could come up with a list of main indoor environmental problems according to the different types of buildings. For example, public buildings (schools, official public buildings/offices,…) have a higher occupancy and hence higher related emissions and sinks but also implications to occupants exposure (hospitals would be a particular case due to the vulnerability of occupants, the use of aggressive disinfectant methodologies, high potential risk of germs, infectious agents and microbes,…).
- Other buildings such as public swimming pools, buildings attached to garages due to their specific emissions and requirements (specific filtration methods) should be considered. The fact that there are different types of buildings have been treated throughout WP1 as a limitation to attain proper characterisation of the indoor environment. This fact requires that a proper classification is established in order to attain an adequate characterisation of the different types of buildings (in a similar way as the outdoor environment is categorized in urban, rural, pristine locations, Chinese mega-urbans, marine environments…).
- Large-scale measurement campaigns focusing on indoor air chemistry are scarce. Prior studies were performed primarily in climate chambers, test houses or classrooms. These campaigns should be extended to residential environment, offices and special non-occupational environments such as e.g. hospitals.

- Prior studies were mainly performed in the USA, in air conditioned schools or a test house in warm climate (Texas) or in Europe (natural ventilation, mechanical ventilation) in schools or test house in moderated temperatures (Paris). Differences in buildings (volume, ventilation type and rate, building materials, climate), culture and lifestyle (occupant behaviour such as venting or cooking practices, consumer products, occupants themselves,…) will likely result in a large impact on indoor chemistry.
- The differences are larger across Europe than the USA and future measurement campaigns might focus on mapping some of the regional differences in IAQ.
- People spend two third of their time in private homes (residential environments). Studies in private homes have not been performed on large scale. Such studies are warranted, both with occupants absent and present.
- In residential buildings, differences in local sources and their characteristics should be taken into account. E.g. i) Short term indoor activities such as cooking, cleaning, smoking, vaping, burning candles and incense, and personal care products (e.g. kitchens, living rooms); ii) long term activities such as heating furnaces, indoor painting and air fresheners (e.g. children's rooms, living rooms); iii) Indoor products, such as furniture, toys, electronic devices etc. (e.g. children's rooms, bedrooms, living rooms, study rooms). The main sources in public buildings, schools and offices are somewhat different, e.g. cleaning (i); painted walls (ii); electronic devices (iii).
- For evaluation of building material related pollution new buildings should be taken into consideration.
- The orientation of the building and the type of windows and artificial light may impact the chemical processes and should be considered.
- For source apportionment/receptor modelling applications, large-scale measurement campaigns of the *same type* of building (residential or school or hospital environment) can produce adequate data to identify common microenvironment-specific sources
- The selection of buildings and their systems have to be supported with information on how people use it, with description of occupants' habits and equipment they use. Large regional differences are to be expected and will likely influence indoor air chemistry.
- Identification of "problem" buildings with respect to microbial colonisation should be done in conducting comprehensive studies.
- Measurements should be made in multiple indoor locations within a building. This should include chemical as well as physical measurements (e.g. light, temperature, humidity). This will provide input for computational fluid dynamics (CFD) models as well as help initialise different zones in detailed chemical models.

Recommendations for planning a blueprint of a field campaign for characterization of indoor air chemistry (WG 6)

- Identify different types of campaigns (what, how, where) as a function of the scientific question to study
- Make a link between laboratory studies/conditions and the real environment to highlight unknown/unidentified processes. Field experiments in real 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.
- Select conditions to identify the processes involved (part of the campaign with and without occupancy, different building conditions, e.g. ON/OFF; AC ON/OFF …).
- Measure in occupied buildings during the time people are present in the buildings (occupancy time) and when they perform various activities (i.e. active indoor sources are present). Measurements in

unoccupied buildings can help in understanding the infiltration and indoor sources and their emissions, and contribution to exposure, but they do not fully represent occupant exposure. Occupancy periods are relevant for exposure assessment and subsequent risk and health effects assessment.

- Studying the link between the chemical and microbiological human emissions, impact of skin microbial activity on chemistry and the impact of a range of environmental and personal factors on this relationship, is warranted.
- Quantifying how indoor environments change with occupancy is not well established. Occupancy leads to changes occurring on indoor surfaces. Little is known about the accumulation on indoor surfaces of the less volatile products of ozone/skin oil chemistry.
- The effect of occupant-initiated reactions on secondary organic aerosols deserves attention.
- Modifying factors of occupant emissions and associated reactions need better understanding in real environments. These include both environmental factors (temperature, humidity, ozone levels, ventilation, concentration of environmental pollutants…) as well as personal factors (age, sex, smoking habit, dermal health condition, nutrition, metabolism, health condition, hygiene, emotional state, clothing as sink and source…). 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.
- Measurements should focus on surface reactivity and the importance of SVOC enhanced surface films, as well as on secondary pollutant emissions following surface interactions indoors including materials such as carpets, furniture and painted walls.
- Novel building materials having pollutant binding properties and their impact in indoor air should be given attention. For example, the impact of nanomaterials on the chemistry indoors deserves attention. This includes the characterization of by-products of photo-catalytic materials used as remediation measures for NOx removal.
- Source apportionment for size resolved indoor particle concentrations should be obtained.
- Mass spectra/signatures for individual indoor sources should be determined and open access mass spectra library should be established to enable source apportionment studies.
- Study the physicochemical characteristics (chemical and size resolved parametrisation) of particles upon infiltration.
- Linking environmental measurements of microbial emissions to overall indoor composition and oxidative capacity of indoor environment is warranted. What is the chemical and physical lifetime of e.g. organic acids and alcohols with respect to main indoor oxidation processes?
- Using a perturbation approach to an environmental study would yield new insights. This could be done by pre-producing known colonies of e.g. fungal species on matched materials and introducing them into experiments to observe perturbations in chemistry and new product formation whilst controlling for the mass and activity of microbes.
- We recommend to link the real environment to chamber and laboratory studies using controlled building-like environments, e.g. micro-buildings and test house facilities for studying the factors controlling microbial emissions in controlled realistic environments.
- It is important that measurement and modelling groups work together to allow modellers to provide further insight into measurement data and guide future campaign goals.