

International Research Journal of Pure & Applied Chemistry

21(9): 40-61, 2020; Article no.IRJPAC.57504 ISSN: 2231-3443, NLM ID: 101647669

Chemistry of Indoor Pollutants and Their Impacts on Human Health

V. Davamani^{1*}, M. Deepasri¹, E. Parameswari¹, S. Arulmani², S. Paul Sebastian¹ and T. Ilakia³

¹Department of Environmental Sciences, Tamil Nadu Agricultural University, Coimbatore, India. ²Bannari Amman Institute of Technology, Sathyamangalam, Erode, India. ³Department of Vegetable Science, HC & RI, Tamil Nadu Agricultural University, Coimbatore, India.

Authors' contributions

This work was carried out in collaboration among all authors. Author VD designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors MD, EP and SPS managed the analyses of the study. Authors SA and TI managed the literature searches. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IRJPAC/2020/v21i930197 <u>Editor(s):</u> (1) Dr. Farzaneh Mohamadpour, University of Sistan and Baluchestan, Iran. <u>Reviewers:</u> (1) Bilash Chandra Roy, ICFAI University, India. (2) Irwan Suriaman, Indonesia. Complete Peer review History: http://www.sdiarticle4.com/review-history/57504

Review Article

Received 06 April 2020 Accepted 11 June 2020 Published 22 June 2020

ABSTRACT

Indoor air pollution refers to the deterioration of indoor air quality by harmful chemicals and other products, which can be up to 10 times worse than the outdoor air pollution. Almost 90% of the modern human time is spent indoors. In India, out of 0.2 billion people using fuel for cooking; 49% use firewood; 8.9% cow dung cake; 1.5% coal, lignite, or charcoal; 2.9% kerosene; 28.6% liquefied petroleum gas (LPG); 0.1% electricity; 0.4% biogas; and 0.5% any other means. The negative consequences of indoor air pollution result in around 2 million premature deaths every year, with 44% are due to pneumonia, 54% from chronic obstructive pulmonary disease (COPD), and 2% from lung cancer. The so-called "natural" or "ecologic" goods are not inherently free of adverse health effects. Certain other constituents such as terpenoids and linseed oil may be chemically reactive than those from non-ecologic products. Secondary emissions from these products may present a greater risk to human health than those compounds which are substitutes for their precursors.

*Corresponding author: E-mail: vsdavamani@gmail.com;

Keywords: Air pollution; human health; air quality; emission.

1. INTRODUCTION

Most of the air that humans encounter is indoor air, almost 90% of the modern human time is spent indoors. Moreover, most of that time is spent in one's own house. Humans directly contribute to indoor air chemistry, through their metabolism, their skin, hair, clothing, their use of personal care items, and activities such as cooking, cleaning, etc. [1]. Thus, the human emissions to the atmosphere occurs indoors.

In addition to those entering from outdoors along with ventilation, a variety of species are emitted from furnishings, building materials, cleaning products, the indoor microbiome, human metabolism and personal care products are among other sources. Pesticides, plasticizers and flame retardants are among the large group of compounds found indoors, where the concerns arise due to exposures to endocrine disruptors, many of which are semi volatile organic compounds (SVOCs) present in the indoor environments [2]. The physicochemical behavior of SVOCs indoors is challenging to understand and also likely to be of considerable significance for human health and wellbeing.

Several processes occurring indoors such as indoor emissions, exchange with outdoors, indoor surfaces deposition, removal by filtration and indoor chemistry determines the concentration of an indoor air pollutant.

Indoor air pollutant concentration is a measure of several processes including indoor emissions, exchange with outdoors. indoor surface deposition, elimination by filtration and "indoor chemistry." The "Indoor chemistry" refers to the physical and chemical reactions which occurs in the indoor environments. It varies from those that influence outdoor atmospheric chemistry for reasons such as absence of direct sunlight and rain, less extreme temperature variations, high surface-to-volume ratios (about three levels), and higher organic compounds concentrations. This chemistry is correlated with three of the top ten global risk factors for negative health outcomes:

- Household air pollution from solid fuels
- Tobacco smoking
- Ambient particulate matter pollution

2. INDOOR AIR POLLUTION IN INDIA

Indoor air pollution refers to the deterioration of indoor air quality by harmful chemicals and other

products, which can be up to 10 times worser than the outdoor air pollution.

The primary sources of indoor air pollution are: Combustion, bioaerosols and building materials. While in developed countries radon, asbestos, pesticides, volatile organic compounds, and environmental tobacco smoke are considered as major indoor pollutants, whereas in developing nations the products of biomass fuels combustion contribute most to indoor air pollution.

The products such as suspended particulate matter, carbon monoxide, polyaromatic hydrocarbons, polyorganic matter, formaldehyde, etc., are released due to incomplete combustion of biomass fuels which have adverse health effects.

Various products like resins, waxes, polishing materials, cosmetics, binders etc, produce various pollutants such as aldehydes, volatile and semivolatile organic compounds. The biological pollutants like dust mites, molds, pollen and other infectious agents generating from stagnant water, mattresses, carpets, and humidifiers too pollute indoor air.

3. SIGNIFICANCE OF INDOOR POLLUTANTS

Indoor air pollution is one of the major environmental issues in the world. Based on figures from the Institute for Health Metrics and Evaluation (IHME), 2.6 million people died prematurely in 2016 from illness related to household air pollution.

The inefficient use of solid fuels for cooking and heating causes indoor air pollution. It is women and children who are affected by indoor air pollution widely. According to the World Health Organization (WHO) these deaths are attributable to the following diseases.

- Pneumonia
- Stroke
- Ischaemic heart disease
- Chronic obstructive pulmonary disease (copd), and
- Lung cancer.

Indoor pollutant consists of several toxic gases such as volatile organic compounds (VOC), Trichloroethylene (TCE), xylene, toluene and formaldehyde, octane, α -pinene, benzene, Carbon monoxide (CO), Nitrogen dioxide (NO₂), pesticides etc.



Fig. 1. Death rates from indoor air pollution in India [3]

The status of socio-economic development is closely related to determinants of indoor air pollution (IAP). There are significant discrepancies between developing and developed countries where the IAP comes from the use of solid fuel in the former, and from "new substances" "chemicals" and (e.g. formaldehyde, insecticides and phthalates) in the latter. Yet, the second-hand tobacco smoke is a common pollutant to both settings. Due to different economic levels and lifestyles in rural and urban areas, IAP also differs to those places. In agricultural areas dust and organic particles are more common and in closed unventilated urban buildings, mites or fungal contaminants are common. The local climatic conditions should also be considered, as they have an impact on architecture (structure of the buildings and materials used, room distribution).

Indoor air quality is altered by outdoor air pollutants concentrations, indoor emissions, building characteristics and the activities of the residents. Certain other pollutants include construction materials such as asbestos and cement, wood preservatives and others. Various sources such as paints, resins, polishing materials, glues, perfumes and cleaning agents releases volatile organic compounds (VOC). Formaldehyde is a component of some household products used which can irritate the eyes, nose and airways [4].

4. SOURCES OF CHEMICALS REACTIVE INDOORS

The indoor air contains multiple sources of reactive chemicals, including the outdoor air.

Pollutants like O_3 , nitrogen oxides (NO_x), particulate matter (PM) and organics enter with the ventilation air or through infiltration into the building window frames, doors and other openings. The chemicals carried in with outdoor air depends on the location and leakage of the building. For example, the traffic generated pollutants will be found in higher concentrations in homes nearer to busy roads and/or with higher ventilation/infiltration rates. The various sources of reactive chemicals indoor are:

- Cleaning agents and air fresheners (e.g., sodium hypochlorite, ammonia, terpenes, acetic acid)
- Electronic devices such as photocopiers and laser printers (O₃)
- Smoking
- Cooking, heating and combustion appliances (e.g., nitrogen dioxide (NO₂), nitric oxide (NO), nitrous acid (HONO), acrolein, polycyclic aromatic hydrocarbons (PAHs))
- Painting
- Building materials like wood, PVC pipes and cable insulation
- Furnishings that includes carpets, other floor coverings and wall coverings
- Pesticides
- humans (e.g., squalene, unsaturated fatty acids, isoprene, NO, ammonia)
- pets
- bacteria and fungi, including mold (e.g., microbial organics)

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Limits (OSHA, 1979 & USEPA, 1980) S. no. Pollutant Sources Health Effects [6,7] 1 Asbestos fibres Fireproofing 0.2 fibres/mL for fibre larger than5 µm Skin irritation, . • insulation, lung cancer . vinyl floor, cement products, vehicle brake linings . 2 Microorganisms Infectious agents, Not available Disease. ventilation. . weakened immunity . air-conditioning system 3 1,000 ppm Carbon dioxide • Motor vehicles. . Dizziness, headaches. • gas appliances, smoking . nausea 10,000 µg/m3 for 8 hours; 40,000 4 Carbon monoxide Motor vehicles. . µg/m3 for 1 hours kerosene and gas heater, Dizziness, headaches, gas and wood stoves. nausea. fireplaces; death smoking 5 Formaldehyde 120 µg/m3 Foam insulation; Skin irritant, . plywood. carcinogen . particleboard, ceiling tile. panelling construction materials 6 55-110 µg/m3 annual; 350 µg/m3 for 1 Particulate matter Respiratory and mucous irritant, . Smoking, . fireplaces, hour carcinogen . dust. Combustion sources (burning trash, etc.) 2 µg/m3 for 24 hours 1.5 µg/m3 for 3 7 Metal particulates Smoking, Toxic, carcinogen . months 2 µg/m3 for 24 hours 100 pesticides, Respiratory and mucous irritant . rodent poisons µg/m3 annual Smoking,

Table 1. Sources, permissible limits and possible health impacts of indoor air pollutants [4]

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S. no.	Pollutant	Sources	Limits (OSHA, 1979 & USEPA, 1980) [6,7]	Health Effects
		 fungicides fossil fuel combustion Gas and kerosene heaters, gas stoves, 		
8	Ozone	 Photocopying machines, Electrostatic air cleaners, outdoor air 	235 μg/m3 for 1 hour	 Respiratory irritant, causes fatigue
9	Pesticides	 Sprays and strips, outdoor air 	5 µg/m3	Possible carcinogens
10	Sulphur dioxide	 Coal and oil combustion, kerosene Space heater, outside air 	80 μg/m3 annual; 365 μg/m3 for 24 hours	 Respiratory and mucous irritant Irritant
11	Nitrogen dioxide	 Smoking, fossil fuel combustion Gas and kerosene heaters 		 Toxic, carcinogen Respiratory and mucous irritant
12	VOC's	 Smoking, cooking, solvents, paints, varnishes, cleaning sprays, carpets, furniture, draperies, clothing rubber lubricants 		 Possible carcinogens



Fig. 2. Various sources and types of indoor pollutants [5]

4.1 Other Sources

Paints, including epoxy latex paints, flexible plastics such as shower curtains and pillow and mattress covers are indoor pollutants. Hair sprays, electrical equipment's, depilatories, antiseptics, drain, oven and lavatory cleaners, polishes, bleaches, some tooth paste, non-stick pans, moth repellents, air fresheners, radiations from various sources especially from colour television, lap tops, Desk top, smart phones, etc. Many air purifiers, containing the pesticide paradi-chloro-benzene are in use today. The vapours produced by this insect-repellent can accumulate to toxic levels in the environment [4].

4.2 Volatile Organic Compounds (VOC)

The increasing emissions of various forms of VOCs are attributable to the rapid growth of urbanized population and the exaggerated usage of synthetically prepared chemical-based products by the consumers. Among the various VOCs observed indoors, the compounds like 1,4dichlorobenzene. naphthalene, benzene. chloroform, ethyl benzene, styrene, isopropylbenzene, 1,2-dichloroethane, tetra-chloroethene, trichloroethylene etc., are identified as carcinogens [8,9]. The most commonly found VOCs in indoor air are acrolein, benzene,

acetaldehyde, 1,4-dichlorobenzene, 1.3butadiene, naphthalene and formaldehyde [8]. The World Health Organization (WHO) have recognized benzene. styrene. toluene. trichloroethylene and tetrachloroethene as the threat pollutants in indoor atmosphere. Similarly, benzene, naphthalene and formaldehyde are commonly identified in indoor air samples and considered as threat pollutants in most of the European countries. The maximum concentration of most commonly identified VOCs in indoor air samples are given in Fig. 3.

The concentration of VOCs present in indoor is much higher than those present in outdoor. Indoor concentration of VOCs is controlled by many factors such as the nature of source, outdoor air quality, degree of ventilation, air exchange rate, and pollutant depletion mechanisms. Chemical reaction of VOCs in indoor environment is mainly influenced by the presence of O3 and •OH or other radicals.

4.3 Ozone

Pollutant common in indoor and outdoor environments is the ozone (O_3). In the outdoors there is a 97% probability that the O_3 molecule will react with nitric oxide (NO), versus ~ 1% probability that it will react with an unsaturated

volatile organic compound (VOC), ~ 1% chance that it will deposit on surface, and ~ 1% chance it will be photolyzed. Whereas, in the indoor conditions, the same molecule has a slightly more than 40% chance for reaction with NO, a slightly less than 40% chance for surface deposition, a 20% chance for removal by air exchange, and a 1% chance of reacting with unsaturated VOCs (ozone photolysis is generally negligible indoors) [11].

Table 2. Sources of VOC [10]

S. no	Source	Volatile organic Compounds
1.	Adhesives	Toluene, xylene, styrene, ethylbenzene, formaldehyde, butyl ether, vinyl cyclohexane, 2-propenoic acid and propylene glycol
2.	Carpet	Formaldehyde, 4-phenyl cyclohexane, vinyl acetate styrene, dodecanol and acetaldehyde.
3.	Paints	Toluene, benzene, p-xylenes, o-xylene, styrene, ethylbenzene, 2- methylhexane, cyclohexane, 2,4 dimethyl penate, methyl cyclopenate, n-heptane, methyl cyclohexane and n-octane.
4.	Printers/ copiers	Formaldehyde, styrene, ethylbenzene, xylene, benzene, 2-ethyl-l- hexanol and toluene etc.
5.	Cleaning products	Limonene, isopropanol, butoxyethanol, 1,4 dichlorobenzene, ethanol, toluene, decane, phenol, I-propanol, o-xylene and chlorobenzene.
6.	Household spray products	Propane, acetaldehyde, butyraldehyde, methyl ethyl ketone, ethyl alcohol, iso-valeraldehyde, benzene, valeraldehyde, methyl isobutyl ketone, toluene, isobutyl alcohol, p-xylene, m-xylene, ethylene acetal and o-xylene, styrene.
7.	Textiles	Formaldehyde, acrylonitrile, acetaldehyde, toluene, o-xylene, 1,2,4- trimethylbenzene, ethylbenzene and m,p-xylene.
8.	Wall covering	Naphthalene, methyl pyrrolidinone, styrene, phenol, formaldehyde, acetaldehyde, tetradecane, toluene, o-xylene, 1,2,4-trimethybenzene and m, p-xylene.
9.	Barbecue charcoal	Benzene, toluene, ethyl benzene, meta para xylene, styrene, formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, butyraldehyde, benzaldehyde and valeraldehyde.
10.	Furniture	Formaldehyde, acetaldehyde, benzene, benzaldehyde, toluene, tetrachloroethylene, xylene, trimethyl benzene, dichloro benzene, ethyl benzene, butoxy ethanol, styrene, butylacetate, hexanal and cyclohexanone.
11.	Window shades	Ethylhexanoic acid, decanol, dodecene, ethyl hexanol and naphthalene
12.	Flooring adhesives	Vinyl acetate, 1,2-propanediol, 2-ethyl hexanol, 2-(2-butoxyethoxy) ethanol, 4-phenylcyclohexene, 2-(2-butoxyethoxy) ethyl acetate, β -caryophyllene, α -humulene, longifolene, formaldehyde and acetaldehyde.
13.	Cleaning products	Polyfluorinated compounds, ethanol, methanol, toluene, styrene and limonene
14.	Cooking activities	Acetaldehyde, propionaldehyde, butyraldehyde, iso-valeraldehyde, toluene, styrene, para-xylene, methyl ethyl ketone, methyl isobutyl ketone, butyl acetate, isobutyl alcohol, propionic acid, butyric acid, isovaleric acid and valeric acid
15.	Personal care products	Air freshener and body wash: alcohol, aldehyde, terpene, organic acid, hexane, benzene, toluene, ethylbenzene, m,p-xylene, styrene, α -pinene, camphene, β -pinene, β -myrcene and n-decane and 3-carene.

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Fig. 3. The concentration (µg m⁻³) of commonly identified VOCs present in indoor air (Adopted and modified from U.S. EPA, (2011))



Fig. 4. Reaction of O_3 , NO_3 and OH radicals with alkenes and other VOCs, and formation of SOA, stable intermediates and other possible reaction [10]

4.4 Secondary Organic Aerosols

Terpenes and terpene alcohols concentrations are often higher indoors than outdoors, reflecting the use of scenting agents in personal care products, cleaning agents and air fresheners. Ozone, generated indoors or transported from the outside, reacts with these terpenoids, developing products with a range of volatilities. The less volatile condense on existing particles or nucleates, generating SOA. The SOA are usually ultrafine particles (UFP, < 100 nm diameter) when initially formed, but grows with time into larger but still relatively small particles (300 - 700 nm). For indoor environments these processes can produce a significant amount of SOA.

The SOA production varies with ozone concentration and can be episodic, as when using a scented cleaning product, or a fairly steady situation, as in the case of plug-in air

fresheners. Despite being commonly initiated by ozone. SOA production is enhanced by hydroxyl radicals (·OH) formed by the reaction of ozone with the double bonded precursors of terpenoids. SOA production can also be influenced by the nitrate radicals which is illustrated bv experiments investigating reaction of ozone with a-pinene in different concentrations of NO. The highest yield of SOA was obtained under the environment predicted to generate the highest nitrate radical concentration. Surface chemistry can be a source of SOA, as shown in the reaction of ozone with surface sorbed d-limonene and squalene. In these situations, the rate of production of SOA from ozone-initiated surface chemistry were much lower than those for the gas phase ozone/terpenoid reactions.

On an average, SOA formed by indoor chemistry adds only a small fraction to the total mass of fine-mode indoor particles (6% with a probability of 50%). Such high SOA situations with low air exchange rates, have elevated levels of ozone and terpenes, like limonene. Under conditions such as washing, the cause of SOA is the thermal desorption of SVOCs from surfaces they have sorbed onto. The accumulated organic compounds will desorb from the surface while heating objects such as cooking utensils, stovetops, clothes irons, and radiators. As the air plume containing these organic substances rises and cools, many of the organic substances supersaturate and nucleate and forms SOA.

5. CHEMISTRY OF INDOOR POLLUTANTS

Reactions between indoor pollutants may produce products which would otherwise might be absent in indoor environment. In an indoor environment, a chemical reaction must occur for a packet of indoor air within a period shorter than or equal to the time of residence. The reactions that satisfy these criteria includes reaction of ozone with nitric oxide, nitrogen dioxide and certain unsaturated hydrocarbons at normal air exchange rates, thermal decomposition of peroxyacyl nitrates, various free radical reactions and selected heterogeneous processes.

Stable products such as aldehydes, ketones, carboxylic acids and various organic nitrates are formed. These reactions also produce free radicals, beginning with radical nitrate, criegree biradicals and peroxyacyl radicals, and leading to radicals such as hydroxyl, alkyl, alkylperoxy, hydroperoxy and alcoxy radicals. Such radicals

can react to other species indoors that produce additional aldehydes, ketones, carboxylic acids, dinitrates and peroxyacyl nitrates. The potential of few products are known or suspected to be irritating.

The time available for indoor pollutants to interact is determined by the air exchange rate along with the air change effectiveness (mixing factor), which also influence the reactants concentration. When a reactant primarily has indoor origins, greater indoor-outdoor interaction and further mixing reduces its concentration indoors. The converse is true if a reactant primarily has outdoor sources. In addition, the concentrations of the reactants affect the rate at which a chemical transformation takes place [12].

The existence of the reactants determines the chemistry in which they participate. Certain volatile organic compounds (VOCs) are relatively inert (e.g., fully halogenated species) whereas other VOCs are relatively reactive (e.g. alkenes). Many indoor reactions continue faster as temperature rises. The reactions between alkenes and the hydroxyl radical is an example for the reactions which show little or no temperature dependence [13]. The relative humidity influences both the water concentration in the gas phase as well as the absence / presence / thickness of aqueous surface films.

Some chemical bonds can be broken through the action of light (photolysis). Outdoors, photolysis is important; indoors, it is less important. Nevertheless, under indoor illumination certain species can photolyze (especially fluorescent lights). These involve the radical nitrate, NO_3 (~ < 580 nm) and nitrogen dioxide, NO_2 (X < 398 nm). As the Surface-to-Volume ratio (S/V) increases, reactions on indoor surfaces become more important. Small spaces and fleecy fabrics (carpets, drapes etc.) are associated with high S/V's. Surface reactions can serve indoor contaminants both as sinks and as sources.

Owing to the reactive aspect of the indoor atmosphere the chemical composition of the indoor air varies. Reactive chemicals as reactants plays an important role in driving the indoor air chemistry. Different types of reactions occur indoors are

- Oxidation,
- ➢ Hydrolysis,
- Acid/base,
- Photolysis,

- Decomposition,
- Dehalogenation (gas phase and on surfaces).

The indoor reactions that have gained the greatest attention are reactions of ozone with terpenoids in the gas-phase as well as with the surfaces of some common materials, furnishings, and the occupants themselves. It has become apparent that surface reactions frequently impact indoor settings more than gas-phase processes do.

The indoor gas-phase reactions that have been most thoroughly investigated are those involving ozone, especially reactions between ozone and terpenoids. Additionally, ozone-initiated reactions are the source of other two important indoor oxidants—hydroxyl and nitrate radicals. Reactions of ozone with alkenes and nitrogen dioxide are the major sources of hydroxyl radicals and nitrate radicals indoors, respectively [14].

5.1 Reactive Chemistry

The important reactions occurring in indoor environment are (i) O_3 reacts with unsaturated

hydrocarbons, (ii) production of •OH radicals by the reaction of O_3 and NOx, (iii) decomposition of PAN (peroxyacetyl-nitrate), (iv) free radical reaction with VOCs, and (v) other heterogeneous reactions [11,15-17]. Note that the reactions in the indoor environment mentioned above are thermodynamically favourable. Hence, due to the absence of sun light, their reaction rate is very less when compared to outdoor condition.

Reactive chemistry itself is a source of origin for various chemicals that otherwise would not be present indoors. Examples of the reactive chemicals generated by indoor air chemistry are short-lived radical species such as hydroxyl (OH), hydroperoxy (HOO·), organic peroxy (where the generic term, ROO, denotes the sum of all the peroxy radicals present) and nitrate (NO₃) radicals, as well as Criegee intermediates formed from the indoor ozone-terpene reaction. Some note species are secondary ozonides, nitrated and oxygenated VOCs (such as organic nitrates, carbonyls, dicarbonyls, and hydroxy carbonyls), and secondary organic aerosols (SOA). Most of these species are expected to be irritating or even carcinogenic, and there are even more species recognized than we detect currently known as 'stealth pollutants'.



Fig. 5. Reactive chemistry indoor [18]

Dominant indoor processes involve Oxidation reactions involving oxygen, ozone, radicals of hydroxyl and nitrate; acid-based reactions, hydrolysis reactions and decomposition, often induced by ultraviolet light and/or heat. Hydrolysis reactions are relatively slower and mostly occurs on surfaces. The other processes may occur both in the gas phase and also on the surfaces [19].

Indoor oxidative chemistry contributes to the formation of many commonly found organic compounds such aldehydes as (e.g. formaldehyde), ketones (e.g. acetone), carboxylic acids, esters, epoxides and dicarbonyls [20] when their vapor pressure is low enough, SOA is formed.

The oxidation processes of indoor chemicals can be powered by oxidants such as ozone (O_3) . hydroxyl radicals (OH) and nitrate radicals (NO_3) in the gas phase, which may contribute to the generation of oxygenated species (e.g. formaldehyde) and secondary organic aerosols (SOA). Such oxidants need to be detected and guantified in combination with oxidant precursors, reactants and reaction products (such as oxygenated organics, organic nitrates, SOA) to understand indoor oxidation processes [21].

The reaction time scale is extensively long for indoor surface chemistry and may persist for longer periods whereas for purely gas phase reactions it is only few hours because of the air exchange rates. Yet, the chemistry that is too slow to be important indoors during the gas phase might be fast enough to be important if either or both of the reactants are bound to the surface.

5.2 Gas Phase Chemistry

Indoor oxidative chemistry is driven by ozone that can react at significant levels with nitric oxide (·NO), nitrogen dioxide (NO₂), and unsaturated organic compounds (e.g., terpenoids. sesquiterpenes, unsaturated fatty acids) in the gas phase to produce excited intermediates, radicals OH and NO₃, and oxygenated organic compounds [15]. The use of cleaning products containing both terpenes and glycol ethers in the presence of O₃ that allows oxidation of the glycol ethers through OH and possibly NO₃ [22]. The resulting products can contain potential allergenic peroxides and hydroperoxides [23].

To date, a lot of indoor air chemistry work has concentrated on the reactions between oxidants (O_3 and OH radicals) and VOCs that generate thousands of complex and sometimes multifunctional gas-phase products. The high concentrations of HONO near sunlit windows, or during cleaning operations, indoor OH concentrations are likely to increase. When formed, OH is able to react with terpenes and any other organics present, often at levels close to those observed outside.

5.3 Surface Chemistry

Surface-to-volume ratios are significantly higher indoors than outdoors (about 3 vs. $0.01 \text{ m}^2/\text{m}^3$) and therefore surface-to-volume reactions turn to be more severe indoors than out. There are various indoor surfaces, including construction materials, wall cavities, ducts, skin, clothes, dust, and airborne particulate matter [19].

Surface interactions impact the subsequent human inhalation exposures to environmental tobacco smoke [24], for instance, acid-base chemistry impacts surface desorption of nicotine [25].

Indoor surface reactions occurs at the interfaces, including air/particle and air/surface films. The ozone-reactivity of certain terpenoids (e.g., Δ 3-carene) is significantly more on surfaces compared to the gas phase. It has a greater effect on lower volatility terpenoids such as α -terpeniol and dihydromyrcenol that have a greater affinity for surfaces than their more volatile cousins of terpene. Benzo[a]pyrene (BaP) is one of the PAHs formed during combustion activities like cooking, smoking, etc. In the gas phase the reaction between BaP and ozone is negligible, but when BaP is sorbed on to glass it reacts with ozone to form mono- and diolepoxides.

5.4 Aqueous Chemistry

Moisture plays a significant part in indoor chemistry. Numerous chemicals present in materials and products used indoors are prone to base-catalyzed hydrolysis. These include esters of sebacate and organophosphates, phthalate, adipate used as plasticizers; p- hydroxybenzoic acid esters (parabens) used as antioxidants; bisphenol A diglycidyl ether (BADGE) used in personal care items and coatings; and acrylatebased copolymers used in adhesives. High humidity outside, water leakage into homes, pipe leakage, flooding, water penetration into building materials, and humidity resulting from human activities such as cooking and bathing contributing to increase in dampness and high RH indoors that lead to respiratory infections such as cough, wheeze, asthma. Dampness is related to mold exposures. Two scientific reports shows that the dampness or mold exposures have resulted in increased respiratory symptoms. HONO production in residences provides conclusive proof that concentrations of indoor liquid water are sufficient to drive aqueous chemistry, at least in some homes / times, because HONO is formed on surfaces (from NO₂ hydrolysis) only in the presence of liquid water.

Aqueous chemistry can influence the exposure by acting as a sink for some water-soluble gasses in indoor air and a source of certain volatile products (altering inhalation exposure) and condensed phase products (altering particulate inhalation and dermal exposure) [26].

5.4.1 Water-soluble organic gases in indoor air

Indoor WSOG concentrations were found to be 15 times higher on average than outdoor concentrations, indicating that the vast majority of indoor WSOGs are emitted or produced indoors. In addition to WSOG released directly into indoor air, WSOG will also be generated indoors from the gas phase VOC oxidation and oxidation of organic surfaces. Gas-phase oxidation was observed to form WSOGs, for example from d-limonene, on time scales that are competitive with the air exchange rate. Oxidation of surface materials is found as the important pathway of formation for WSOGs as surface oxidation can create indoor WSOGs even though reaction times are long relative to the time-scale for air exchange. Three important oxidants responsible for the production of WSOG indoors are ozone, hydroxyl radical (OH·) and nitrate radical (NO₃). Ozone enters from outdoors while OH and NO₃ are produced indoors. Occasionally, nitrogen pentoxide (N₂O₅) and chlorine radical might also play an important part like in homes with combustion using natural gas and ozone $(NO_2 + O_3)$ or in cleaning and photolysis processes, respectively [26].

In case for aqueous chemistry in indoor, air surfaces are an important part of indoor chemistry. Indoor surface area-to-volume (S/V) ratios are greater than $3 \text{ m}^2/\text{m}^3$, and much higher

when considering internal surface areas for materials such as carpets and upholstery. This is of magnitude greater than the standard < 0.01 m^2/m^3 of outdoor ambient air. Even a 1 nm water film on indoor surfaces, a film consistent with simple water adsorption, will provide more than 200 times the volume of liquid water as is found in aerosols in outdoor air (assuming 20 m^2/m^3 of surface in a 300 m^3 home).

The HONO measurements indoors provides strong evidence that ample liquid water is present in residences to drive aqueous chemistry, and that aqueous chemistry will change the composition of indoor air. HONO has been measured in several homes over the last few decades and found that HONO is generated from the heterogeneous hydrolysis of NO₂ whose concentrations ranging from 2 to 8 ppb. Recently, indoor OH radical concentration was measured as 1.8×10^6 molecules/m³ which is related to photolysis of HONO on windows. This suggests that OH radicals can also be formed through photolysis in indoor liquid water films on windows. Those OH radicals can further oxidize aldehydes (e.g., glyoxal), organic acids (e.g., acetic, lactic) and phenols (e.g., guaiacol, phenol) in the aqueous phase to form oxalic acid, oligomers and other products.

The gas phase formic acid is produced by the aqueous OH oxidation of formaldehyde. It is also expected that ammonia/amines, which has varying water-solubilities and can also be increased indoors, will react with aldehydes as water evaporates from indoor surfaces. These reactions will form brown surface films water can be present indoors for a variety of reasons. Few indoor locations are always wet, such as the toilet bowl and sink, but they have limited interfacial surface areas for chemical mass transport. Other spots that are seasonally wet includes air conditioning coils during summer and windows/exterior walls during winter that are cooler than the indoor air and condense moisture from that air. Also, various types of hygroscopic materials (e.g., clothing, furniture, building materials, aerosols and surface grime) absorb water vapor, creating highly concentrated aqueous solutions [26].

5.5 Photochemistry

A typical misunderstanding about the indoor condition is that the absence of direct daylight implies the non-occurrence of indoor photolysis responses. However, photolysis still occurs inside, simply more gradually than outside. In some cases, photolysis of HONO indoors can be a source of hydroxyl radicals. It has been observed that HONO is formed by the reaction between NO_2 and water on indoor surfaces and also light can enhance indoor HONO production from interfacial reactions between NO_2 and household chemicals. HONO, could also respond with nicotine sorbed on surfaces of indoor to deliver cancer-causing tobacco-explicit nitrosamines (TSNAs).

Kowal and his team took a different type of lighting used in residences and measured the distance-dependent and wavelength-resolved photon fluxes. They found significant difference among various light sources, both in terms of intensity and wavelength dependence. Highest intensities were found from fluorescent tubes, whilst the LED light source had zero emission below 400 nm [27]. The effect of various sources of indoor lighting on projected indoor OH concentrations was explored using models. The OH concentration predicted depending on the type of indoor lighting shows that using an uncovered fluorescent tube is likely to lead significantly more chemical processing than using an LED. Also the non-zero concentration of OH was predicted in dark and this shows that this essential oxidant is ubiquitous indoors.

6. IMPACTS OF OCCUPANTS ON INDOOR CHEMISTRY

Human inhabitants emit skin oils at an astounding pace, and shed their skin flakes, rich in skin oil. A typical adult releases sebum at ~500 mg / h107, and sheds 30-90 mg / h skin flakes. Ozone and nitrate radicals rapidly react with double bonded constituents of skin oil.

The oxidation chemistry between ozone and skin oil produces various gas-phase products, including acetone, 6-methyl-5-heptene-2-one (6-MHO), geranyl acetone, and 4-oxopentanal (4-OPA). These reactions also produce low volatile chemicals, including levulinic, succinic, adipic and suberic acids, that remain on the skin, clothes, or surfaces Oxidation levels are high, suggesting the presence of these less volatile products on skin and surfaces soiled with skin oil and skin flakes. Breath is also an important source of reactive chemicals indoors, which includes isoprene, nitric oxide (NO) and ammonia. Isoprene gradually reacts with ozone, more easily reacts with hydroxyl and nitrate radicals, producing methacrolein and methyl vinyl ketone among other products. Ammonia is also

produced from the skin of the inhabitants and breath. Ammonia from occupants affects the pH of airborne contaminants indoors, as well as indoor surface acid-base chemistry [28].

7. EFFECTS OF INDOOR POLLUTANTS ON HUMAN HELATH

The negative consequences of indoor air pollution result in around 2 million premature deaths every year, with 44% are due to pneumonia, 54% from chronic obstructive pulmonary disease (COPD), and 2% from lung cancer. Women and younger children, who spend most of the time at home are the most affected groups. The morbidities related to indoor air pollution are respiratory illnesses, viz., acute respiratory tract infection and COPD, low birth weight and still birth, leukaemia, nasopharynx, larynx and lung cancer. The formaldehyde might cause harmful health effects being an acute reducing vital capacity. irritant. causing bronchitis, to be a carcinogen causing leukaemia and lung cancer [29].

The commonly observed harmful effects are irritation of eyes, nose and throat. Also cough, wheeze, chest tightness and increased responsiveness of airways to allergens.

Potential avenues leading to health effects in the airways and the cardiovascular system include: Sensory irritation, inflammatory reactions in the airways, sensitization, heart rate effects, delayed physiological response, and possibly dermal exposure routes [30,31].

Harmful effects of IAP are manifested as Asthma, cancer, cardiovascular diseases, Sudden infant death syndrome (SIDS). Some of the common indoor pollutants and their harmful effects have been summarized below:

- Volatile Organic Compounds: (VOC) -Cause respiratory tract diseases, nerve diseases, irritation of eyes, and loss of coordination, visual disorders, nausea, allergic reactions and asthma.
- Formaldehyde Causes breathing difficulties, Skin rash, other allergic reaction.
- Moulds Conjunctive irritation, nerve diseases, Hypersensitivity reactions, asthma, Systemic infections, asthma.
- Carbon Monoxide: Causes fatigue, vomiting, irritability, sleepiness, confusion, Unconsciousness, coma and Death.

 Biomass smoke, especially metal ions, and polycyclic aromatics, contributes to cataract development. The use of biomass fuel for cooking has been found to be correlated significantly with a high occurrence of active tuberculosis.

Studies in western India reported that use of wood was found to be a major cause for agedependent cataract. The risk of stillbirths has increased up to 50% due to use of biomass fuels during pregnancy. An increased risk of low birth weight babies by 49 per cent was associated with the biomass fuel exposure. In contrast with those using cleaner fuels, women from households using high emission fuels were 1.4 times more likely to give birth to a baby with low birth weight.

A pollutant's water solubility influences its effect on the airway: highly water-soluble chemicals affect the lips, nose, and throat; low watersoluble chemicals impact the middle airway (bronchial tubes); and much lower water-soluble chemicals damage the lower airway (deep lungs and alveoli).

Based on the inherent characteristics, respirable particles and gases impact various regions of the respiratory tree. For gases it is essential to have relative solubility whereas size is important for particles. Note that, extremely water-soluble, sulfur dioxide initially affects the upper airways, while medium-soluble ozone initially affects the middle airways and low solubility nitrogen dioxide affects the lower airways. Chemesthesis refers to the "feel" of a chemical, usually in the eyes, mouth, or throat describes discomfort that have been chemically provoked. threshold exposure The for short to chemesthesis is usually > 1 ppm, which may be lower for reactive molecules. In the case of a mixture of limonene / O3 (at reasonable concentrations), the chemesthesis response of the subjects increased over time. The exposure duration has a deep effect on both magnitude and sensitivity of chemesthesis [33].

Dermal reactions are also very concerning. Oxidation of limonene has been reported to cause contact allergens [34].

A variety of indoor sources and occupants' activities, including furniture, paints, lacquers, waxes, carpets, solvents, cleaning supplies, office equipment such as copiers and printers, gas cook stoves and cigarettes, can release potentially harmful gasses and particular matter (PM). Air pollutants common to different indoor environments include carbon monoxide and dioxide (CO and CO₂), volatile organic compounds (VOCs; e.g., formaldehyde and benzene), nitrogen oxides (NO and NO₂), and polycyclic aromatic hydrocarbons (PAHs) one of the priority concerns for human health today.

The continuous exposure to air pollutants, the concentration of which can be even higher indoors, may eventually cause respiratory and cardiovascular diseases leading to the so called 'sick building syndrome' and 'building-related illnesses' [35].



Fig. 6. Impact of pollutants on the airway [32]

8. MITIGATION MEASURES OVERCOME THE IMPACTS

8.1 Phytoremediation

Phytoremediation is emerging as an important way for the mitigation of indoor air pollutants (IAP). Plant mitigates indoor pollution through different processes which involve phytoremediation, adsorption, and absorption and stomata uptake. These activities depend upon the surface area of plant leaf and also the plant variability, temperature, humidity, water available, light source etc.

8.2 Removal Mechanism

Different mechanisms by which plants remove indoor pollution include

 Microbial degradation (rhizospheric microorganisms)

- Plant-liquid extraction (phytoexteraction),
- Plant-gas extraction (stomatal uptake),
- Enzymatic catalysis inside tissues,
- Direct evaporation through leaves or indirect transpiration by plant.

Five common indoor plants have been reported (Peace Lily, Ficus, Calathia, Dieffenbachia, Golden Pothos) for mitigating ozone from indoor area by moderate ozone removal from indoor environment (Figs. 8 and 9). The leaf surface area was the important factor for ozone removal [37].

Particulate matter ($PM_{2.5}$) alone accounts for more than 2 million deaths a year worldwide [38]. PM also affects the circulatory and respiratory systems [39] and are also the second biggest reason of lung cancer (European Environmental Agency (EEA) 2007) and autism [40].



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Fig. 7. Mechanism of pollutant removal in plants [35]

Plant name	Scientific name	Known pollutant removed
Spider Plant	Chlorophytum Comosum	Benzene, Formaldehyde CO Xylene
ZZ Plant	Zamioculcas zamiifolia	Benzene, toluene, ethylbenzene, and xylene (BTEX)
Snake Plant	Sansevieria trifasciata	Ethylbenzene toluene VOC
Golden Pothos	Scindapsus Aures	Toluene Benzene CO NO2
Aloe	Aloe barbadensis	Benzene Formaldehyde.
Chrysanthemum	Chrysanthemum indicum	Formaldehyde
Gerber Daisy	Gerber Daisy	Trichloroethylene Benzene
Areca Palm	Chrysalidocarpus lutescens	Toluene Xylene Formaldehyde Dibutyl phthalate

Table 3.	Plants th	nat remove	indoor	pollution	[36]
				0011011011	



Fig. 8. Ozone deposition velocity of indoor plants



Fig. 9. Comparison of different indoor plants for their ozone removal efficiency

Particulate matter will persist in the air after emission for a time ranging hours to several weeks and may remain in the emission site and even be transported over long distances [41]. There are several classifications of PM, depending on their aerodynamic diameter. The classification with four fraction sizes as cited in literature are as follows. Large-Ø 10 - 100 µm; Coarse—Ø 2.5 -10 um (PM10); Fine-0.01-2.5 µm (PM2.5) and Super (or ultra) fine-less than Ø 0.01 µm. It was observed that spider plants accumulate PM of both types (water washable and trapped in waxes) in all three sizes and the amount differed depending on the activity taking place in the particular rooms ranging from 13.62 to 19.79 µg/cm² [42].

From the 120 plant species assessed for phytoremediation of pollutants from indoor air,

Chlorophytum comosum L. (spider plant) has the ability to eliminate formaldehyde, nitrogen dioxide, carbon oxide, ozone, benzene, toluene, cigarette smoke and ammonia [45]. This reduces the risk to human health to a greater extent.

The volatile formaldehyde removal by aerial and root parts of two common indoor plants *Ficus japonica* and *Ficus benjamina* have been studied and reported that during the daytime, the amount of formaldehyde removed by the aerial sections of the plant was considerably greater than at night [43].

Formaldehyde, a widespread hazardous air pollutant which is emitted from aged furniture and pressed-wood products over the long term and which is likely to have carcinogenic effects in humans is one of the major concerns. Pioneer experiments carried out by NASA during the 1980s have shown successfully that plants are capable of eliminating airborne pollutants. Although these results were based on a simplified experimental approach - recently, more precise studies simulating long-term foliage exposure to traditional indoor air pollutant concentrations showed that stomatal (dependent) absorption is 30-100 times higher than that passively adsorbed by non-stomatal deposition. These findings further indicate that certain pollutants are metabolically degraded and/or translocated to shoots and roots after they have entered the plant leaf. Plants have enzymes which can catalyze pollutant degradation, such as formaldehyde oxidation or hydroxylation and cleavage of the benzene and toluene aromatic rings. Airborne pollutants absorbed via leaf stomatal uptake can undergo transformation followed by enzymatic oxidation and conversion into various bioproducts through conjugation with plant endogenous



Fig. 10. Removal of volatile formaldehyde by aerial and root parts [43,44]

Plant	Voc reduction %	Removal of other pollutants
Hemigraphis alternata	44%	Formaldehyde, CO ₂
Hedera helix	38%	Methanol, NO and NO ₂
Tradescantia pallida	34%	Particulate matter (PM), black carbon (BC)
Asparagus densiflorus	31%	NOx, TVOC
Hoya carnosa	26%	SO ₂ and N ₂ O

Table 4. Plants with VOC and other chemical removal potential [36]

compounds (i.e., sugars, amino acids, organic peptides). The acids. and assimilated contaminants can be either re-expelled after being catabolized (re-emission into the air or ejection through root exudates) or metabolized further to be used both as carbon and as energy sources. Plant enzymatic scavenging and detoxification processes manage a decreasing concentration gradient of pollutants between the air and the inside of the leaves, allowing consistent and steady absorption when stomata are open. However, only a few enzymes currently exist which are accountable for the metabolic degradation of airborne pollutants.

8.3 Ventilation Systems

Buildings are diverse, and it is vital to understand the impacts that variations in building construction, location and operation can have on indoor air chemistry.

A key issue affecting indoor air chemistry is the building ventilation rate. Mechanically ventilated buildings often employ heating, ventilation and air conditioning (HVAC) systems and it is necessary to understand when the system is running, the air exchange rate, the fraction of recirculated air, whether the outdoor air fraction used for ventilation is fixed or variable, humidification/dehumidification. filtration efficiencies and temperature set-points throughout the day. Even in buildings with natural ventilation, it is necessary to measure air exchange rates, temperature and relative humidity to properly understand the chemistry. Another consideration is the chemistry that occurs in "hidden" building spaces (e.g., wall cavities, basements, crawl spaces, attics) and/or how this can influence the chemistry in occupied spaces.

9. MODELLING STUDIES ON INDOOR CHEMISTRY

Indoor environments have changed significantly in the last 50 years and will continue to do so. An emerging research field focuses on low or zeroenergy buildings which turn to have low ventilation levels and thus more room for gasphase chemistry. With growing use of 'green materials' and products containing synthetic nanoparticles, it is necessary to look at their emissions / reactions and how these chemical interactions develop with age. Ongoing and drastic changes in indoor environments are more significant than ever to understand indoor chemistry and ensure that building occupants and building contents are safe from accidental exposures and harmful chemicals.

Indoor air models are being used to evaluate findings, identify gaps and limitations in knowledge and design experimental programs. The indoor chemical box model contains around 5000 species and 20,000 reactions. Measurements are available for perhaps only 100-200 indoor species; model predictions provide insights that would be absent otherwise.

Development of a modelling consortium for indoor chemistry integrates models over a range from molecular to room scales (spatial) and from sub-nanosecond to days (temporal). The MOCCIE methods include simulations of molecular dynamics (MD), modeling of kinetic processes, modeling of gas-phase chemistry, modeling of organic aerosols, and simulations of computational fluid dynamics (CFD).

Using these models, it is possible to study ozone reactions with skin and clothes, oxidation of volatile organic compounds and production of secondary organic aerosols and mass transport and partitioning of indoor species to surfaces. MD simulations include molecular representations adsorption of limonene on SiO₂ and ozone interactions with skin lipid squalene, providing kinetic metrics such as coefficient of surface accommodation, lifetime for desorption and bulk diffusivity.

For simulating α -pinene ozonolysis with enhanced representation of gas – particle partitioning, a comprehensive indoor chemical



Fig. 11. Modelling approaches in MOCCIE [46]

box model is used. Application of the 2D-volatility base set shows that OH-induced aging often results in increased concentrations of indoor organic aerosols due to organic mass functionalization and increased partitioning. CFD simulations show that primary ozone concentrations shift rapidly near the human surface, implying the non-uniform spatial distributions from the surface to ambient air, while secondary ozone product is fairly wellmixed across the space. This development provides a basis for combining various modelling tools and experimental measurements, opening up an avenue for development of integrated detailed and models with representations of various chemistry in indoor environments.

10. CONCLUSION

Due to modern technology the rate of indoor air pollution has significantly increased. Urban people spend up to 85–90% of their time indoors [45], often unaware that they can be subjected air pollution continuously. Indoor air pollution levels can be more than 10 times higher compared to outdoor and, in regarding to some hazardous substances, their concentrations can also surpass acceptable levels by up to 100 times. According to the United States Environmental Protection Agency (US EPA), indoor air pollution is one of the top five risks to public health. Indoor air pollution is very detrimental to health but the use of indoor plants will save us. Indoor plants can provide a powerful tool in combating elevated indoor air pollution levels. Plants in our office or home are not only for decorative purposes, but NASA scientists find them fairly useful in absorbing potentially harmful gases, and in cleaning up the air inside the buildings [47]. Phytoremediation technology is a simpler, cheaper, environmentally friendly purification process that can be used for a wide variety of both organic and inorganic impurities. However, the time of purification is longer.

Building materials emit a range of reactive constituents and secondary products (derived from initial constituents) which includes terpenoids, aliphatic aldehydes, phthalates, phenol, mono-and dicarboxylic acids and so on, which have adverse health effects on the inhabitants.

An example of secondary pollution exists in buildings constructed with pentachlorophenol (PCP)-treated wooden studs. Over time, PCP is converted into tetra-chloroanisole, which gives occupants a very unpleasant odour [48]. The socalled "natural" or "ecologic" goods are not inherently free of adverse health effects. Certain other constituents such as terpenoids and linseed oil may be chemically reactive than those from non-ecologic products. Secondary emissions from these products may present a greater risk to human health than those compounds which are substitutes for their precursors.

Future indoor field campaigns regarding indoor oxidant chemistry should have goals of:

- Continued characterization of oxidant sources and sinks.
- Measures to confirm the presence of species that the models predict and their concentrations relevant for occupant exposure and also to minimize the uncertainties in photolysis.
- The rates of deposition and surface production.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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> Peer-review history: The peer review history for this paper can be accessed here: http://www.sdiarticle4.com/review-history/57504