Secondary Pollutants from VOCs in Urban Indoor Air

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Abstract

People spend most of their time in indoor environment. Volatile organic compounds (VOCs) are commonly found in indoors due to the presence of several indoor sources. Besides, outdoor VOCs, when infiltrate into the indoors, increase indoor levels of VOCs. Some studies have reported that VOCs in indoor air may be involved in the production of secondary pollutants. This study investigates the role of VOCs in forming secondary air pollutants and identifies the critical environmental factors, which favor the reactions. It was found that VOCs form secondary organic aerosols (SOAs), which remain in particle form in the ultrafine size range. In this, pollutants like ozone (O_3), oxides of nitrogen (NOx) and hydroxyl radicles (OH) take part. SOA constitutes major portion of particulate matter in indoors and as it has fine size, it is suspected to cause severe health effects. The article is, therefore, focused on the importance and challenges that SOAs pose to indoor environment. Mitigation measures and research gaps are also discussed.

Keywords: Indoor, Pollutants, VOCs, SOA, Particulate matter.

Introduction

Indoor air pollution is as important as the outdoor air pollution, since an average person spends more than 80% of the time in indoor environments [1]. It is either residence or workplace. So, any air pollutant in the indoor environment can cause more damage because of prolonged period of exposer. With rapid urbanization, numbers of residences and workplaces are increasing in Indian cities particularly near trafficked roadways. Poor air quality inside the residences and workplaces is the cause of severe health risk to the users and can also reduce work efficiency and increase absenteeism [2].

Amongst the pollutants, volatile organic compounds (VOCs) are a major class of air pollutants generally found in both outdoor and indoor environments. Indoor VOC sources are building materials, furniture, cleaning products, insect repellents, solvents, fragrances and hobby supplies [3] and smoking [4]. Attached garages are also a source of indoor VOCs [5]. VOCs are released from day-to-day indoor activities like cooking or cleaning [6, 7]. VOCs migrated from outdoor air are also a major source [8]. Vehicular exhausts containing VOCs infiltrate indoor and increase the indoor concentration [9]. Contaminated water used for shower bath also increases VOC concentration, especially benzene concentration in indoor area [10]. VOCs have several health effects. Many VOCs are toxic and some are reported as carcinogenic [11]. Benzene is classified as human carcinogen group 1 by the International Agency for Research on Cancer, 1982. It should also be noted that the major indoor sources of VOCs like solvents, cleaning products, and infiltrated vehicular exhaust are common in urban areas than in rural areas.

Besides VOCs, ozone is found in indoor environments of urban areas. Several types of office equipment, photocopier machines and printers generate ozone [12]. Ozone generators are also used as air cleaners in urban houses [13]. Ozone generating outdoor also infiltrates into indoor spaces, which increases ozone concentration even in absence of indoor sources. Ozone reacts with VOCs to form several sets of compounds and finally forms a group of semi-volatile compounds, which are suspended in air [14]. Such reactions also form hydroxyl radicals, which further react with more

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VOCs and form secondary compounds in aerosol form [15]. These aerosols are termed as secondary organic aerosols (SOAs). Less air exchange rate, high temperature, variable humidity and more VOC sources can increase the SOA concentration in indoor air. High aerosol concentration in a building may create many health issues and lead to formation of sick building syndromes.

In India, indoor air quality studies are mostly focused on the release of air pollutants from cooking processes using traditional biomass cook stoves in rural and semi-urban areas [16, 17].

Compared to rural and suburban areas, indoor air quality of Indian cities has got less attention, because of less use of biomass based cooking stoves [18]. The studies on SOAs in India are scarce. Most buildings near roadways particularly in urbanized areas have high occupant density, poor ventilation and use no air cleaning equipment. Hence, higher SOA in such buildings is more likely. The scope of this study is to develop a scientific perspective and find the fundamental processes of SOA formation under typical environmental conditions so that ways of mitigation can be understood.

VOCs in Indoor Environment

In different studies, different types of VOCs are identified in indoor areas. Chlorinated, aromatic, terpenoid, aliphatic and carbonyl compounds are found in buildings used for mixed purposes. BTEX (benzene, toluene, ethylbenzene, and xylene) and terpenoid are found in buildings used for both office and residential purposes [19]. VOCs in indoor are generally found to be twice of the outdoor [20, 21]. In preoccupied buildings, VOC concentration is found larger than already used buildings [22].

Smoking is a major source of VOCs in indoor buildings, which mainly contribute to benzene [23]. Toluene is found in very high concentration in indoor area [24-26]. Cleaning products, washing products and cosmetics are major terpenoid sources. The commonly found VOCs used in such products are limonene [27] and αpynene [28].

Formaldehyde is another important VOC found in indoor air. It is emitted from wood adhesive where urea formaldehyde copolymer is used. It is also a constituent of tobacco smoke [29]. Along with these, other VOCs found in indoor area are ethanol, n-decane, nonanal, styrene, campene, etc. [30].

SOA Formation from VOCs

Studies on VOCs have shown that in indoor area there are chemical pathways, which cause degradation of these compounds. VOC degradation generally occurs in presence of hydroxyl radical, ozone or nitrate radical [31]. Generally for many VOCs, the reaction half-life is longer when it reacts with ozone at normal air exchange rate of a common building. But a subset of VOCs competes with air exchange rate and as a result they react rapidly with ozone. This subset contains one or more unsaturated carbon bond and ozone reacts at these unsaturated bonds. This subset includes camphene, isoprene, d-limonene, α-pyrene and styrene [32]. The reactions are:

$O_3+R_1R_2C=CR_3R_4$----Ozonize

Ozonide $\longrightarrow R_1C(O)\ R2+[R_3R_4C.OO.]^*$ Or

Ozonide $\longrightarrow [R_1R_2C.OO.]^*+R_3C(O)R4$ [32]

The bi-radicals form [R3R4C.OO.]* and $R_1R_2C.OO.]^*$ go on continuous reactions and form hydroxyl radical, hydroperoxyl radical and alkylperoxyl radical as intermediate products. The forms of the stable products are generally aldehyde or carbonyl products. Alcohol and carbonyls have lower volatility than their precursors and are condensed to form aerosol [33].

The forms of hydroxyl radical react with VOCs by abstraction of hydrogen atom from the atom or add hydrogen or functional groups to the C-C bonds. In addition, reaction volatility generally decreases and SOA form [33]. In case of aromatics, OH radical plays the role in bond cleavage during photo oxidation [34], which forms low-volatile compounds. Proxy radical can also form lower-volatile products. Peroxy radical and hydro-peroxy radicals formed as intermediate products can react with each other to form hydro-peroxide, which behaves as aerosol due to low volatility.

$RO_2+HO_2=ROOH+O_2$ [35]

NOx plays an important role in SOA formation. SOA formation increases in low concentration of NOx from mono-tarpenes, isoprene and aromatics [36, 37]. NOx level determines the initial oxidant concentration and in higher concentration it competes with the VOC to get itself oxidized. It also acts a scavenger of hydroxyl and peroxyl radical. Peroxyl radical reacts with NOx to form alkyl nitrate. However, this reaction forms an isomerization channel which causes formation of SOA from sesquetarpenes and large aromatics [38]. For relatively small hydrocarbon, when NOx level is low, less alkyl nitrates are formed and rest of alkoxy radicals react with oxygen and form low-volatile compounds. The formation of less volatile compounds such as hydro-peroxides and acids increases SOA concentration [39].

There is another process of formation of SOA known as particle-phase reaction. This is non-oxidative pathway where higher molecular weight SOA is formed. In the experiments, when acidic seed particles are used, it causes increase of SOA concentration. It occurs because of accumulation of volatile compounds on the seeds and behaving as aerosol [40]. In chamber experiments, it is also seen that ammonium sulfate seeds absorbs the gas phase products and forms particles [41]. The kinetics of particle-phase reactions contains uncertainty in terms of comparison with atmosphere. In real world, particle-phase reactions are found less.

Size Distribution of SOA

United States Environmental Protection Agency (USEPA), in 2007, considered SOA a fraction of PM2.5. But in different laboratory experiments, it is found that the particle diameter generally lies below 1 μm. Sarwar et al. found that with the addition of VOC, rapid burst of particles occurred in the range of 0.02-0.1 μm and gradually size increases up to 0.7 μm [42]. Weschler and Shields also found the same trend in the particle growth. In their experiment, the sizes of particles were in the range of 0.1-1.0 μm [43]. Coleman et al. found in a chamber experiment that major particle size is below 0.4 μm; however, high concentration of particulate matters of size 1 μm was also detected. [44]. Hovorka and Branis, in their study in a large hall found increased number of particles of less than 0.1 μm. The ultrafine range of 15-80 nm was found to appear at the release period of ozone and VOCs. These cumulative particle concentrations increase the PM2.5 concentration in indoor than outdoor [45].

Factors Affecting SOA Formation

Increasing temperature causes volatilization of VOCs and also enhances SOA formation [46]. Huang et al. found that total particle count increased from 15 to 23 °C and decreased at 30 °C. At 30 °C particle formation was found to be delayed [47]. Warren also found same kind of results where SOA formation was 5-6 times higher at 17 C than at 40 C. Walkoff et al. reported that RH favors SOA formation while Weinmann et al. found that RH affects particle growth. Huang et al. showed that when RH was more than 50%, more particles of size range 6-225 nm were formed. Their findings were supported by the study of Johnson et al., which reported that particle formation increases with RH increasing from 2 to 80% [48]. In contrast, Na et al. found RH inhibiting formation of SOA. They reported that water vapor might stabilize the radical which is the intermediate product of the process of formation of SOA and thus stop the reaction [49].

Air exchange rate also plays a major role in SOA formation process. Whesler and Shields found that at higher air exchange rate both number and mass concentrations of the particles were less. Their study was later supported by Huang at al. In their study, when the ACH was reduced to 1.08 and 0.36 h^{-1}, the growth and number of particles were found to be increased. But in real world study of Hovorka and Branis, in high air exchange rate the number of small particles was found to be increased with the increasing air exchange rate. Therefore, in case of parameters there lie uncertainties because the effect of same factor was found different in different experiments.

Mitigation Measures

In indoor environment, the precursor VOCs of SOA formations are identified as cleaning products and air fresheners. So, to control SOA the use of such cleaning products should be limited. But it is somewhat different because all available cleaning products either herbal or chemical-based contain such VOCs. Weschler reported that use of ozone as air purifier is misleading; instead it increases the SOA concentration in indoor spaces. His opinion was that modest increase of ventilation rate may decrease the indoor air pollutant concentration than introduction to 50-100 ppb of ozone to indoor. Goddish reported that climate control can be the easiest mean to control precursor VOCs. The control and application of temperature and RH at a level at which least amount of SOA forms can be a good control option. As the particle sizes are small, so conventional techniques are not that much suitable for control of SOA. Moreover, application of big and expensive control systems is also not feasible to use in residential buildings.

Research Gaps and Future Scope

Least work on SOA is done in the field of its impact on human health. It is due to the lack of suitable exposure technique of SOA in in vitro studies. For that reason, there is no biomarker of SOA identified. But it is believed that SOA causes severe health effects because of its smaller size.

There are different precursors of SOA that occur in field in mixed conditions. Laboratory analysis generally uses pure form of one or two VOCs. So, the real-world study may not match with chamber experimental results. In that case, it will be difficult to validate the models also. As the researchers found OH radicals in indoor also, so there will be chance of occurring of reactions like smog, which is prominent in outdoor. One factor that differentiates smog reactions from indoor conditions is light. In indoor, light intensity is generally lower than in outdoor. Leungsakul et al. found that ozone-limonene reaction occurred in both presence and absence of light [50]. But the impact of light on SOA formation is very less studied so far. Because of presence of unidentified SOA precursors, it is also difficult to estimate the budget of SOA. The aging of SOA under different conditions is also not well studied. It, therefore, creates a constraint in case of predicting episodes of SOA. The effects of intermediate gas products and radicals are still unknown.

Conclusion

VOCs are found in less concentration in the environment but in that much concentration also that they can cause pollution and severe health effects. A mixture of VOC, NOx, Ozone and OH radical can change the chemistry of the indoor species and can form SOA. In urban areas, outdoor pollutions are well known, but indoor pollution is still understudied. Developing economic conditions and living standard of urban dwellers make them buy more products which are easily available in urban markets that contain precursors of SOA.

Due to rising urban population, residences are becoming more compact with lower air exchange rate. It is increasing the chance of more SOA formation. The size of SOA is ultrafine, so such particles can easily enter into human lungs. So, there is much chance of deteriorating human health of urban dwellers. So, the study on SOA is important for urban centers of India.

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