Indoor Photochemistry Involving Ozone in Rural Location of Kannur—A Tropical Site in India

V. LEKHA^{1,*} and P. PUSHPALETHA²

¹Department of Chemistry, K.M.M. Government Women's College, Kannur-670004, India

²Department of Chemistry, Government College, Kasaragod-671123, India

*Corresponding author: E-mail: lekhaavdkm@gmail.com

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This study reports the indoor ozone (O₃) pollution in the rural location of Kannur, a tropical site in India, during March 2018 and the influence of their most important determinants. Measurements of indoor O₃, NO, NO₂ and NO_x were carried out in a residential building for a period of one week. Measurements were taken from the kitchen, as it had been identified as the most polluted spot. The background concentrations of O₃, NO, NO₂ and NO_x were also monitored. Indoor O₃ originates mainly from the outdoor environment and is also produced from indoor sources. The results show that there is a higher level of indoor O₃ during cooking hours. The study indicated that cooking activities in the kitchen had a strong impact on the indoor O₃ level. Ozone is an important gaseous pollutant which may lead to severe health problems such as decreased lung function and respiratory symptoms.

Keywords: Combustion, Fossil fuels, Indoor air quality, Nitrogen dioxide, Ozone, Photochemistry.

INTRODUCTION

In the context of urban smog, ozone chemistry has been studied extensively since 1950s. Ground level ozone is considered as an important gaseous pollutant which may lead to severe health problems [1,2]. Tropospheric ozone or ground level ozone is created when emissions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) interact in the atmosphere in the presence of sunlight [3]. These air pollutants are catalyzed by the sunlight and converted to ozone (O₃). The ultraviolet and visible fraction of the sunlight initiates photochemistry in the atmosphere by photolysing certain molecules into highly reactive species such as hydroxyl radicals (•OH) [4]. The photochemistry of ozone formation in the simplified form:

Volatile organic compound and carbonyl compounds play the role of hydrocarbons in additional oxidation phases. •OH and HO₂• are short-lived radicals, which play a significant role in the ozone formation process.

Ozone is generally considered as a gas present in the upper atmosphere or as a pollutant in the outdoor air, but it is also present in the indoor air. Various factors influence the indoor ozone concentration are the outdoor ozone concentration, its air exchange rates, indoor sources, surface removal reactions and the reactions between O₃ and other chemicals [5]. The variation in the indoor ozone concentration is often directly proportional to the outdoor ozone concentration [5].

The major source of indoor ozone is outdoor ozone, where it is formed through photochemistry by sunlight. Depending upon various factors like air exchange rate, ventilation type, etc. the outdoor ozone penetrated into the indoor environment [5] and the indoor ozone ratio is 10 % to 90 % to that of outdoor ozone [6]. Indoor ozone levels often less than outdoor levels, due to indoor surface reactions [7]. Electrical equipment like photocopiers or air cleaners are sources of indoor ozone [6]. Ozone levels above 10 ppb are associated with some health risk [8].

The composition of atmosphere is determined largely by photochemistry initiated by sunlight. Indoors photochemistry has long been thought to be unimportant since the high energy photons that drive photochemistry outdoor are largely absent in indoors. However, it was recently demonstrated that sunlight filtered through windows can photolyze nitrous acid (HONO) to form hydroxyl ($\bullet\text{OH}$) radicals [9]. It has been argued that the UV light fraction of solar spectrum is largely attenuated within indoor environments [10]. The Marseille field campaign found that wavelength between 340 and 405 nm were readily available within the indoor environment.

There are some studies measured spectral irradiance in indoors [9,10,11]. The investigators found that the penetrated spectral irradiance in the range 340-400 nm was about 1/3rd of outdoor light [9,11-13]. These studies support that sufficient amount of sunlight penetrates indoors that can produce photochemical reactions, such as photolysis of HONO and NO_2 . The radiation emitted by a vegetation flame is predominant in the infrared region [14]. During the combustion of a hydrocarbon (wood or fossil fuels such as oil and natural gas) much heat is released.

High indoor $\bullet\text{OH}$ concentrations indicated the possibility of photolysis of HONO, due to the penetration of sunlight through the windows and the indoor electric lighting (CFL, incandescent, LED) [15]. Compact fluorescent lamps (CFL) and lamps using light emitting diodes (LED) provided enough light energy for indoor photochemical reactions [9]. NO_2 is one of the very few atmospheric molecules that absorbs and photolysis in the visible range of solar spectrum [9]. Considering the glass walled buildings, indoor concentrations of many species, including O_3 are increased markedly over the base values due to indoor photolysis of NO_2 [16].

The HONO is produced directly by combustion of fuels [17,18] and also enhanced by the photo excitation of NO_2 [19]. The photo-excited NO_2 chemistry enhance the concentration of O_3 in several studies [20-24]. In a controlled environment, an elevated indoor/outdoor ozone concentration ratio (about 2.0) was reported in a study of the effect of cigarette smoking in indoor ozone concentrations [25].

A study by the National Institute of Occupational Health in Ahmedabad, India [26], reported the gaseous by-products

such as SO_2 , NO_2 , O_3 , have been the most implicated pollutants found in indoor air due to combustion of biofuels [27]. NO_2 is an important trace gas, since the photolysis leads to the formation of O_3 , which may also be an important process indoors (eqn. R₄). Biomass study clearly revealed that LPG gas is the least contributor of O_3 than biomass fuel. The higher O_3 concentration contributor follows the following sequence: Coal cake > twigs > wood > dry leaf > straw > cow dung > gas stove [28]. During the burning of biomass many gaseous pollutants such as CO , CO_2 and O_3 including humidity and temperature are produced [28].

There is a common misconception that absence of indoor photolysis reactions means the absence of indoor photolytic reactions. Light can propagate through indoors by many ways, such as indoor lightening, combustion of fuels, through open windows and doors, through windows with some attenuation, *etc.* So photolysis occurs indoors in a slower way than outdoors. Reactions requiring higher energy light such as O_3 photolysis are attenuated more indoors relative to outdoors than those reactions requiring less energy, such as HCHO photolysis to produce $\text{HO}_2\bullet$ [29]. Highest peak intensities were found from fluorescent tubes, whereas the LED light source had zero emission below 400 nm.

EXPERIMENTAL

The location of the study is at Azhikode (11.9074°N, 75.3255°E), 5 km north of Kannur town of India, and a location along the coastal belt of Arabian sea (Fig. 1) and lies at a height of 5 m above mean sea level. The chosen investigated area is a rural place without major industrial activities and in the west coast region of the Indian subcontinent. The air distance to the seashore is 2 km and that to the western ghats is 50 km. This region is strongly influenced by the marine as well as mountain environmental boosts containing high amounts of vegetation.

Data sets—indoor and outdoor O_3 , NO and NO_2 : The data on concentrations of O_3 , NO and NO_2 were obtained. The concentrations of ozone and nitrogen oxides were measured by using portable analyzers that based on the well-known techniques of UV absorption and chemiluminescence, respectively and the data were taken at 30 min intervals. The instruments

Fig. 1. Location of observation site

were placed 1.5 m away from the stove. Indoor formaldehyde concentration, before and during cooking, were also measured.

RESULTS AND DISCUSSION

As kitchen had been recognized as the most polluted room, measurements were taken from there. Measurements of indoor O_3 , NO , NO_2 and NO_x were carried out in a residence over one week (March 2018), in a low ventilated circumstance. During cooking, LPG and solid biomass fuels were used. Apart from chemical transformations occurring indoors, no other indoor sources for O_3 have been identified except cooking processes. The outdoor concentrations of O_3 , NO , NO_2 and NO_x were observed from a neighbouring rural area of Azhikode, situated in Kannur, during the same period.

Ozone is rarely produced indoors because it involves UV sunlight to photolyze the NO_2 and hydrocarbons. Cooking and heating are the main domestic activities that lead to an excessive concentration of NO_2 , due to the use of solid biomass fuel in general. Unvented or poorly vented gas fired appliances are a strong source of indoor NO_2 and it plays a critical role in determining O_3 concentration in the troposphere because photolysis of NO_2 is the only key initiator of the photochemical formation of ozone [30]. From Fig. 2, it is evident that for indoor concentrations of O_3 three peaks dominate, one in the morning, the other at the noon time and the third one during the evening/night. The results show that there is a higher level of indoor O_3 during cooking hours. Comparing with indoor O_3 concentration, the outdoor O_3 concentration has only one peak, which is during the noon time (Fig. 3).

Fig. 2. Indoor ozone concentration at Azhikode, Kannur during the period of study

The predominant source of indoor ozone is outdoor air where ozone is formed through photochemistry. The outdoor ozone can be transported to indoor environment by ventilation and infiltration [5]. Generally, the indoor ozone concentration is lower than that in the outdoors due to ozone removal by indoor surfaces and indoor gas phase reactions. Ozone may be generated by high tension electrical equipment like photocopiers, laser printers, air cleaners, *etc.* are absent in this residence. Among the three peaks (Fig. 2), significantly bigger one was observed at the noon time, which may attribute to the higher outdoor O_3

Fig. 3. Outdoor ozone concentration at Kannur during the period of study

concentration at that time (Fig. 3). Various other determinants for increased indoor O_3 concentrations are mainly related to cooking and combustion processes.

Indoor photochemistry: Indoor photochemical reactions have been ignored due to the assumption that there was not sufficient light energy to initiate a photochemical reaction. But there are various possibilities for the presence of indoor light energy.

Solar radiation: A common misconception about the indoor environment is that the absence of direct sunlight means the absence of indoor photolysis reactions. However, there are many ways that solar light can propagate through indoor environments: either directly through open windows and doors or through transparent windows and doors with some attenuation. The Marseille field campaign found that wavelength between 340 and 405 nm were readily available within the indoor environment.

Radiations from combustion flame: As the sun is very hot (6000 K), so it emits radiation at many different wavelengths. At 700 K, a hot object starts to emit visible light (380–750 nm). A fire emits radiation, which the human eye experiences in the form of flames and heat. During a fire, relatively little UV energy and visible light energy are emitted, related to the emission of infrared radiation. A normal orange flame can burn at 600 K or less. It is not hot enough to irradiate UV rays, but radiates in the visible and infrared parts of the electromagnetic spectrum. The LPG gas stove burns in the heat range of 800–1200 °C and the flame can react with air to form various gaseous products.

Radiations from electric light sources: In early morning and evening, the kitchen is lighted by incandescent bulbs. All of the light sources studied, with the exception of LED bulb, had significant emission at wavelengths shorter than 400 nm, and may be able to induce photolysis of radical precursors indoors. Emissions from halogen and incandescent bulbs extended almost to 300 nm and fluorescent tubes had significant emission at approximately 315 nm. Intensity decreased rapidly with distance from all light sources, except for sunlight and fluorescent tube. The intensity of sunlight did not display a distance dependence and intensity from fluorescent tubes, was not reduced until a distance of approximately 60 cm.

In the lower troposphere, only molecules with dissociation energy corresponding to $\lambda > 290$ nm are photo chemically active. Between 398 nm and 415 nm, room temperature NO_2 still partially photo-dissociates because of contribution of internal energy to the process, but the quantum yield declines rapidly with the availability of wavelengths. NO_2 is one of the very few atmospheric molecules that absorbs and photolysis in the invisible range of the solar spectrum.

Combustion emissions: Indoor fuel combustion has been identified as one of the most important factors that influences indoor air pollution. Indoor air pollutants arising from gas combustion include NO_2 and other nitrogen species. NO_2 is produced by oxidation of atmospheric nitrogen during high temperature fuel combustion. In combustion processes, primarily NO is emitted to the air, which is converted in open flames and in the air to NO_2 (eqn. R₆ and R₇).

Pollutant gases from fuel burning include CO_2 , CO, CH_4 , NO_x , HONO, carbonyl compounds, VOCs, etc. Ozone is a major air pollutant produced from chemical reactions between NO_x and VOCs from burning fossil fuels or biomass. NO_2 plays a critical role in determining O_3 concentration in the troposphere because photolysis of NO_2 is the only key indicator of photo-chemical formation of O_3 . NO_2 in the indoor environment is the result of both infiltration of outdoor NO_2 and NO_2 produced by combustion sources within the house. For homes with gas ranges, indoor nitrogen dioxide concentrations are frequently twice as high as outdoor concentrations.

The NO_2 produced during combustion, photo-excited (650 nm $> \lambda > 420$ nm) and reacted with water vapour in kitchen to form HONO and OH radicals.

The OH radicals oxidize VOCs to produce peroxy radicals and in the presence of NO_x , peroxy radicals convert NO to NO_2 . Subsequently, photolysis of NO_2 to yield O_3 .

Several studies showed that photo-excited NO_2 enhance the concentration of O_3 . Ozone enhancement is permissible only in a region of high NO_x emissions. HONO produced directly by combustion, absorbs light in the wavelength region 300-405 nm, which is readily available within indoor cooking environments, also produce $\text{OH}^\bullet$ and follow the reactions R₁, R₂, R₃, R₁₁ and R₁₂ to produce excess ozone.

In this low ventilated residence, formaldehyde (HCHO) concentration was 45 ppb at the time of cooking while other times 18 ppb. HCHO produced by combustion and cooking especially frying, produce HO_2 radicals and also $\text{OH}^\bullet$ and follow the reactions R₁, R₂, R₃, R₁₁ and R₁₂ to produce excess ozone.

Oxidation of other combustion products, like CH_4 , CO, VOCs in the presence of NO_x , also produce indoor ozone.

Indoor temperature: Combustion generates heat and light, so indoor temperature rises during cooking. Temperature influences indoor ozone levels. Many studies showed that ozone production is positively correlated to temperature. High temperatures are produced when natural gas and kerosene are burned, wood fires are not so strong sources.

The dynamics of the changes in concentrations showed a need for a targeted air exchange during the combustion process. Dominant indoor processes include oxidation reactions, acid-base reactions, hydrolysis reactions and decomposition reactions, often promoted by light and/or heat. In addition, one can expect the indoor levels of O_3 to be extremely low due to homogeneous chemical reactions with NO_x and heterogeneous surface reactions. Indoor chemistry includes homogeneous reactions such as those of O_3 with both NO (fast, eqn. R₂₅) and NO_2 (slow, eqn. R₂₆) and heterogeneous reactions such as those between NO_2 and indoor surfaces.

Fig. 4 showed that for indoor concentrations of NO_2 three peaks dominate during cooking hours. The NO_2 produced during cooking and heating, plays a critical role in determining ozone concentration. Indoors, ozone reacts with NO_2 , at a rate much slower and is significant only when the indoor concentration of NO_2 is very high (> 100 ppb).

Fig. 4. Indoor O₃ and NO₂ concentration at Azhikode, Kannur during the period of study

Conclusion

The indoor ozone pollution causes severe health problems, and many of them are unaware of its sources and dangers. The indoor O₃, penetrating from the outside or coming from the inside, can generate chemical reactions among the chemical species present inside, generating secondary pollutants that could be more concern for health than the primary pollutants. A small level of indoor ozone itself cause ill effects on human health, materials and art works [31]. In order to decrease the indoor exposure to ozone and its reaction products, we can fit filters for ozone in ventilation ducts and reduce the use of products whose emissions react with ozone. These methods can be useful in childcare centers, schools and hospitals in regions that usually have a high level of outdoor ozone. The outdoor ozone levels highly affected the indoor ozone levels and also on the duration of time windows were opened. So it is more advisable that windows and doors must be opened during the morning and evening hours, in order to dilute indoor pollution. Similarly, windows and doors were closed during noon time, as outdoor ozone concentrations were maximized. Another suggestion to decrease indoor ozone is done by replacing incandescent bulbs with CFL and LED.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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