Role of Biogenic VOCs in Atmosphere for the Production of Tropospheric Ozone in Delhi, India

Pallavi Saxena and Chirashree Ghosh

Abstract— Tropospheric ozone is the most abundant of the photochemical oxidants. It is one of the secondary pollutant which is produced during photochemical processes consists of nitrogen oxides and volatile organic compounds (VOCs) as its precursors. Tropospheric ozone has deleterious effects on plant as well as human health. Its production in the atmosphere is a non-linear process, therefore it can be produced from various sources. Its very interesting to note that biogenic VOCs (bVOCs) mainly isoprene, α-pinene and formic acid emitted from trees which are produced by vehicular emissions as well as plant species are great contributors of tropospheric ozone. Therefore, based on this concept, our present study focuses on assessment of biogenic VOCs like isoprene, α-pinene and formic acid and tropospheric ozone levels at three different selected sites in Delhi which are categorized on the basis of near to traffic intersection with dense vegetation (Site I), away from traffic intersection with dense vegetative area under Riverine zone (Site II) and away from traffic intersection with dense vegetation under Hilly Zone (Site III) during winter season. The results showed that Site II & III had found high concentrations of bVOCs (isoprene, α-pinene and formic acid) and ozone concentrations as compared to Site I. Hence, our present study set as an example, that policy makers and scientists have given more attention towards those ignored areas which seems to be like free from pollution but after monitoring they were found to be having high concentrations of tropospheric ozone which can further act as an example that there are still some more pathways of producing this type of pollutants by biogenic VOCs like isoprene, α-pinene and formic acid.

Index Terms— Biogenic VOCs, Delhi, tropospheric ozone and vegetation.

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1 INTRODUCTION

Tropospheric ozone is considered as strong oxidant [1,2] which produces high risk to human beings [3], plant health [4] and materials both globally, locally as well as regionally [5]. According to US EPA (United States Environmental Protection Agency), ozone is a significant component in tropospheric photochemistry and classified as one of the criteria pollutant. The precursors responsible for its high production are volatile organic compounds and nitrogen oxides ($NO+NO_2$) [6]. But, the tropospheric ozone production rate in the lower atmosphere not only depends their concentrations but also on their ratios [7]. At high NOx/VOC ratios, an increase in O_3 is observed due to decreasing NOx and this stage is called as VOC-limited regime. On the other hand, O_3 photochemistry present in high VOC/NOx regime is called as NOx-limited [8].

Among all VOCs, biogenic VOCs (particularly isoprene, monoterpenes etc.) represented an important portion of total ambient VOC, especially in urban and rural areas [9, 10]. Global BVOCs emissions are estimated to be about 1150 teragrams of carbon per year which increases those of their manmade sources by about a factor of 10. Generally, BVOCs have much lesser atmospheric lifetimes than manmade VOCs due to faster reaction rates with OH [11]. In typical dense vegetative zones, isoprenes and monoterpenes (α – pinene and β – pinene) are the dominant VOCs which are reactive relative to lighter hydrocarbons. Among all the largely found BVOCs, only isoprene and monoterpenes contributed about 44% and 11% respectively, to the global budget of biogenic emission. BVOCs emissions are largely dependent on meteorological parameters like solar radiation and temperature [12].

In India, numerous plantation and afforestation programmes have been initiated since 1979 to increase the forest cover [13]. Under such programmes, a number of trees, shrubs and herbs have been planted both in urban and rural areas. Greenbelt development programme is used for mitigation purpose of air quality as per their selection of plant species. But sadly in developing countries like India, very less attention has been given on the selection of plants based upon their BVOC emission rates. Very less studies have been reported in India on estimation of BVOCs emissions from plant species [14,15,16,17,18,19]. But not a single study has been reported in India on role of BVOCs in the production of tropospheric ozone. Hence our present study focuses on assessment of biogenic VOCs like

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isoprene, α-pinene and formic acid and tropospheric ozone levels in Delhi, India during winter season and also correlates them with the production of tropospheric ozone.

METHODOLOGY

a. Study area and sampling sites: Delhi, the capital city of India is one of the largest cities which lies at an altitude of between 700 and 1000 ft. having area of around 1500 km^2. Delhi is a main centre of business and commerce and a hub of main offices of many companies [20].

Delhi has tropical climate with comparatively dry conditions and harsh summers. Monthly mean temperature ranges from 13.5ºC in January (2ºC minimum) to 34.5ºC in June (48ºC maximum) with annual mean temperature is 25ºC. It has three main seasons viz. summer, monsoon and winter with annual rainfall of 715 mm. Wind Speeds are generally high in summer and months than in winters.

Delhi ranks among 10 most polluted cities in the world in terms of air pollution. Population and transportation are two major reasons behind the high concentrations of air pollutants in Delhi. Delhi has got the highest traffic density among all the Indian cities and consequently some of the major air pollutants like NO_x, O_3 and CO are still crossing the permissible limits even after the implementation of control policies like use of Compressed Natural Gas (CNG) [20].

Selected sampling sites were differentiated on the basis of volume of traffic flow (Table 1) and availability of vegetation cover, e.g. Site I (IT – institutional area with moderate vegetation cover; 500m from traffic zone); Site II (RZ – riverine zone with dense vegetation cover; 1.5 km away from traffic zone) and Site III (HZ – hilly zone with dense vegetation cover; 1 km away from traffic zone). At all the selected sites, naturalized trees and shrubs were there.

b. Sample collection and analysis: Isoprene, α-pinene and formic acid were sampled among all BVOCs in two phases - Phase I (morning hours: 0800-1100) and Phase II (evening hours: 1500-1800) - alongwith meteorological parameters (temperature, relative humidity and wind speed)with the help of a pocket weather monitor (Kestrel, K3000-342127,USA). The criteria for the selection of above mentioned compounds is that, they are the representatives of terpenoids and aldehyde groups. Moreover, terpenoids are highly responsible for tropospheric ozone production than any other class of organic compounds.

For Sampling of selected BVOCs, Organic Vapor Sampler (OVS) APM 856 (Envirotech Instruments Pvt. Ltd. India),

TABLE 1
TRAFFIC FLOW RATE AT DIFFERENT SAMPLING SITES IN DELHI

Site Name	Site No.	Peak traffic volume/h (pcu)[a]	Average vehicle speed (kmph)[b]
Institutional area	Site I	7947[c]	30 - 40
Riverine Zone	Site II	3765[c]	30 - 40
Hilly Zone	Site III	68[c]	20-30

[a]NDMC (1992); bTPA (1994); cpcu (passenger car unit): It is the number of vehicle movement expressed in terms of car (hourly in this case). The value of `pcu' for different vehicles is given below: Car, Taxi, Van and Matador: 1.0, Trucks and Buses: 3.7, Auto Rickshaw and Vikram: 2.0, Scooter, Motor Cycles and Mopeds: 0.75 etc.

including fabricated diffusive glass sampling tube and regulated air suctioning pump was used. The ambient air was trapped in known amount of activated charcoal contained in sealed glass tubes. The activated charcoal samples were transferred from sealed tubes into glass vial and capped immediately to further prevent from adsorption of compounds. These tubes were stored at 4 ºC until analysis. To the sample vial, 2ml of CS_2 was added to the mixture and shaken gently for 40 minutes. Then CS_2 was filtered out with Teflon syringe filter and analysis was done in GC-FID (Shimazdu, GC-2010) equipped with Omega SPTm column. Nitrogen was used as carrier gas with flow rate of 1.21 ml / min. The standard calibration mixture containing isoprene, α-pinene and formic acid were procured from Supelco was used for calibration. Calibration standards were prepared by diluting the stock standard mixture. The QA/QC measures included laboratory and field blank and replicates were taken for measurements of samples. For laboratory blank, unexposed charcoal tubes were analysed for VOCs similar to the exposed ones.

Ground level ozone measurements were done with the help of a UV based ozone analyzer (Model O_3 42M, Environment S.A., France). The instrument was kept at a height of about 10 meters above the ground. A 5 meter long Teflon tube (12mm dia.) was used as the intake tube for air sampling. An inverted Teflon funnel was fitted at the entrance of the tube to prevent dust and rain water going directly into the tube and the system.

c. Statistical analysis: Statistical analysis was performed using SPSS software 19.0. Pearson's correlation

test was done to help us best to confirm the obtained results and also to depict data more easily and correctly.

RESULTS AND DISCUSSION

a. Variation of Meteorological Parameters: Monthly variation of meteorological parameters like ambient temperature, relative humidity, wind speed and wind direction at three different selected sites in Delhi during winter season (Nov'11 – Feb'12) are given in Fig. 1. Lowest temperature was found in the month of January (6-8ºC) and highest in November (23-25ºC), highest R.H. (50-55%) was found in the month of November and lowest in February (32-39%), lowest wind speed was found in the month of December (1.1 – 1.5 m/s) and highest in February (1.8 – 2.1 m/s) at all the sites. Highest level of RH was found in November due to prevailing foggy weather condition and mostly wind direction is from south-west to north-easterly in all the selected months.

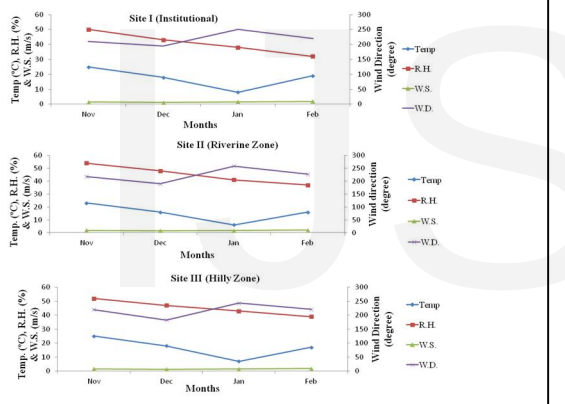

Fig. 1. Monthly Average Variation of Meteorological Parameters at Sampling Sites.

b. Diurnal Variations in Ozone during winter months: From Fig. 2 it has been clearly stated that at all the sites viz. Site I (IT), Site II (RZ) and Site III (HZ) during winter months i.e. November 2011 – February 2012, during daytime, ozone peaks were found during noontime and then gradually starts decreasing. It may be due to the photoxidation of precursors like VOCs, NO_x and CO [21]. Interestingly, Site II (RZ) and Site III (HZ) had reported high concentrations of ozone of 49.74 and 45.77 ppb respectively as compared to Site I (IT) of 43.55 ppb. Site RZ and HZ are dense vegetative sites where ozone production is controlled by availability of nitrogen oxides and dominated by terpene hydrocarbons emitted from different plant species (Biogenic VOCs) [22]. Hence, Biogenic VOCs are largely responsible for tropospheric ozone production especially in these areas [23]. Similar result has also been reported by Andrews [24], where ozone concentrations were found to be lower in high traffic areas than those in away from traffic intersection areas and dense vegetation zones, occur mainly due to scavenging of ozone by NO originating from traffic. However, as per the nitrogen oxides and ozone chemistry, NO_x are involved in both the formation and destruction processes of ozone and its involvement is relatively more complicated. Therefore, in high traffic density areas, where NO_x concentrations are high, the duration of all the reactions involved means that high NO concentrations destroy ozone faster than NO_2 can create it [25]. Another interesting feature to note that, during late afternoon hours at all the sites, high ozone concentrations were found as compared to other peak hours. This might be due to peak traffic hours are there i.e. 16:00 – 21:00 hours in Delhi which are responsible high gasoline exhaust emissions resulted in high concentrations of precursors like NO_x, CO and VOCs to produce tropospheric ozone [26]. Sites II and III area away from traffic intersection and dense vegetative sites and they are about 1.5 km away from traffic zone (outer ring road) and a huge number of heavy duty vehicles pass through it which ultimately leads to the emissions of air pollutants. These emissions can travel fast to accumulate at these sites, resulting in high precursor concentrations and consequently leads to high ozone levels [27].

Among all selected winter months, highest concentration was found in the month of January followed by December, November and February at all the sites (Fig. 2). This is due to higher amounts of precursor gases, inspite of lower solar radiation than in summer months. Moreover, due to convection, fickian transport, mixing heights and lower temperature inversions which affects the mixing, dilution and accumulation of localized ozone which occurs especially during January month [24]. In addition to that, the photochemical lifetime of ozone especially in midlatitudes in winter than in summer [28, 29].

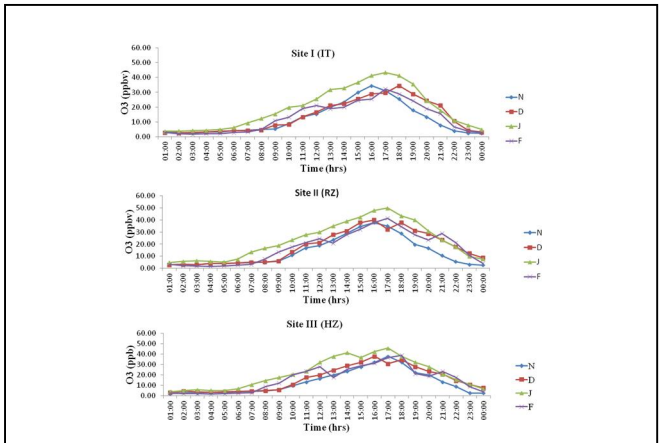

Fig. 2. Diurnal variation of ozone during winter season at selected sites

c. Correlation between meteorological variables and ozone: Pearson correlation statistical test were performed in order to understand the relationship between ozone and meteorological parameters at all the sites during winter season. From Table 2(a) it is observed that significant positive correlation of ozone with temperature at Site I was found with r = 0.564* at P≤ 0.05. Moreover, with relative humidity significant negative correlation was found with r = -0.608** at P≤ 0.05. At Site II, significant positive correlation of ozone was observed with temperature with r = 0.754* at at P≤0.05 while with wind speed significant negative correlation was found with r = -0.688** at P≤0.05 (Table 2(b)). Similar results were found at Site III with temperature r = 0.712* at P≤0.05 and with relative humidity r = -0.722** at P≤0.05 (Table 2(c)). Similar observations were also reported by several studies [30,31]. Moreover, with increase in temperature, there is increase in O_3 concentrations because it is a photochemical reaction. With decrease in relative humidity, ozone concentrations were found to be high due to less scavenging of OH radicals and with low wind speed, dispersion of pollutants would be very less, hence, concentrations of O_3 were found to be high [32].

d. Biogenic VOCs and Tropospheric Ozone Production: From Fig.3 it has been clearly depicted that at all the sites concentrations of isoprene were found to be higher as compared to α-pinene and formic acid in all the winter months. This is due to the reason that isoprene is most abundant hydrocarbon emitted at a rate of about 500 Tg/yr, mostly from deciduous vegetation in the presence of photosynthetically active radiation as compared to monoterpenes like α-pinene and oxygenated VOCs like formic acid [33] and at selected sites most of the vegetation are isoprene emitters as compared to other ones [17]. All of these selected hydrocarbons makes them susceptible to attack by O_3 as well as NO_3^- and OH^- radicals that's why all of them are very reactive and mostly responsible for the production of tropospheric ozone [34]. Moreover, as per the previous studies done earlier, NO_2 concentrations were found to be low at sites II and III and still ozone concentrations were found to be high [27,31,35].

Therefore, under high BVOCs concentrations, tropospheric ozone concentration remained high. In addition to that, BVOCs concentrations were found to be high at Site II and III as compared to I, might be due to Site II and III are dense vegetation zones, instead relatively less vegetation is found at Site I.

According to correlation graphs as shown in Fig. 4, 5 and 6, significant positive correlation of ozone with isoprene at all the sites with r = 0.6307, 0.5668 and 0.7967 at P≤0.05 while

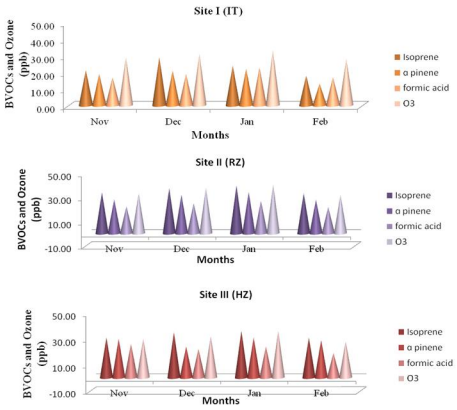

Fig. 3. Monthly variation of ozone and BVOCs during winter season at selected sites

weak positive correlation was found with α-pinene and formic acid at all the sites at P≤0.05. This is due to the reason that as compared to α-pinene and formic acid, isoprene has more OH-isoprene rate constant (100 x 10-12 cm^3/molecule/s), therefore more chances to produce tropospheric ozone in the atmosphere. Moreover, estimated atmospheric lifetime of isoprene is 1.5 hours while that of α-pinene and formic acid is 3 hours and 1 week respectively [18] which also confirms that isoprene is highly reactive as compared to other two selected BVOCs and hence, leads to ozone formation.

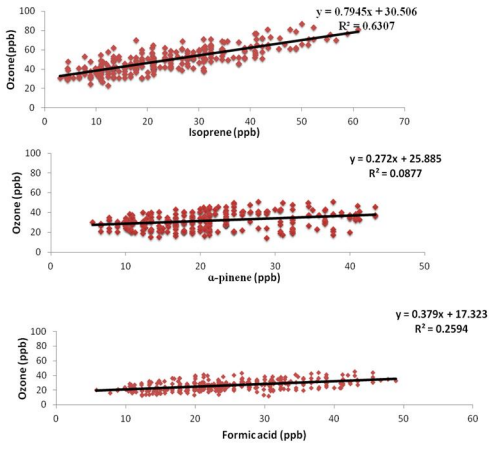

Fig. 4. Correlation graphs between ozone and BVOCs during winter season at Site I (IT)

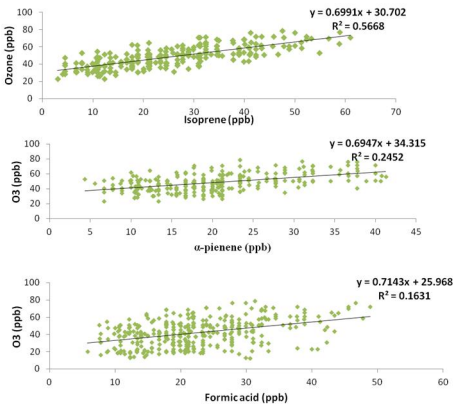

Fig. 5. Correlation graphs between ozone and BVOCs during winter season at Site II (RZ)

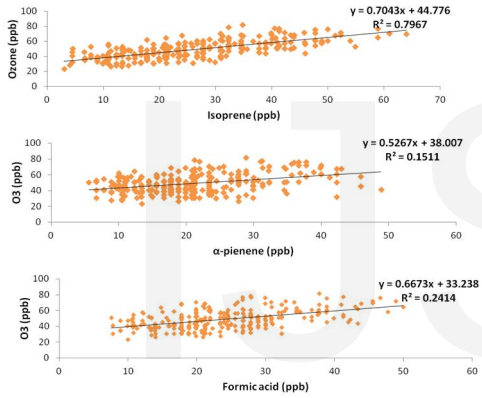

Fig. 6. Correlation graphs between ozone and BVOCs during winter season at Site III (HZ)

TABLE 2(A,B,C)
CORRELATION MATRIX OF OZONE WITH METEOROLOGICAL VARIABLES AT DIFFERENT SITES (I, II, AND III)

Meteorological Variables	Karl Pearson's Correlations
	Winter 2a
T_{max}	0.564*
RH_{avg}	-0.608*
WS_{avg}	-0.465

Meteorological Variables	Karl Pearson's Correlations
	Winter 2b
T_{max}	0.712*
RH_{avg}	-0.213
WS_{avg}	-0.722*

Meteorological Variables	Karl Pearson's Correlations
	Winter 2c
T_{max}	0.754*
RH_{avg}	-0.408
WS_{avg}	-0.688*

Correlation is significant at 0.05 level (2-tailed)

CONCLUSION

The present study concludes that biogenic VOCs are highly responsible for the production of tropospheric ozone as compared to other precursors present in the atmosphere. Among all the BVOCs, isoprene concentrations were found to be high at all the sites viz. Site I, II and III but Site II and III (dense vegetation sites) were having relatively high isoprene concentrations than other selected sites. Temperature, relative humidity and wind speed are the most favourable meteorological factors at all the sites which are responsible for increasing the concentration of tropospheric ozone. Diurnal variations of tropospheric ozone concentrations showed that ozone peaks were found during late afternoon hours and highest found to be in January month due to lower temperature inversions, lower boundary layer and mixing heights. In addition to that, as per correlation coefficients, ozone is significantly positively correlated with isoprene as compared to other BVOCs like α-pinene and formic acid which confirms that isoprene is highly responsible for the ozone production.

Hence, by taking all the above points into consideration, this study sets up a platform for policy makers and scientists to give more attention towards those ignored areas which seem to be free from pollution but actually they are having high concentrations of tropospheric ozone.

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