

Emissions of volatile organic compounds from biomass burning sources and their ozone formation potential over India

Kumud Pandey¹ and L. K. Sahu^{2,*}

¹FIT Engineering College (Applied Science Department), Mawana Road, Meerut 250 001, India

²Physical Research Laboratory, Navrangpura, Ahmedabad 380 009, India

Thousands of volatile organic compounds (VOCs) in the Earth's atmosphere exist which play an important role in various photochemical processes. However, the global model simulations of tropospheric chemistry deal with limited data of speciated VOCs. In the present study, we have used the Global Fire Emissions Database inventory of VOCs emitted from biomass burning in India during the period from 1997 to 2009. We have also analysed data of some VOCs measured in the upper troposphere over India for the year 2008. In this study, the major species analysed are C₂H₄, C₂H₄O, C₂H₆, C₂H₆S, C₃H₆, C₃H₆S, C₃H₈, C₅H₈, CH₃OH, higher alkanes, higher alkenes, terpenes and toluene lumps. The biomass burning emissions of VOCs show large inter-annual variation. For example, the annual emission estimates of non-methane hydrocarbons (NMHCs) and CH₃OH varied in the range 100–470 and 46–211 Gg yr⁻¹ respectively. The major biomass sources were broadly categorized as deforestation, fuel-wood, forest and agricultural residues. The agricultural residue burning is the most dominant among the several biomass burning sources contributing to the emissions of CH₃OH (59%), isoprene (80%) and toluene (72%). On the other hand, the major sources for NMHCs emission were agricultural residues and deforestation during all the years. The fire count data detected using the satellite-based Along Track Scanning Radiometer have been used to directly refer to the seasonal and inter-annual variations of biomass burning activities. We have estimated the propylene-equivalent concentrations of different light NMHCs measured in the upper troposphere over India. Role of stratospheric intrusion in the distribution of NMHCs has been analysed using the potential vorticity data.

Keywords: Biomass burning, non-methane hydrocarbons, volatile organic compounds, ozone.

Biomass burning is one of the most important sources of trace gases and particles in the global atmosphere. Many pollutants emitted from biomass burning can affect the radiation budget and cause climate change. On the other

hand, reactive trace gases like volatile organic compounds (VOCs) control the photochemistry and influence the budget of tropospheric ozone (O₃). The vegetation fires impact 8 (long-lived greenhouse gases, O₃, stratospheric water vapour, surface albedo, aerosols (direct), aerosols (indirect), linear contrail and solar irradiance) out of 14 identified radiative forcing terms which further contribute to interannual variability (IAV) in growth rates of many trace gases^{1,2}. The long-range transport and deep convection of these emissions can significantly impact the budget of organic trace constituents in the remote oceanic and upper troposphere respectively. The emissions of VOCs from biomass burning have a significant impact on the health of the population living near the sources or in the downwind regions. Therefore, it is important to estimate the contribution of biomass burning in the global budget of trace gases to assess the environmental and climate change impacts. In addition to bottom-up approaches, measurements using aircraft, satellite and ground-based instruments are also used to estimate the emissions from biomass burning with different spatial and temporal resolutions. On both regional and global scales, several studies have assessed the seasonal and inter-annual variability of biomass burning emissions using satellite data.

Among the Asian countries, India is the second largest contributor to the emission of non-methane VOCs (NMVOCs)^{2,3}. The major sources of biomass burning in India can be categorized as forest fire, deforestation, agricultural waste and wood burning. Therefore, study of emission variability of NMVOCs from biomass burning sources in India is of great interest considering spatio-temporal variation of these sources. In India, the fire season in the forested areas starts from February to May, but the cropland fires vary with the region and harvesting practice. Typically, the crop residue burning practices peak in the period April to October. Overall, the amount of biomass burnt is largest in Central India, but fire frequency is highest in the east–northeast⁴. Unutilized crop waste and cropland fires are predominant in the western part of the Indo-Gangetic Plains (IGP), which includes random field burning^{5,6} leading to high uncertainty of estimates⁷. However, qualitatively, the seasonal and

*For correspondence. (e-mail: lokesh@prl.res.in)

inter-annual variations of open biomass burning activities have been studied using the active fire count data. In this study, we have investigated the biomass burning emission estimates over India during the years 1997–2009 using the Global Fire Emissions Database (GFED version 3.1). The GFED 3.1 data is mainly based on the satellite-driven Carnegie–Ames–Stanford Approach (CASA) biogeochemical model modified to account for fires. The percentage contributions of various NMVOCs from different biomass sources are also analysed in this study. Emission of speciated NMVOCs from all sources has been summed to estimate the total emission from each source for the specific category of NMVOC. The annual emissions of different categories of VOCs have been calculated in the unit of Gg yr^{-1} .

The remote sensing data can significantly enhance the information available from traditional data sources. The disadvantages of satellite remote sensing include the inability of sensors to obtain data and information through cloud cover. Satellite-detected World Fire Atlas (WFA) data have been used to investigate the seasonal and inter-annual variation of fire count detected over India. We have also analysed *in situ* measured data of several light NMHCs from the Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container (CARIBIC) observations conducted on-board the flights from Frankfurt (Germany) to Chennai (India) during April–December 2008 (ref. 8). The CARIBIC observations provide the first detailed *in situ* measurement data of light NMHCs in the upper troposphere over India. We have estimated the propylene-equivalent concentrations of different light NMHCs using CARIBIC data. This estimation provides relative contribution of different NMHCs in O_3 production under a given photochemical condition (NO_x , sunlight, other radicals, etc.).

Data and analysis

Fire count data

The fire counts detected by the satellite sensors provide a useful proxy to study the seasonal and inter-annual variation of biomass burning. In this study, active fire count data from the European Space Agency (ESA) has been used (<http://dup.esrin.esa.int/ionia/wfa/index.asp>). The ESA Along Track Scanning Radiometer World Fire Atlas (ATSR-WFA) project provides a global fire monitoring service by using data acquired by the ATSR-2 and Advance Along Track Scanning Radiometer (AATSR) sensors from the ESA satellites. The WFA consists of a global collection of hot spots detected using the ATSR-2 of ERS-2 from November 1995 to December 2002. The extended data since the beginning of 2003 till present have been detected using the AASTR sensor. The WFA is based only on the $3.7 \mu\text{m}$ channel, which is highly sensi-

tive to radiation at a threshold of 312 K (algorithm 1) or 308 K (algorithm 2). The overall ATSR-WFA project detects hot spots in the thermal bands of the ATSR family instruments for night-time observations.

The spatial resolution of the ATSR sensor is $1 \times 1 \text{ sq. km}$ and completes global coverage every three days. In comparison to the daytime observations from the AVHRR, the number of fires detected from the ATSR night-time scans is considerably smaller. Therefore, many of the fires detected during daytime are relatively small controlled burns which attribute little to the large-scale regional burned area. The active fires detected from ATSR cannot be directly translated into the amount of burnt material or released trace substances. The ATSR dataset contains a number of events from heat sources other than vegetation fires.

The ATSR fire detection algorithm cannot detect multiple fires within a pixel or differentiate sub-pixel fires of different sizes. The main drawback with ATSR is the night-time overpass, given that fire activity peaks in the afternoon due to both human activity and meteorological conditions⁹. On the other hand, the night-time fire detection reduces the difficulties or errors associated with daytime such as sun glitter, warm surface detection, high reflectivity surfaces and reflection off cloud edges. Despite several shortcomings, the ATSR fire count data provide the best current information on the seasonal and spatial variation of fire activity in many regions of the world.

GFED 3.1 emission inventory and aircraft data

The emissions from open biomass burning sources are an important source of atmospheric trace gases and aerosols. In addition to absolute amount, the emissions of species from biomass burning sources are highly variable in space and time domain. In spite of so many parameters controlling the amount of emissions, efforts have been made to quantify the global emissions. In this study, the long-term emission data of NMVOCs from the GFED version 3.1 over India for the years 1997–2009 has been analysed. The annual GFED 3.1 data is a revised version of the CASA biogeochemical model which includes the improved estimate of area burned, fire activity, and plant productivity to calculate fire emissions with a resolution of 0.5° . The NMVOCs emissions have been broadly categorized as deforestation, wood fire, forest fire and agricultural waste burning, particularly for India. In spite of large uncertainty and several limitations, GFED is one of the best updated data available for the global biomass burning emissions.

The CARIBIC project is a long-term measurement programme on-board a commercial aircraft. This program is based on the use of an instrument container deployed on Lufthansa Airbus A340–600 for a series of four long-

distance flights between Frankfurt, Germany and various destinations across the world. The CARIBIC instrument container houses a range of *in situ* trace gas and aerosol analysers, complemented by an aerosol sampler and a whole-air sample collection system¹⁰. In the present study, we have used NMHC data collected on the Frankfurt–Chennai route between 14°N and 30°N over the Indian subcontinent¹¹. Further details of analysis are provided elsewhere^{8,12}. Air samples were analysed for NMHCs using a gas chromatograph (GC) coupled with a flame ionization detector (FID) system. The CARIBIC container also houses a proton transfer mass spectrometer (PTRMS) for the measurement of VOCs, though with high noise reported during monsoon. In any case, we are not using CARIBIC PTRMS data in the present study. On the other hand, the PTR-based technique such PTR-QMS and PTR-TOF-MS are useful for the detailed characterization of VOCs.

In order to assess the importance of individual NMHCs in the formation of O₃, we have estimated the propylene-equivalent (Propy-Equiv) concentration using the following equation

$$\text{Propy-Equiv } (j) = \text{conc } (j) \frac{k_{\text{OH}}(j)}{k_{\text{OH}}(\text{C}_3\text{H}_6)},$$

where $\text{conc } (j)$ is the concentration of species j expressed in ppbC, $k_{\text{OH}}(j)$ is the reaction rate constant for the reaction between species j and OH, and $k_{\text{OH}}(\text{C}_3\text{H}_6)$ is the rate constant for the reaction between OH and propylene (propene)¹³. The rate constants used in this study are presented in Table 1.

Results

Seasonal and inter-annual variations of fire count and NMVOCs

Typically, biomass burning occurs mainly in the dry season and the extent of activity can differ from year to year. The monthly mean of fire count data detected during the years 1997–2009 over India is shown in Figure 1 *a*. This figure presents the mean annual variation of fire count data detected over India. The monthly mean values of fire count are higher in the pre-monsoon season (March–May) and lower in the monsoon season (July–September). Similar seasonal variation of biomass burning has been reported in previous studies^{13–15}, where it was found that the fire events were mainly confined to March–May. In Figure 1 *b*, the time series of annual mean fire count during the years 1997–2009 over India is presented. The number of fire counts detected over India was highest during 1999 and lowest during 2002. Almost similar trend has been found by Arino *et al.*^{16–20}. The impact of El Niño events was also demonstrated in these

studies. However, the increasing trend of fire counts from 2006 onwards can be noticed. Similar trend has been found by Kharol *et al.*¹³. They have analysed satellite data for 2006 and found maximum number of forest fires between February and April, with a significant peak in March.

In Figure 2, the annual mean emissions (Gg) of various NMVOCs are shown separately for the years 1997–2009. The species included in this figure are non-methane hydrocarbons (NMHCs), toluene, terpenes, higher alkanes and higher alkenes. Here NMHCs are the sum of all lower hydrocarbon (C₂–C₆) air pollutants such as alkanes (except methane), alkenes, alkynes and aromatics ring (C ≤ 6). It is clear from the figure that the annual emissions of NMHCs were lowest in 1998 and highest in 1999. The contributions of different species also vary from year to year. We have found that from biomass burning NMHCs are most dominant pollutants compared to oxygenated VOCs and aromatic compounds in India. The mean of each species during 1997–2009 was also estimated and is shown in Figure 3. The vertical bars are the ±σ variation with respect to the mean of the entire study period.

The major biomass burning sources are categorized as deforestation, forest fire, agricultural waste and wood burning. There is difference between forest fire and wood fire. The wood fire is burning of dry logs for cooking, heating, and the production of charcoal. In India, human activity is the principal cause of forest fires. It is done for clearing land for farming and to regenerate certain tree species, for example, oak and pine. Forest fire happens mainly in summer and autumn. They are particularly destructive when there is a drought because branches and twigs die and become dry, creating plenty of fuel for the fire.

The emission of some speciated VOCs from different sources of biomass burning is presented in Figure 4. The pie charts have been made by taking the average of contributions for each source from 1997 to 2009. It is found

Table 1. Estimated lifetimes of light non-methane hydrocarbons with respect to the reaction with OH. Values are calculated for a 12 h day-time average, where OH radical concentration of $2 \times 10^6 \text{ mol cm}^{-3} \text{ s}^{-1}$ is used. The rate constants at 298 K for reactions of NMHCs with OH are available with Atkinson^{40,41} and Sahu⁴²

Species	Lifetime (days)	Reaction rate with OH ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)
Ethane (C ₂ H ₆)	45	0.254
Propane (C ₃ H ₈)	10	1.12
<i>n</i> -Butane (<i>n</i> -C ₄ H ₁₀)	4.7	2.44
<i>n</i> -Pentane (<i>n</i> -C ₅ H ₁₂)	2.9	4.0
Acetylene (C ₂ H ₂)	14	0.82
Ethene (C ₂ H ₄)	1.4	8.52
Propylene (C ₃ H ₆)	5.3	26.3
<i>i</i> -Butane (<i>i</i> -C ₄ H ₁₀)	4.7	2.34

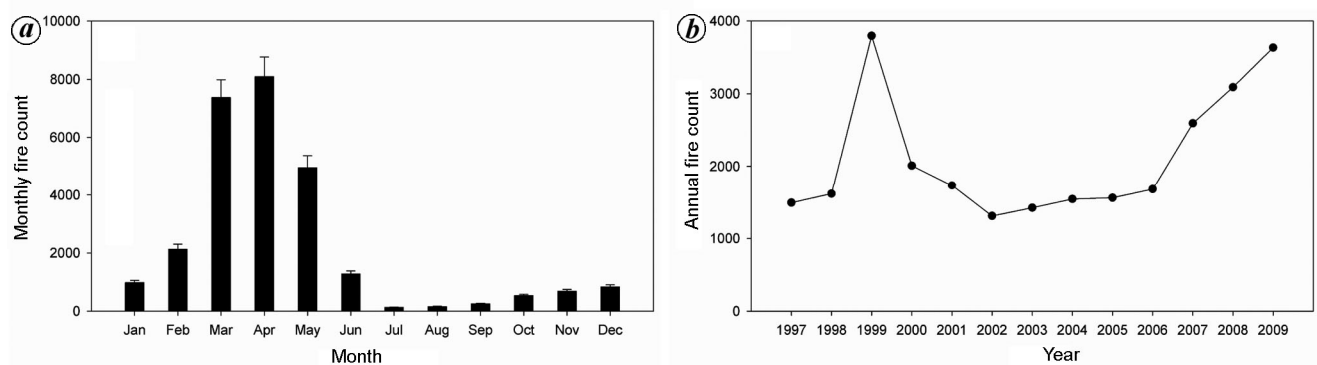


Figure 1. *a*, Month-to-month variation of fire counts for the period 1997–2009. *b*, Time series of annual fire count data over India.

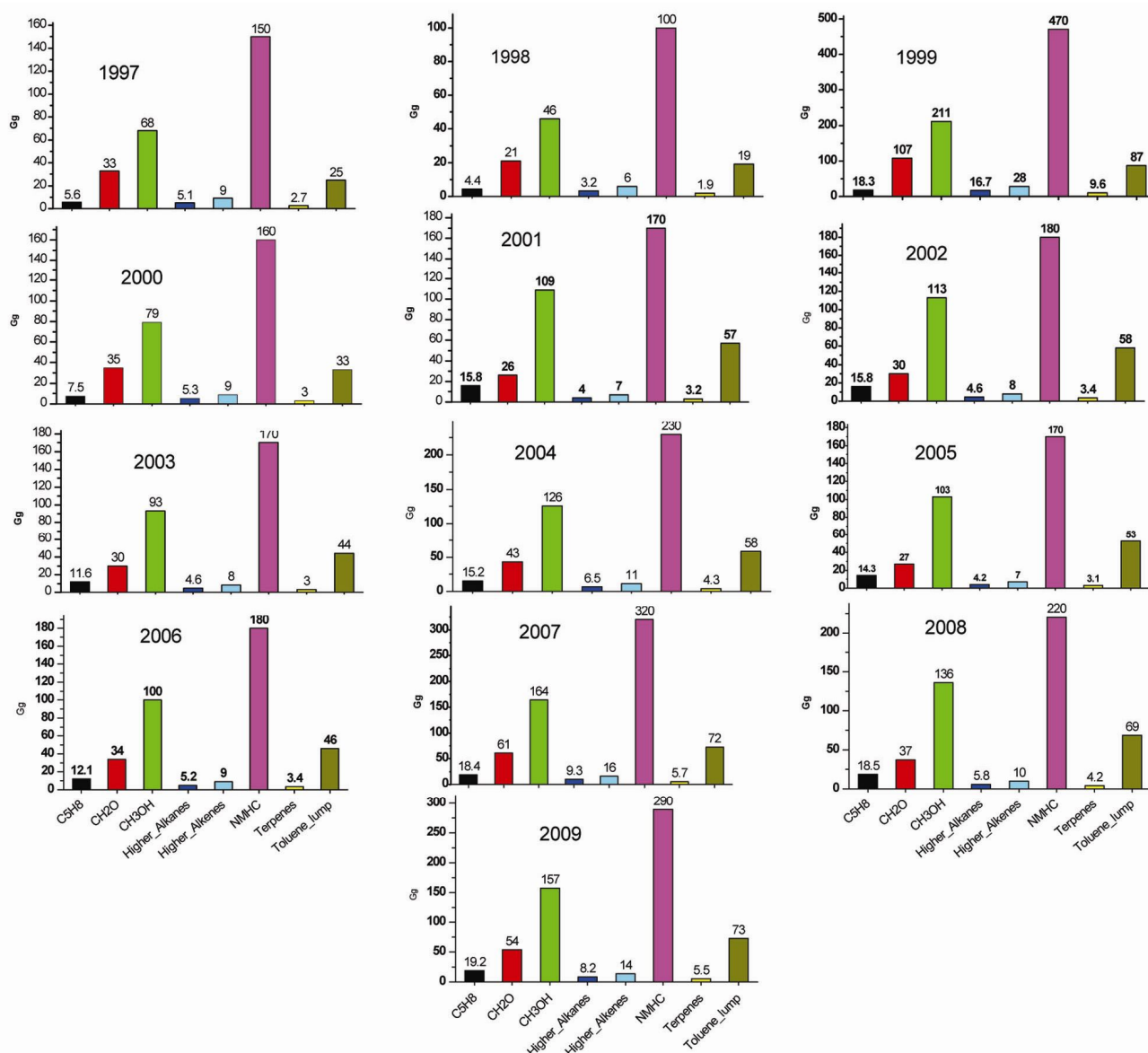


Figure 2. Year-wise emission of different species over India during 1997–2009.

that NMVOCs are primarily produced by agricultural waste burning (41%) and deforestation (47%). On the other hand, agricultural waste burning is the major source

for isoprene (80%), toluene (72%) and methyl alcohol (59%). In addition to biomass burning, emissions from other sources like biofuel and fossil fuel combustion

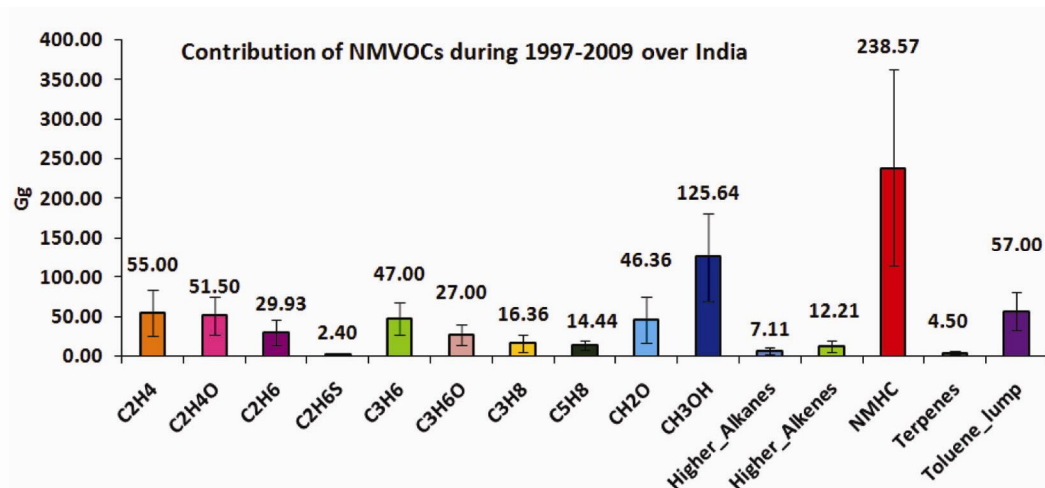


Figure 3. Mean inter-annual variation of NMVOCs.

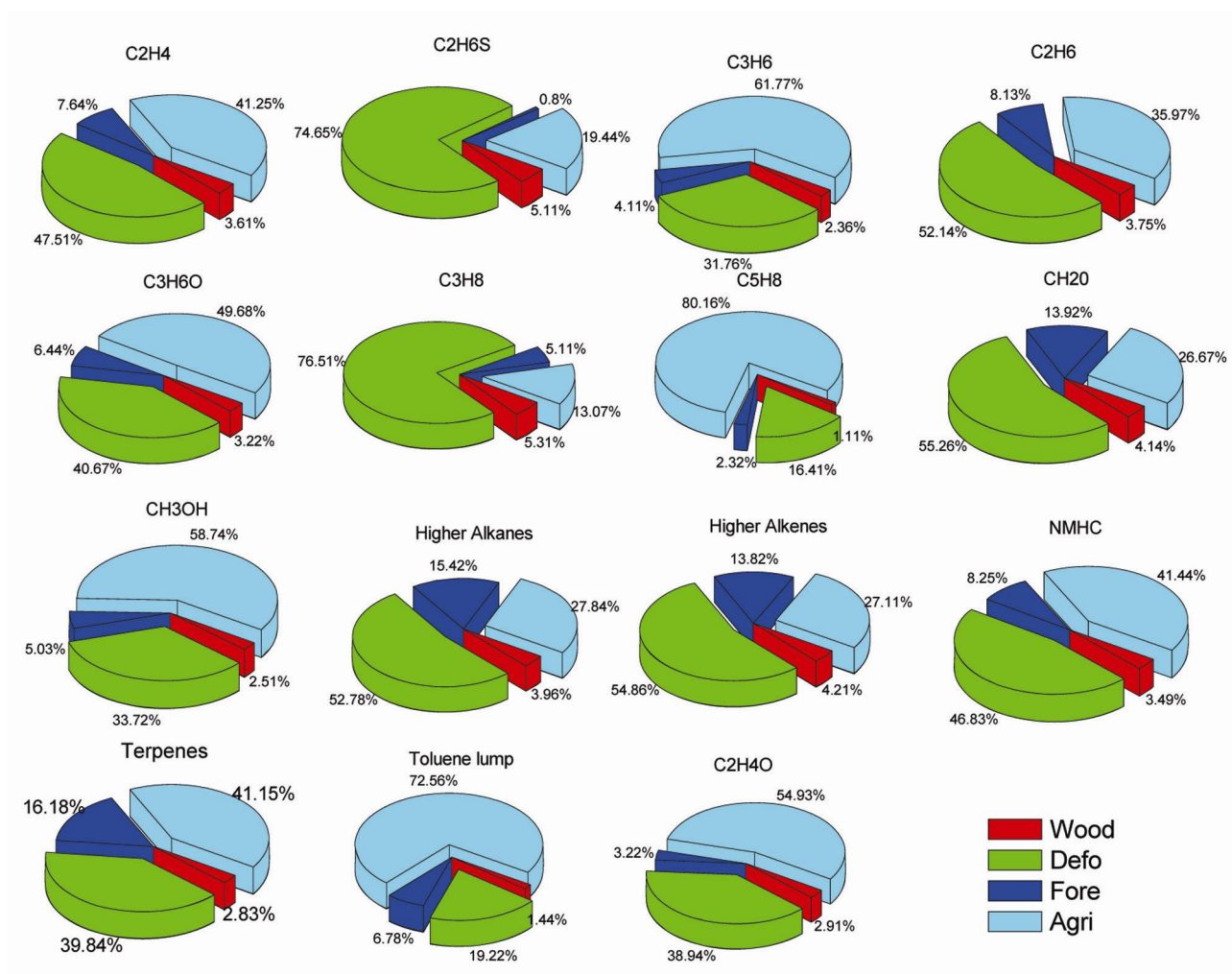


Figure 4. Major sources of NMVOCs.

contribute to NMHCs. During the monsoon season, the emission from biomass burning is lowest in India and

hence contributions from biofuel and fossil fuel combustion are expected to be high.

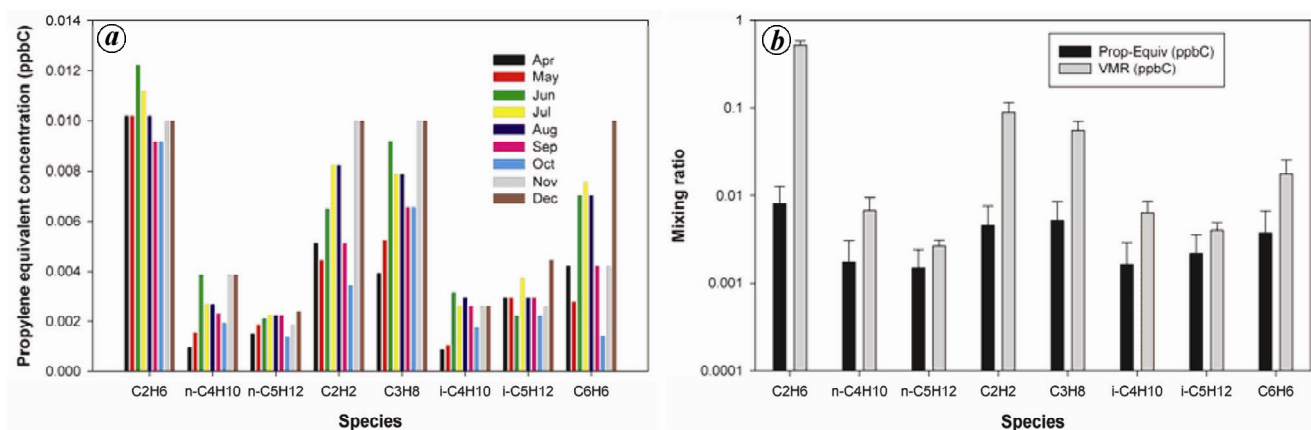


Figure 5. *a*, Pre-monsoon, monsoon and post-monsoon variability of light NMHCs. *b*, Monthly mean propylene equivalent for the year 2008. Vertical bars are the $\pm\sigma$ variation from mean.

Table 2. Propylene equivalent concentration for long-lived and short-lived NMHC species in the upper troposphere over India

Volatile organic compounds	Propylene equivalent concentration (ppbC)							
	C ₂ H ₆	<i>n</i> -C ₄ H ₁₀	<i>n</i> -C ₅ H ₁₂	C ₂ H ₂	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>i</i> -C ₅ H ₁₂	C ₆ H ₆
April	0.0102	0.0010	0.0015	0.0051	0.0039	0.0009	0.0030	0.0042
May	0.0102	0.0015	0.0019	0.0044	0.0052	0.0010	0.0030	0.0028
June	0.0122	0.0039	0.0021	0.0065	0.0092	0.0031	0.0022	0.0070
July	0.0112	0.0027	0.0022	0.0082	0.0079	0.0026	0.0037	0.0076
August	0.0102	0.0027	0.0022	0.0082	0.0079	0.0030	0.0030	0.0070
September	0.0092	0.0023	0.0022	0.0051	0.0066	0.0026	0.0030	0.0042
October	0.0092	0.0019	0.0013	0.0034	0.0066	0.0017	0.0022	0.0014
November	0.0102	0.0039	0.0019	0.0051	0.0092	0.0026	0.0026	0.0042
December	0.0122	0.0039	0.0024	0.0086	0.0098	0.0026	0.0044	0.0070
Average (ppbC)	0.0105	0.0026	0.0020	0.0061	0.0074	0.0023	0.0030	0.0051
Standard deviation	0.0011	0.0011	0.0004	0.0019	0.0020	0.0008	0.0007	0.0022
Average (ppbv)	0.5167	0.0068	0.0026	0.0889	0.0561	0.0064	0.0041	0.0180
Standard deviation	0.0527	0.0026	0.0005	0.0257	0.0141	0.0022	0.0009	0.0074

Propylene equivalent concentration of NMHCs and impact of STE

The Propy-Equiv concentrations of NMHCs have been used to estimate their relative contributions in O₃ production²². The Propy-Equiv concentration is calculated by multiplying the concentration of each NMHC by the ratio of its OH rate constant to the OH rate constant for propylene. In Figure 5*a* the Propy-Equiv concentrations (ppbC) of different NMHCs are shown over India for the year 2008. Most of the species such as C₂H₆, C₂H₂, C₃H₈, etc. showed higher propylene equivalent concentrations during the monsoon season. Figure 5*b* shows that ethane, propane, acetylene and benzene are the most abundant hydrocarbons (which are relatively long-lived species). The reactive species such as ethene, propylene and butanes have less pronounced seasonal variations. Among all long-lived species, ethane shows high mean value of 0.51 ppb compared to acetylene (0.088 ppbC) and propane (0.05 ppbC). The Propy-Equiv estimates of different species are given in Table 2. On the other hand, for quan-

titative estimates, the role of other parameters such as NO_x and intensity of solar flux is also important. The sensitivity of photochemistry leading to production of O₃, whether VOCs-limited or NO_x-limited is usually estimated by the ratio of VOC/NO_x. In the tropical region, deep convection can transport the surface-emitted precursors in a very short time. Therefore, the photochemical process can play an important role in the O₃ distributions in the upper troposphere.

Discussion

Vadrevu *et al.*¹⁴ found that the biomass burning season in India is highest during the pre-monsoon period (March–May). The frequency and intensity of fire can vary according to the vegetation type, climate conditions and socio-economic factors. In North East India, severe forest fires take place during the January–May period every year. The main reason for such fires could be slash-and-burn style of farming. Venkataraman *et al.*⁴ using MODIS active-fire maps over India, detected seasonal variability

of forest and crop waste burning. They found that the peak in forest biomass burning occurs in February–May, and crop waste burning varied with geographical location, with peaks in April and October, corresponding to the two major harvest seasons. Giriraj *et al.*⁵, while quantifying fire regime in India, found that the bio-geographic zones (Deccan, Central Plateau and North East) and states of India (Andhra Pradesh, Chhattisgarh, Madhya Pradesh and Mizoram) have a regular seasonal maximum during March and April. The rising summer temperatures and dry weather conditions promote the occurrences of fires and as summer progresses to March and April, parts of Central India and the Western Ghats predominantly covered with deciduous forests, become dry and leaf-fall aids in quick ignition of fire. In May, fires almost subside in the south and become predominant in the northern pine forests of the Himalayan zone. The Himalayan zone forests, situated in northern part of India, predominantly composed of *Pinus roxburghii* experience heavy fire episodes every year during May and June. High summer temperatures in this region occur around mid-April to May. The results of Vadrevu *et al.*¹⁴ and Giriraj *et al.*⁵ are consistent with those of the present study.

For example, in 2006, using the Defense Meteorological Satellite Program – Operational Line Scan system (DMSP-OLS), Kharol *et al.*¹⁴ derived peak frequency in the month of March. During the study for the years 2007, 2008 and 2009 over the northwest region of India, Kumar *et al.*²¹ found that the fire counts were highest in spring for all three years. Moreover, the total fire counts in the year 2007 were relatively smaller than in the years 2008 and 2009, which is similar to our results (Figure 1 b).

On an annual basis, higher number of fire counts was recorded during 1998–1999 and lower number during 2002–2003. The two anomalous periods of 1998–1999 and 2002–2003 have been explained with a strong correlation between fire activity and El Niño/La Niña²². The largest number of fire counts found in 1998–1999 coincides with El Niño events²⁰. Several studies, for example, in Indonesia have demonstrated that such large fires in peat areas are of particular importance for overall fire emission products. The fires in peat areas may release up to 50 times (or even more) higher emissions per unit area burnt than fires in surface vegetation^{23,24}; Levine *et al.*²³ estimated that 20% of the total area burnt in 1997 produced 94% particulate matter. Such trend in particulate matter emitted by the fires are the dominant pollutants which can deteriorate air quality on a regional scale²⁵. Kirono *et al.*²⁶ noted that during the 1997 El Niño, virtually entire Indonesia had rainfall below the 10th percentile, with many locations receiving the lowest rainfall on record since 1950. These conditions contributed to a pronounced lowering of the water table in peat. The episodes of El Niño could cause abnormal drought conditions in Indonesia. In Indonesia fire is also used during the long fallow rotation of the so-called jungle rubber in Sumatra

and Kalimantan to remove most of the biomass, including the woody parts.

For global fire the year-to-year variation has been reported by Arino and co-workers^{18,19}. We have considered mid-infrared region (MIR) (3.7 μm), whereas Arino and co-workers have considered short wavelength infrared region (SWIR) (1.6 μm) measurements. The years 1997 and 1998 showed unusually high fire counts due to El Niño. This was followed by a cold phase from late 1998 through 2000, is associated with the opposite influence in SE Asia. The El Niño/Southern Oscillation (ENSO) is the most important coupled ocean–atmosphere phenomenon to cause global climate variability on inter-annual timescales. The MEI is sensitive to ENSO and identifies events not detected by other indices. The time series of MEI are available from 1948 to the present, from the National Oceanic and Atmospheric Administration (NOAA; <http://www.cdc.noaa.gov/people/klaus.wolter/MEI/>). MEI has six main observed variables over the tropical Pacific. These are: sea-level pressure (P), zonal (U) and meridional (V) components of the surface wind, sea surface temperature (S), surface air temperature (A), and total cloudiness fraction of the sky (C). In recent times, the observed maximum for the strongest El Niño events is of the order of 3.0. Typically, most events fall between 1 and 2. The fire counts data, in the view of a set of MEI, also indicate the role of El Niño in 1997–98 and the subsequent La Niña from 1999 to 2001 (refs 27 and 28).

Among different categories of VOCs, the contribution of NMHCs is most significant in India. In addition, we have found that the contributions of oxygenated VOCs like CH_3OH and HCHO are significant compared to other oxygenated species. It may be pointed out that the annual variability of NMHCs and CH_3OH during 1997–2009 is roughly two times that of other species. The major sources of biomass burning in India during the period 1997–2009 are deforestation, forest fire, wood fire and agricultural waste. On the basis of emission of NMVOCs from different biomass burning sources, we have found that deforestation and agricultural waste are two major sources of biomass burning in India. To minimize pollution, these major sources must be controlled adequately. Similar observation has been made by Fuller and Murphy²⁸ for Southeast Asia.

A recent study identifies that Swedish agriculturists were largely responsible for the related problems of plantation fires and deforestation during the 1997–98 El Niño event²⁹. It is to be noted that the NMHCs are precursors for O_3 formation. They are oxidized by the hydroxyl radical (OH) to form a complex mixture of peroxy radicals that oxidize NO to NO_2 without consuming O_3 and thus allow O_3 to increase in the troposphere. The composition and concentration of various NMHCs depend and vary with the type of sources like biogenic and anthropogenic emissions. Concentrations of NMHCs were studied to

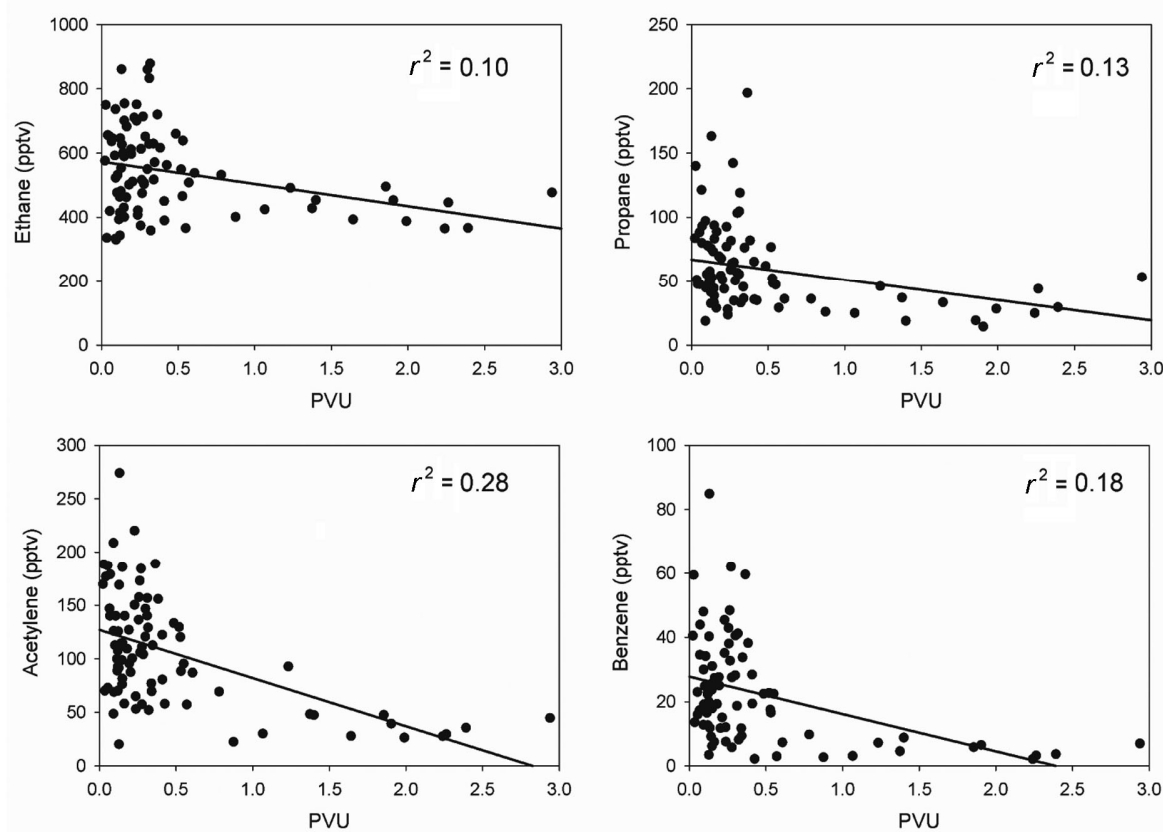


Figure 6. Relation between the mixing ratios of some NMHCs and potential vorticity in the upper troposphere over the Indian subcontinent.

explore the O_3 formation potential (OFP) of each NMHC in 2008 for India. In the upper troposphere, the mixing ratio of NMHCs showed elevated values during summer compared to winter⁸. This variability was most likely the result of rapid convection of surface air to the upper troposphere during the monsoon season.

The trends for individual species over India are shown in Figure 5 a. Similar work was done by Tan *et al.*³⁰ for Foshan, China. They found ethane, propane, *n*-butane, *i*-pentane, ethene, propylene, ethyne, benzene and toluene to be the most abundant hydrocarbons and also account for Prop-Equiv of each species. They concluded that alkenes played the most important role in O_3 formation, followed by aromatics and alkanes during the study period in Foshan³⁰. Lal *et al.*³¹ also worked in this direction taking propylene equivalent as a key tool for studying mixing ratio of some light NMHCs at two sites in IGP, namely Hissar and Kanpur and found that ethane and propane are most abundant.

In India, aromatics are most preferred because they decay by reaction with the OH radicals more rapidly. It may be pointed out that the reactive aromatic species such as benzene are more effective in O_3 formation than butanes, pentanes and long-lived species such as ethane and propane acetylene. Similar result has been obtained by other workers using observation data^{15,32–34}.

It has been found that the mixing ratio (ppb) of ethane is higher compared to other light-weight NMHCs, but in view of large mixing ratio (ppb) the rate of reaction with OH radical, e.g. propylene equivalent concentrations is relatively low. Similar work by Doskey and Kotamarthi³⁵ is based on measurements of NMHCs at tall building sites in Nashville (Polk Building), Houston (Williams Tower), and Phoenix (Bank One Building) USA, for 1999 and 2000.

In the tropical upper troposphere, the dominant role of convection in the distribution of trace constituents has been reported in various studies. On the other hand, mainly limited over the higher latitudes of the tropical region, the episodes of stratosphere–troposphere exchange (STE) can impact the levels of many trace gases. In context of this study, NMHCs are primary species and have relatively short lifetimes to reach in the stratosphere. Therefore, under the influence of STE, lower levels of NMHCs are expected in the upper troposphere. In this study, we have used the potential vorticity ($1 \text{ PVU} = 10^{-6} \text{ km}^2 \text{ kg}^{-1} \text{ s}^{-1}$) data to study the influence of STE events in the distributions of NMHCs over India. The relation between the potential vorticity (PVU) and the mixing ratios of some NMHCs (ethane, propane, acetylene and benzene) is shown in Figure 6. On an average, the levels of these species tend to decrease with

increasing PVU value. The drastic decline in the levels of NMHCs can be noticed in air mass having PVU value greater than 0.5. The least square regression linear fit has been also plotted in the figure. In spite of poor correlation coefficient values ($r^2 = 0.10\text{--}0.28$), the rapid decline in NMHCs with the increasing potential vorticity can be clearly noticed.

Summary

In the present study, emission of VOCs from biomass burning sources during the period 1997–2009 over India has been analysed. This study and growing interest in the measurement of VOCs in the tropical region suggest the following key points:

1. Satellite-derived fire count data and emission estimates have been used to study the seasonal and inter-annual variability of biomass burning in India during 1997–2009. The highest fire count was detected in the period 1998–1999. The present results based on ATSR also compare fairly well with the other nighttime observations^{36,37}.
2. The emissions of NMVOCs from biomass burning sources in India show large year-to-year variation during the study period. The contribution of NMHCs was most significant. It was found that the contribution of oxygenated VOCs (e.g. CH₃OH, HCHO, etc.) and to some extent aromatics was also significant compared to other species. It may be pointed out that the variability of NMHCs, C₂H₄, C₂H₄O, CH₃OH and toluene lump during the study period is roughly two times higher than that of other species.
3. Typically, the biomass burning sources are categorized as deforestation, forest fire, wood fire and agricultural waste. It has also been found that NMHCs are mainly produced by agricultural waste burning (41%) and deforestation (47%). On the other hand, agricultural waste burning is the major source for isoprene (80%), toluene (73%), formaldehyde (80%) and methyl alcohol (59%). Therefore, major contributors of VOCs in India are both deforestation and agriculture waste burning. It may be due to slash-and-burn agriculture, which is a major practice in North East India^{38,39}. In Central India, in addition to agriculture waste burning forest fire also contributes significantly.
4. *In situ*, CARIBIC measurement data was used to analyse a suite of trace gases that included a number of C₂–C₈ NMHCs. Seasonal variations in the mixing ratios of NMHCs are predominantly controlled by their reactions with the OH radical. The real time measurement covering a large spatial and temporal domain can help study the role of regional biomass burning and its ozone formation potential over India.

Effects of two different dynamical processes, namely convection and STE were noticed in the distribution of NMHCs over the Indian region.

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