Non methane hydrocarbon (NMHC) fingerprints of major urban and agricultural emission sources active in South Asia for use in source apportionment studies

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Abstract

In complex atmospheric emission environments such as urban agglomerates, multiple sources control the ambient chemical composition driving air quality and regional climate. In contrast to pristine sites, where reliance on single or few chemical tracers is often adequate to resolve pollution plumes and source influences, comprehensive chemical fingerprinting of sources using non-methane hydrocarbons and identification of suitable tracer molecule/molecules and emission ratios is necessary. Here, we characterize and present "chemical fingerprints" of some major urban and agricultural emission sources active in South Asia such as paddy stubble burning, garbage burning, idling vehicular exhaust and evaporative fuel emissions. Whole air samples were collected actively from the emission sources in passivated air sampling steel canisters and then analyzed for 49 NMHCs (22 alkanes, 16 aromatics, 10 alkene and 1 alkyne) using thermal desorption gas chromatography flame ionisation detection (TD-GC-FID). Based on the measured source profiles, chemical tracers were identified for distinguishing varied emission sources and also for use in PMF source apportionment models. Thus, we were able to identify chemical tracers such as i-pentane for petrol vehicular exhaust and evaporative emissions, propane for LPG evaporative and LPG vehicular exhaust emissions, and acetylene for the biomass fires during the flaming stage. Furthermore, we observed propane to be a major NMHC emission (8%) from paddy stubble fires and therefore in an emission environment impacted by crop residue fires, use of propane as a fugitive LPG emission tracer requires caution. Isoprene was identified as a potential tracer for distinguishing paddy stubble and garbage burning in the absence of isoprene emissions at night from biogenic sources. Diesel vehicular exhaust comprised of >50% alkenes and alkyne by mass composition while diesel evaporative emissions were enriched in C5-C8 alkanes and aromatics. The secondary pollutant formation potential and human health impact of the sources was also assessed in terms of their OH reactivity (s^{-1}), ozone formation potential (OFP, $gO_3/gNMHC$) and

fractional BTEX content. Petrol vehicular exhaust emissions, paddy stubble fires and garbage fires were identified as the most polluting among the sources studied in this work. Source specific inter-NMHC molar ratios which are often employed for identifying ambient air pollution emission plumes and assessing photochemical ageing were also examined. Toluene/benzene (T/B) ratios

5   were a good tracer for distinguishing the paddy stubble fire emissions in flaming (0.42) and smoldering stages (1.39), garbage burning emissions (0.21-0.32) and traffic emissions (3.54). While i-butane/n-butane ratios were found to be similar (0.20-0.30) for many sources, i-pentane/n-pentane ratios were useful for distinguishing biomass burning emissions (0.09-0.70) from the traffic/fossil fuel emissions (1.55-8.77). The results of this study provide a new foundational

10 framework for quantitative source apportionment studies in complex emission environments such as South Asia.

1 Introduction

Non-methane hydrocarbons (NMHCs) are an important class of volatile organic compounds (VOCs) that drive atmospheric chemistry and contribute towards formation of tropospheric ozone

15 and secondary organic aerosols (SOA) (Poisson et al., 2000; Hallquist et al., 2009; Derwent et al., 2010; Ortega et al., 2016). Ground level ozone affects ambient air quality, human health and climate thus making it a primary target in air quality regulations (EPA, 1990). Furthermore, by reacting with hydroxyl radical (OH) they can also affect the oxidative capacity of the atmosphere (Atkinson, 2000). NMHCs have a wide variety of anthropogenic, pyrogenic and biogenic sources.

20 In the urban areas, anthropogenic sources such as vehicular emissions, industries and fugitive solvent evaporation dominate the emissions (Barletta et al., 2005; Baker et al., 2008; Kansal, 2009; Jaimes-Palomera et al., 2016). However, in an agrarian and developing economy like India and other parts of South Asia, other major anthropogenic activities like crop residue burning and

garbage burning have emerged as poorly regulated emission sources. Every year the North West-Indo Gangetic Plain experiences episodes of large scale open burning of paddy stubble in the post-harvest months of October and November wherein > 12,685 km^2 of area of Punjab alone is estimated to be burnt in the open farm fields (Badarinath et al., 2006). This results in emission of

5   a large number of gaseous and particulate pollutants into the air and causes severe deterioration in regional air quality (Sarkar et al., 2013; Chandra and Sinha, 2016; Kumar et al., 2016; Garg et al., 2016; Kumar et al., 2018; Sharma et al., 2019). Previous studies have characterised the emissions of selected VOCs, greenhouse gases and primary air pollutants like benzenoids, carbon monoxide, nitrogen oxides and black carbon (Venkataraman et al., 2006; Sahai et al., 2007) from paddy

10   stubble burning over NW-IGP. However, there is still a considerable deficit in knowledge concerning the speciated non-methane hydrocarbons, which are co-emitted in the smoke (Andreae, 2019; Sinha et al., 2019). The NMHC emissions from different sources when expressed as emission source profiles (Watson et al., 2001; Hong-li et al., 2017) provide detailed insights for quantitative source apportionment in source receptor models. Moreover, they are helpful for

15   assessing human health risks due to exposure to toxic and hazardous compounds and secondary pollutant formation tendencies, and therefore assist in prioritization of pollution control strategies and policies.

The ratio of two NMHCs having different chemical lifetimes can also be used for constraining the photochemical age of air masses and atmospheric transport times (Parrish et al., 1992; McKeen

20   and Liu, 1993). Several source profiles have been compiled for different emission sources in North America (Dallmann et al., 2012; Gentner et al., 2012), Europe (Passant, 2002; Niedojadlo et al., 2007), East Asia (Na et al., 2004; Liu et al., 2008; Zhang et al., 2013; Zheng et al., 2013; Hong-li et al., 2017) and other areas (Doskey et al., 1999), however there is still considerable gap in data

of speciated NMHCs from active emission sources in South Asia. Using the emission source profiles from different regions of the world for modelling and estimation studies can result in large uncertainties in source apportionment and emission quantification as the emissions can change from country to country depending upon the quality and composition of fuels, combustion practices and vehicular fleet. Therefore, it is essential to have a comprehensive database of regional and local source profiles which can be used to yield more accurate data for calculation of emissions and source apportionment tools such as positive matrix factorization.

In this study, we report the NMHC fingerprinting of paddy stubble burning emissions, garbage burning emissions, fuel evaporative emissions and idling exhaust emissions of vehicles powered by liquefied petroleum gas (LPG), compressed natural gas (CNG), diesel and petrol using 49 speciated NMHCs (22 alkanes, 16 aromatics, 10 alkene and 1 alkyne). These compounds were measured using thermal desorption gas chromatography flame ionisation detection (TD-GC-FID). Based on the measured source profiles, chemical tracers were identified for distinguishing varied emission sources and also for use in PMF source apportionment models. Further, we assessed the secondary pollutant formation potential and health risks of the sources in terms of their OH reactivity (s^{-1}), ozone formation potential (OFP, $gO_3/gNMHC$) and fractional BTEX content.

2 Materials and Methods

2.1 Whole air sampling from specific sources in passivated steel canisters

Table 1 summarizes the details of the whole air sample collection experiments for emissions from paddy stubble burning, garbage burning, busy traffic junctions, idling vehicular exhaust emissions and fuel evaporation. The paddy stubble burning samples (three flaming and smoldering each) were collected at an agricultural field in Kurari, Mohali (30.605° N, 76.744° E) on 4 Nov 2017

between 16:30-18:30 LT. The garbage burning samples (five flaming and smoldering each) were collected at waste sorting and disposing stations in Mohali and surrounding villages (30.642-30.699ºN, 76.713-76.729ºE) between 7 - 17 February 2017. Figure S1 shows the flaming and smoldering fires were distinguished based upon the visual inspection of presence of flame and white smoke as per previous studies (Chandra et al., 2017; Kumar et al., 2018). The fire in flaming stage showed clear flame with little smoke while in the smoldering stage there was white smoke and no flame. The traffic samples were collected from three busy traffic junctions in Chandigarh and Mohali (Sohana Gurudwara Chowk, 30.691º N, 76.698º E; Sector 79/80 Chowk, 30.678º N, 76.721º E; and Transport Chowk, 30.717º N, 76.812º E) from 3-15 March 2017. Although the vehicular emissions are known to be dependent upon several factors, their idling operation results in particularly higher emissions and fuel residues in the exhaust (Yamada et al., 2011; Shancita et al., 2014). This is because in idling operations the engine does not work at its peak operating temperature and efficiency (Brodrick et al., 2002) resulting in incomplete fuel combustion (Rahman et al., 2013). In this study, prior to vehicular exhaust sampling, the engine was left running for about 5 minutes until it warmed up to normal working temperature (70-90ºC) and then the air was sampled directly from the mouth of the tailpipe exhaust with the car being in stationary position and engine left running at idle speed. The idling vehicular exhaust samples were collected from 23 Petrol vehicles (14 two wheelers and 9 light duty four wheelers), 33 diesel vehicles (6 three wheelers, 12 light duty four wheeler and 15 heavy duty wheelers), 9 LPG vehicles (three wheelers) and 7 CNG vehicles (6 three wheelers and 1 light duty four wheeler) from Mar 2017-Oct 2018 in Chandigarh and Mohali (30.660-30.750ºN, 76.700-76.840ºE). For a better representation, the most common vehicle models on Indian roads were selected for this study based upon the personal field observations and motor vehicle data provided by Ministry of Road

Transport and Highways (MoRTH 2017). The fuel evaporative emissions samples (one each from the headspace of LPG, petrol and diesel) were collected in the IISER Mohali campus on 5 Jul 2017. In addition, prior to the lighting of fires or turning on the engine, ambient air samples were also collected from the aforementioned sites to correct for ambient background concentrations.

5   The whole air was actively sampled in commercially available 6L passivated SilcoCan air sampling steel canisters (Restek, USA) and then analyzed using a thermal desorption gas chromatograph equipped with a flame ionisation detector (TD-GC-FID) within one day of sample collection as per collection procedure described in previous works (Chandra et al., 2017; Vettikkat et al., 2019). Stability tests of compounds in the canisters were also conducted which showed that

10   all the measured compounds reported in this work including alkenes and alkyne remained stable for upto 3 days. The air was sampled actively into the canisters using a Teflon VOC pump (Model − N86 KT.45.18; KNF Germany) operating at a flow rate of ~5500 ml/min and pressurized upto 30 psi. The steel canisters were protected from dust and air particles using a Teflon membrane filter (Pore size 0.45μm) in the sample inlet line. Prior to each sampling the canisters were cleaned

15   and preconditioned as per EPA Method TO-15 using TO-Clean canister cleaner (Wasson ECE Instrumentation, Colorado, USA) and humidified nitrogen.

2.2 NMHC measurements by Thermal Desorption - Gas Chromatography-Flame Ionization Detection (TD-GC-FID):

NMHCs in the sample air were measured using gas chromatograph equipped with two flame

20   ionization detectors (GC-FID 7890B, Agilent Technologies, Santa Clara, United States). Sampling and pre-concentration was performed using a thermal desorption (CIA Advantage-HL and Unity 2, Markes International, UK) unit coupled to the GC-FID system. Helium (99.999% pure, Sigmagases, India) was used as the carrier gas. Hydrogen (99.9995%, Precision Hydrogen 100 -

H$_2$ Generator, Peak Scientific, Scotland, UK), Synthetic air (99.999%, Sigmagases, India) and

Nitrogen (99.9995%, Precision Nitrogen Trace 250 – N$_2$ Generator, Peak Scientific, Scotland, UK)

were used as the FID gases (Table S1). Synthetic air (99.9995%, Precision Zero Air 1.5 - Gas

Generator, Peak Scientific, Scotland, UK) was also used as the purge gas for the Markes Thermal

5   desorption unit.

At a first stage, the sample air was passed through a Nafion dryer (integrated in CIA Advantage)

to remove water (Badol et al., 2004; Gros et al., 2011). It was then preconcentrated at -30°C

(maintained by a Peltier cooling system) at 20 ml/min, on an Ozone precursor trap (U-T17O3P-

2S, Markes Internatioal, UK). The trap was a 2 mm-internal diameter, 60 mm-long quartz tube

10   containing Tenax TA, Carboxen 1003 and Carbosieve SIII as adsorbents. Preconcentrated trap was

thermally desorbed by heating the trap rapidly to 325°C and held at this temperature for 20 min,

so that all the preconcentrated NMHCs were thermally desorbed. Thermally desorbed NMHCs

were then transferred via a heated inlet (130°C) line onto the GC instrument consisting of two

capillary columns (DB-1, dimethyl polysiloxane, 60 m x 0.25 mm, 1.00 μm film thickness;

15   Alumina Plot, Al$_2$O$_3$/Na$_2$SO$_4$, 50 m x 0.32 mm, 8 μm film thickness, Agilent Technologies, Santa

Clara, United States). Table S1 lists the settings at which the FIDs were operated and the oven

temperature was ramped. Initially a temperature of 30°C was maintained for 12 min and thereafter

it was increased at two subsequent rates of 5°C/min (upto 170°C) and 15°C/min (upto 200°C). The

two columns were connected via a Dean's switch which was turned on after 17 min of the

20   chromatographic run. In these initial 17 min, the two columns were connected to each other in

series and the eluents from first column (DB-1) were directed onto the second column (Alumina-

PLOT). After 17 min the series connection between both the columns was broken by turning on

the Dean's switch and the eluents from both columns were directed onto their respective FIDs. C6

and higher NMHCs were resolved on DB-1 column and recorded on FID 1 while C2-C5 NMHCs were resolved on Alumina PLOT column and recorded on FID 2. Thus, in a single run, C2-C10 compounds were measured simultaneously in two chromatograms.

Prior to the sampling, the instrument was calibrated by dynamic dilution with zero air at four

5   different mixing ratios (in the range of 2–20 ppb) using a standard gas calibration unit (GCU-s v2.1, Ionimed Analytik, Innsbruck, Austria). A NIST calibrated flow meter (BIOS Drycal definer 220) was used to measure the flows of both the standard gas and zero air mass flow controllers before and after the calibration experiments. Figure S2 shows the plots from the calibration experiments that exhibit excellent linearity over the entire dynamic range ($r^2 \geq 0.99$). For highly

10   concentrated samples, appropriate dilution was performed prior to sample injection so that the measured concentrations were within the range of 5-30 ppb for most of the compounds. However, there were still a few compounds that were 50-200 ppb in some sources even after dilution. The instrument linearity was therefore tested at high concentrations of upto 200 ppb and excellent linearity ($r^2 \geq 0.99$) was observed for all the compounds. Table S2 lists the details of two VOC gas

15   standards; 1) Gas standard (Chemtron Science Laboratories Pvt. Ltd., Navi Mumbai, India) containing 56 VOCs at a mixing ratio of circa 1 ppmv (stated accuracy of ± 5%), 2) Gas standard (Apel-Riemer Environmental, Inc., Colorado, USA) containing VOCs at circa 500 ppb (stated accuracy better than 5%) using which the instrument was calibrated. Instrumental sensitivities can change during a long run deployment owing to change in settings and mechanical wear and tear

20   and therefore regular calibrations are important to ensure the instrumental stability. Table S3 shows the average sensitivity factors (pAs/ppb) and standard deviation derived from thirteen calibrations performed regularly between Dec 2016 and Oct 2018 with no drastic changes observed in the instrumental sensitivities. A reasonable agreement (considering the instrumental uncertainty

error of <15% for respective compounds) was found for the average calibration factors between Feb 2017 - Oct 2018 derived from the two different gas standards for the common compounds such as isoprene (53.2 ± 4.9 and 55.6 ± 5.9 pAs ppb^{-1}), benzene (67.8 ± 5.6 and 69.2 ± 5.5 pAs ppb^{-1}) and toluene (74.6 ± 6.6 and 81.3 ± 7.7 pAs ppb^{-1}). Peak identification and quantification

5   were performed using the PC software (Agilent OpenLAB CDS, Chemstation Edition, Rev. C.01.06(61)). All the chromatograms were manually inspected to ensure correct peak identification, baseline determination and peak area calculation. Individual Peak areas (pAs) were converted to ppb using the calibration factors obtained from calibration experiments. Table 2 lists the compound specific precision errors, limit of detection (LOD) and total uncertainties. The

10   precision of the instrument was evaluated under the identical conditions using the relative standard deviation of five individual measurements of 5 ppb of standard gas mixture and was in the range of 0.1-0.5% for the reported compounds. The limit of detection of the instrument was evaluated according to Eq. (1) at 5% probability, using the standard deviation of 8 zero/blank samples measurements under identical conditions (Penkett, 2007; ACTRiS 2014).

$$LOD = 2t\sigma \qquad\qquad\qquad (1)$$

Here, σ is the standard deviation of 8 blank measurements (manual integration of peaks in the blank sample and if peaks were missing then integration of the baseline corresponding to the same retention time and average peak width) and t is the student's t-value for the 5% probability and 7 degrees of freedom. The instrumental LOD was in the range of 2-104 ppt. The total uncertainties

20   were calculated using the root mean square propagation of individual uncertainties like the 5% accuracy error inherent in the VOC gas standard concentration, error in the linear fit of the calibration curve, the error in the flow reproducibility of the two mass flow controllers, and the precision error of the instrument. The overall uncertainties for all compounds were less than 15%.

3 Results and Discussion

3.1 NMHC chemical fingerprinting of emission sources

3.1.1 Paddy stubble fires and garbage fires

Figure 1a-d shows the normalized emission profiles of the whole air samples collected from paddy

5   stubble and garbage fires under flaming and smoldering conditions. The mixing ratios were

corrected for ambient background levels using samples collected just before the fires, averaged for

the different fires and normalized to the NMHC with the maximum mixing ratio in the respective

source sample.

The largest contributors to the observed mass concentrations in paddy fires under flaming

10   conditions were ethene (15%), ethane (15%), propene (14%), benzene (12%) and acetylene (9%),

while in smoldering conditions ethane (21%), isoprene (13%), propene (13%), propane (8%) and

ethene (6%) were the highest ranked contributors. Acetylene was found to be negligible (<1%) in

smoldering fires and therefore can be used as tracer for fires under flaming conditions. Amongst

alkenes, the fraction of ethene and propene reduced in smoldering while that of isoprene increased

15   by ~2 times. In the garbage fire emissions, under both flaming and smoldering conditions, benzene

(~22%) was the highest emitted NMHC followed by propene (16 and 14% respectively) and ethene

(8 and 14% respectively). Acetylene was again found to be low (~1%) in smoldering conditions

while in flaming conditions it was 11%. Ethane, propane and *n*-butane increased by ~2 times under

smoldering conditions. The garbage burnt in this study mostly comprised of wet vegetable and

20   food waste from households and therefore had less styrene (<1%) (Sharma et al., 2019). Isoprene

was found to be very low (<1%) in the garbage fires as compared to the paddy stubble fires and

therefore could be potentially employed for distinguishing paddy stubble and garbage burning

activities in absence of isoprene emissions at night from biogenic sources. Furthermore, propane

has been widely used as an emission tracer for fugitive LPG emissions (Blake and Rowland, 1995;

Barletta et al., 2002; Apel et al., 2010) but in a complex emission environment influenced by

intensive paddy stubble fires, use of propane as a fugitive LPG emission tracer may not be ideal

5   as it is one of the major species (8% of the total NMHC emissions) being emitted from the paddy

stubble burning.

3.1.2 Fuel evaporative emissions

Figure 1e-g shows the normalized source profiles of the whole air samples collected from the

headspace of liquefied petroleum gas (LPG), petrol and diesel.

10   In terms of mass concentrations, *n*-butane (28%), propane (22%), *i*-butane (16%) and butenes

(20% in total from all isomers) were found to be the major constituents in the LPG evaporative

emissions. The most abundant species in petrol evaporative emissions were *i*-pentane (39%),

ethane (16%), *n*-butane (11%) and *n*-pentane (10%). The total aromatic content in the petrol vapors

was low (1%), which is consistent with previous studies (Harley et al., 2000; Na et al., 2004).

15   Diesel evaporative emissions were quite different from petrol and had high fraction of heavier C5-

C8 alkanes (65%) and aromatics (29%) while unsaturated C2-C6 compounds comprised only

about 1% of the total emissions. *n*-octane (8%), *n*-hexane (7%), *i*-pentane (7%), *n*-heptane (6%),

toluene (5%) and methylcyclopentane (5%) were the major species identified in diesel vapors. C9

aromatics (13%), C10 aromatics (5%) and C8 aromatics (5%) constituted the major fraction of

20   aromatic content in the diesel vapors.

3.1.3 Vehicular exhaust and traffic emissions

Figure 2 shows the normalized source profiles of the whole air samples collected from the tail pipe exhaust of idling vehicles with different fuel types and from busy traffic junctions. Among NMHCs, compressed natural gas (CNG) vehicular emissions (Fig 2 a) had 73 % ethane by mass concentration which is not surprising considering it is mostly composed of methane and ethane

5   (Goyal and Sidhartha, 2003). The other major NMHC emissions from CNG exhaust were propane (14%) and ethene (5%). Overall alkanes (92%) and alkenes (7%) accounted for almost all NMHC emissions from the CNG vehicles.

Figure 2b shows that LPG vehicular emissions were mainly comprised of low molecular weight alkanes, i.e, C2-C4 NMHCs. *n*-butane (26%), *i*-butane (17%), propane (14%), *trans*-2-butene

10   (11%), propene (9%), 1-butene (8%) and *cis*-2-butene (6%) were the major components by mass concentration in these emissions. Alkanes accounted for 62% and alkenes 38% of the total emissions, whereas aromatics were negligible. LPG fuel is known to completely combust at higher driving speeds and therefore the presence of propane and butanes in the exhaust was indicative of incomplete combustion at idling stage (Guo et al., 2011). The major species in LPG-fueled vehicle

15   emissions found in this study were similar to studies in Taiwan (Chang et al., 2008) and Guangzhou (Lai et al., 2009). One major difference observed was that *n*-butane was the most abundant emission in the LPG vehicular exhaust in this study as compared to propane which is reported in aforementioned studies. This could possibly be because of the differences in LPG fuel composition, engine type, and combustion conditions that results in the variations in exhaust

20   emissions.

Figure 2c shows the averaged petrol vehicular emissions for two wheelers and four wheelers fueled by petrol. The emissions majorly comprised of toluene (16%), *i*-pentane (11%), *m/p*-xylene (11%), ethylbenzene (5%), acetylene (5%), 2,2-dimethylbutane (4%) and benzene (4%) which is also

similar to the studies conducted in Taiwan (Guo et al., 2011) and Pearl river delta (Liu et al., 2008). Alkanes and aromatics were the major constituents with 42% and 44% contribution respectively to the total NMHC mass concentration. Unlike evaporative emissions, negligible (<1%) emissions of ethane and butanes and high emission of aromatics (44%) were observed in the petrol exhaust.

5 High content of BTEX (35%) in petrol exhaust emissions is noteworthy considering their impact on air quality and human health.

Figure 2d shows the averaged diesel vehicular emissions of light duty vehicles, heady duty vehicles and three wheelers. The emissions majorly comprised of ethene (22%), propene (17%), acetylene (10%) and benzene (7%). Unlike petrol emissions, alkenes and alkyne were the major constituents

10 of the diesel vehicular exhaust contributing 57% to the total NMHC emissions. Furthermore, the BTEX (16%) and C5-C8 (11%) emissions were also lower than the petrol exhaust emissions possibly due to the better combustion efficiency of the diesel engines (Reiter and Kockelman, 2016). In addition to this, higher emissions from petrol could possibly be explained because of the two wheelers which are known to be high NMHC emitter because of inefficient and incomplete

15 combustion of fuel (Liu et al., 2008). C9-C10 aromatics, however, were found to be 13% of the total NMHCs as compared to 6% in petrol vehicle exhaust. Most of these compounds are likely from the unburnt fuel as they were also found in significant fraction in the diesel evaporative emissions. Since *i*-pentane was found to be negligible (0.2%) in diesel exhaust, it was identified as an ideal tracer for petrol vehicular emissions. In comparison to the petrol, the diesel exhaust had

20 lower fraction of heavier C5-C8 alkanes (11%) which were possibly combusted. Figure 2e shows the averaged source profile of whole air sample collected from three busy traffic junctions which therefore represent the ambient traffic emissions mixture. Although the Indian vehicular fleet comprises of vehicles running on petrol, diesel, LPG and CNG, more than 70% of on-road vehicles

are petrol fueled (Guttikunda and Mohan, 2014; Goel and Guttikunda, 2015; Prakash and Habib, 2018). Therefore, the petrol vehicular exhaust emissions were expected to dominate the ambient traffic mixing ratios. In addition to that, since the traffic samples were collected from busy traffic junctions, these were more likely to be influenced by the emissions in the vehicular idling condition

5   discussed earlier. Alkanes (51%) and aromatics (34%) formed a major fraction of the traffic emissions. Major NMHC species measured from the traffic were *i*-pentane (15%), toluene (10%), *n*-pentane (5%), *m/p*-xylene (5%), acetylene (4%) and 2,2-dimethylbutane (5%). Based upon the emission characteristics discussed earlier for each fuel type, petrol vehicles and LPG vehicles were identified as the most likely sources of *i*-pentane and propane respectively in the traffic plume.

10   Even though the Indian vehicular fleet is dominated by Petrol fueled vehicles, the consumption of diesel in road transport sector is approximately twice as much as petrol (Sadavarte and Venkataraman, 2014; Prakash and Habib, 2018). This is because the maximum diesel consumption (40%) is by heavy duty vehicles (HDVs) which run over large distances and have lower mileage than other vehicle classes. In past three decades, India has undergone rapid economic and industrial

15   growth, which in turn has resulted in increased consumption of diesel to sustain increased freight transport across the country (Nielsen, 2013). As discussed previously, the diesel vehicular exhaust and evaporative emissions were dominated by heavier C5-C8 alkanes, alkenes and aromatics which are key precursors in OH reactivity and ozone formation. Furthermore, secondary organic aerosol (SOA) formed from the diesel vehicular exhaust are estimated to be 2-7 times more than

20   petrol vehicular exhaust in urban areas where diesel generally accounts for 10-30% of total on-road fuel consumption (Gentner et al., 2012). It was estimated in 2009 that transport sector contributed 694 Gg of PM emissions in India, >70% of which came from vehicles fueled by diesel (Sahu et al., 2014). Since LPG and CNG vehicular emissions comprise of mostly C2-C4 alkanes

and alkenes, they have lower SOA formation potentials than petrol and diesel (Derwent et al., 2010) and therefore have emerged as cleaner fuel alternatives. However, the emission of large suit of reactive unsaturated NMHCs due to improper combustion of these fuels results in the high OH reactivity and OFP which can severely impact local air chemistry and quality. Therefore, in order

5   to mitigate the emissions the use of improved technologies (for better combustion and emission reduction like catalytic convertors), cleaner fuels (BSV and BSVI) and reduced idling times of the vehicles should be encouraged. Also, depending on which type of pollution is more acute (PM or gaseous), promoting the appropriate less polluting fuel type for more usage could help improve the overall ambient pollution.

10   **3.2 Assessment of OH reactivity, ozone formation potential (OFP) and BTEX loading from different emission sources**

Figure 3a-d show the comparison of percentage contribution of different chemical classes of NMHCs to the total mass concentrations, OH reactivity (s^{-1}), normalized reactivity ($gO_3/gNMHC$) and total BTEX loading (%) from various emission sources. The hydroxyl radical reactivity

15   reflects the total pollutant loading of the air mass (Sinha et al., 2012) and was calculated as Eq. (2):

$$\text{Total NMHC OH reactivity} = \Sigma \; k_{OH+NMHCi} \; [\text{NMHC}_i] \qquad (2)$$

where, $k_{OH+NMHCi}$ is the first order rate coefficient for the reaction of NMHC_i with OH radicals (Atkinson et al., 1982; Atkinson et al., 2006) and $[\text{NMHC}_i]$ is the measured concentration of the

20   NMHCs.

The ozone formation potential (OFP) is used as metric to measure the contribution of NMHCs in the total O_3 formation potential in urban environments (Carter, 1994). Normalized reactivity R (g

O_3/g NMHCs emitted) is generally used to indicate OFP for NMHCs from emission sources using their source profiles and MIR values as Eq. (3) (Harley et al., 2000; Zhang et al., 2013)

$$R = \Sigma_i \, \omega_i \times (MIR_i) \qquad (3)$$

where, ω_i are the weight percentage of $NMHC_i$ present in the emission source and MIR_i are the

5   maximum incremental reactivity coefficients (MIR) (Carter, 1994; Carter, 2009).

The ranking in the calculated OFP for the emission sources was: diesel vehicle exhaust (6.6 gO_3/gNMHC) > smoldering paddy stubble fire (6.0 gO_3/gNMHC) > flaming paddy stubble fire (5.5 gO_3/gNMHC) > LPG vehicle exhaust (5.3 gO_3/gNMHC) > flaming garbage fire (5.1 gO_3/gNMHC) > smoldering garbage fire (4.6 gO_3/gNMHC) > petrol vehicle exhaust (3.9

10   gO_3/gNMHC) > LPG evaporative emissions (3.7 gO_3/gNMHC) > diesel evaporative emissions (2.9 gO_3/gNMHC) > petrol evaporative emissions (2.2 gO_3/gNMHC) > CNG vehicle exhaust (1.0 gO_3/gNMHC). Although, alkenes were not the largest emissions by mass, they were still the largest contributor to the OH reactivity (67-93%) and OFP (49-83%) in the fire and fuel evaporation emissions. In the paddy stubble and garbage fire emissions, alkenes and aromatics contributed the

15   largest to the total OH reactivity (90% and 6-8% respectively) and OFP (~80% and ~18% respectively). Alkanes have comparatively poor reactivity towards OH radical and therefore despite contributing 23-36% to the total NMHC mass concentration, their contribution to the OH reactivity was negligible (<2%).

In paddy stubble fires under flaming conditions propene (33%), and under smoldering conditions

20   isoprene (46%) were the largest contributors to the total OH reactivity (details in Figure S4 and S5). These two NMHCs were also the largest contributor (~40-50%) to the OFP from paddy stubble fires. In garbage fires under both flaming and smoldering conditions, propene was the

largest contributor to total OH reactivity (46% and 42% respectively) and OFP (38% and 36% respectively). LPG evaporative and vehicle exhaust emissions comprised of 75% and 62% alkanes respectively, however, >90% of total OH reactivity was contributed by the alkenes. Butenes were the largest contributors to total OH reactivity (87% and 72% respectively) and OFP (78% and 65%

5   respectively) for LPG evaporative and vehicular exhaust emissions. 87% NMHC emissions from CNG vehicular exhaust were C2-C3 alkanes, but ~57% contribution to the total OH reactivity and OFP was from propene and ethene. In diesel evaporative emissions there was an approximately equal contribution to the total OH reactivity from alkanes (48%) and aromatics (41%). This is because of the presence of larger fraction of heavier C5-C8 branched alkanes which are generally

10   more reactive towards OH radical as compared to the light C2-C4 alkanes. 1,2,4-trimethylbenzne (13%) was the largest contributor to the total OH reactivity and OFP from diesel evaporative emissions. OH reactivity from diesel vehicular exhaust emissions however were dominated by alkenes (82%), and propene (41%) and ethene (21%) were the largest contributors. Both of these NMHCs also contributed 30% each to the total OFP calculated from diesel vehicular exhaust. In

15   petrol evaporative emissions, largest contribution to the OH reactivity was from butenes (50%) and *i*-pentane (17%). However, in petrol vehicular exhaust both aromatics and alkenes became the dominant contributors (42% each) to OH reactivity and the ranking of NMHC contribution to total OH reactivity was: propene (17%) > *m/p*-xylene (13%) > styrene (11%) > toluene (7%). For OFP from petrol vehicular exhaust, trend in the largest contributing NMHC was: *m/p*-xylene (26%) >

20   toluene (16%) > propene (11%) > ethene (5%). The total OH reactivity from traffic emissions were dominated by alkenes (48%) and aromatics (35%). The NMHCs contributing the largest fractions to the total OH reactivity were Styrene (9%) > trans-2-butene (9%) > isoprene (7%) > 1-hexene

(6%) > m/p-xylene (6%) > propene (6%) and to OFP were *m/p*-xylene (14%) > toluene (11%) > 1,2,4-trimethylbenzene (8%) > ethene (6%) > *i*-pentane (6%).

In order to assess the health risks associated with these sources, we compared the fraction of BTEX compounds in each of the emission sources. Benzene is classified as a human carcinogen (IARC, 2012) whose potential health risk assessments have already been elucidated before in NW-IGP during the periods influenced by intense paddy stubble fires (Chandra and Sinha, 2016). Other benzenoids like toluene and xylenes have also been associated with adverse effects on human health (ATSDR, 2000; ATSDR, 2007) and are classified as group "D" carcinogens by the US EPA. The ranking in the fraction of BTEX in the different emission sources was: petrol vehicle exhaust (35%) > smoldering garbage fire (33%) > flaming garbage fire (31%) > flaming paddy stubble fire (22%) > diesel vehicle exhaust (16%) > smoldering paddy stubble fire (13%) > diesel evaporative emissions (11%) > petrol evaporative emissions (3%). LPG and CNG emission sources had <1% of benzene and therefore were identified as least harmful sources, while petrol vehicular exhaust, garbage fires and paddy stubble fires were the most toxic emissions which could severely impact human health from BTEX emission potential.

3.3 Molar emission ratios of NMHCs in different emission sources

Inter NMHC molar ratios (ppb/ppb) are very useful tools that can not only be used to distinguish between different emission sources but also constrain the identity of the sources affecting ambient mixing ratios in a complex environment (Barletta et al., 2005; Barletta et al., 2017). This is because, for the NMHC species with similar chemical lifetimes, the molar ratios remain preserved during chemical oxidation and ambient dilution (Parrish et al., 1998; Jobson et al., 1999).

Table 3 lists commonly used inter NMHC molar emission ratios for the emission sources studied in this work. Toluene/benzene (T/B) ratio is a widely used ratio in identifying the vehicular emission sources (Barletta et al., 2002; Barletta et al., 2005). T/B measured for traffic in this study was 3.54 and varied between 0.37-6.99 for the idling vehicles of different fuel types. For petrol

5 fuelled vehicles the T/B was 3.41 which is also consistent with the ratios reported for vehicular emissions (Barletta et al., 2002; Barletta et al., 2005; Russo et al., 2010; Guo et al., 2011; Zhang et al., 2013). Furthermore, T/B can also be useful in distinguishing the paddy stubble fire emissions in flaming (0.42) and smoldering stages (1.39). *i*-butane/n-butane ratio (B/B) is another example of a widely used NMHC ratio to distinguish between different fossil fuel related emission sources.

10 However, in our study we found that this ratio is not useful in a complex emission environment influenced by varied emission sources. This is because the ratio exhibits similar values (0.20-0.30) for paddy stubble fires, garbage fires, petrol evaporative, diesel evaporative and petrol vehicle exhaust emissions. Therefore, caution should be applied while using this ratio in complex emission environments where biomass burning, fossil fuel combustion and biogenic emission sources

15 simultaneously occur in significant scale and strength to contribute to the chemical composition of ambient air. *i*-pentane/*n*-pentane can instead be used as a more reliable ratio for distinguishing biomass burning emissions (0.09-0.70) from the traffic/fossil fuel emissions (1.55-8.77).

4 Conclusion

Comprehensive chemical speciation source profiles of 49 NMHCs (22 alkanes, 16 aromatics, 10

20 alkene and 1 alkyne) were obtained for several major emission sources active in South Asia, namely paddy stubble burning, garbage burning, idling vehicular exhaust and evaporative fuel emissions. Many of these compounds like higher C6-C8 alkanes, C9-C10 aromatics and alkenes have been quantified for the first time from the different emission sources in the South Asian

region, which is important to ascertain region to region variability of such common urban and agricultural emission sources. The work highlights the importance of identifying the local emission source profiles as some NMHC emissions were found to be very different to the studies reported from North America, Europe and East Asia. These source profiles can be used for accurate and reliable emissions estimations, source apportionments and assessing the choice of fuels from point of view of air quality impacts both as primary emission source and also formation of secondary pollutants. Useful chemical tracers were identified for various emission sources: *i*-pentane for petrol vehicular exhaust and evaporative emissions, propane for LPG evaporative and LPG vehicular exhaust emissions, and acetylene for the biomass fires in flaming conditions. However, propane was also quantified as a major NMHC emission (8%) from paddy stubble fires and therefore not a reliable chemical tracer for fugitive LPG emission in a complex emission environment influenced by intensive paddy stubble burning. Isoprene was identified as a potential tracer for distinguishing paddy stubble and garbage burning in absence of isoprene emissions at night from biogenic sources. Alkenes and aromatics dominated the fire emissions while alkanes were found to be the major constituents of the fuel evaporative emissions. In the idling vehicular exhaust, higher emissions were observed due to presence of unburnt fuel. LPG and CNG vehicular exhaust comprised majorly of C2-C4 alkanes. The diesel vehicular exhaust emissions contained higher fraction of alkenes and aromatics but the petrol vehicular exhaust emissions were found to contain higher aromatic content than diesel. Ambient traffic emissions were found to be dominated by the petrol exhaust emissions due to the typically higher fraction of petrol fueled vehicles among the on road vehicular fleet in India.

The toxicity and health impacts of the emissions were assessed by using the BTEX fraction as proxy and petrol exhaust, paddy stubble fires and garbage fires were ranked higher in toxicity than

other emissions. Furthermore, the impact of the emissions in the atmospheric environment was assessed by comparing the OH reactivity and ozone formation potentials. The diesel exhaust emissions, paddy stubble fire and garbage fire emissions were identified as the most polluting emission sources. Although LPG and CNG vehicular exhausts were cleaner and non-toxic

5 emissions, however they comprised of large fraction of alkenes due to improper combustion of fuels. Thus they can impact local air quality and atmospheric chemistry and therefore use of improved VOC scrubbing technologies, cleaner fuels and reduced idling times of the vehicles should be promoted.

Finally, we presented the inter NMHC molar ratios for all the emission sources. Toluene/benzene

10 ratios were identified as a good tracer to distinguish the paddy stubble fire emissions in flaming (0.42) and smoldering stages (1.39), garbage burning emissions (0.21-0.32) and traffic emissions (3.54). On the other hand, i-butane/n-butane ratio was found to be similar (0.20-0.30) for many sources and therefore caution must be taken while using it in complex emission environments. i-pentane/n-pentane ratio can instead be used reliably for distinguishing biomass burning emissions

15 (0.09-0.70) from the traffic/fossil fuel emissions (1.55-8.77). The results of this study will aid identification of factor profiles in source apportionment models such as positive matrix factorization yielding more accurate quantitative data for mitigation of ambient air pollution.

Data availability. Data is available from the corresponding author upon request

Author contributions. V.S. and A.K. conceived and designed the study. A.K. carried out the sample collection, field work and performed TD-GC-FID measurements with help of M.S. and H.H. A.K. carried out preliminary analysis and wrote the first draft. V.S. revised the paper and

5   carried out advanced analyses and interpretation of the data and supervised all experimental aspects of the work. V.G. participated in the discussion of the analytical system and commented on the paper and B.B provided valuable inputs concerning the analytical system.

Competing interests. The authors have no competing interests to declare.

Acknowledgements. We acknowledge the IISER Mohali Atmospheric Chemistry facility for data

10   and the Ministry of Human Resource Development (MHRD), India for funding the facility. A.K., H.H. and M.S. acknowledge MHRD and IISER Mohali for PhD (SRF) and PhD (JRF) fellowships. We acknowledge EGU for waiver of the APC through the EGU 2019 OSPP award to A.K. We also acknowledge the help and support of the members of IISER Mohali Atmospheric Chemistry facility: Harshita Pawar, Pallavi, Abhishek Mishra, Abhishek Verma, Bharti Sohpaul and Tess

15   George for technical assistance during field sampling. This work was supported by funding received under the National Mission on Strategic knowledge for Climate Change (NMSKCC) MRDP Program of the Department of Science and Technology, India vide grant (SPLICE) DST/CCP/MRDP/100/2017(G).

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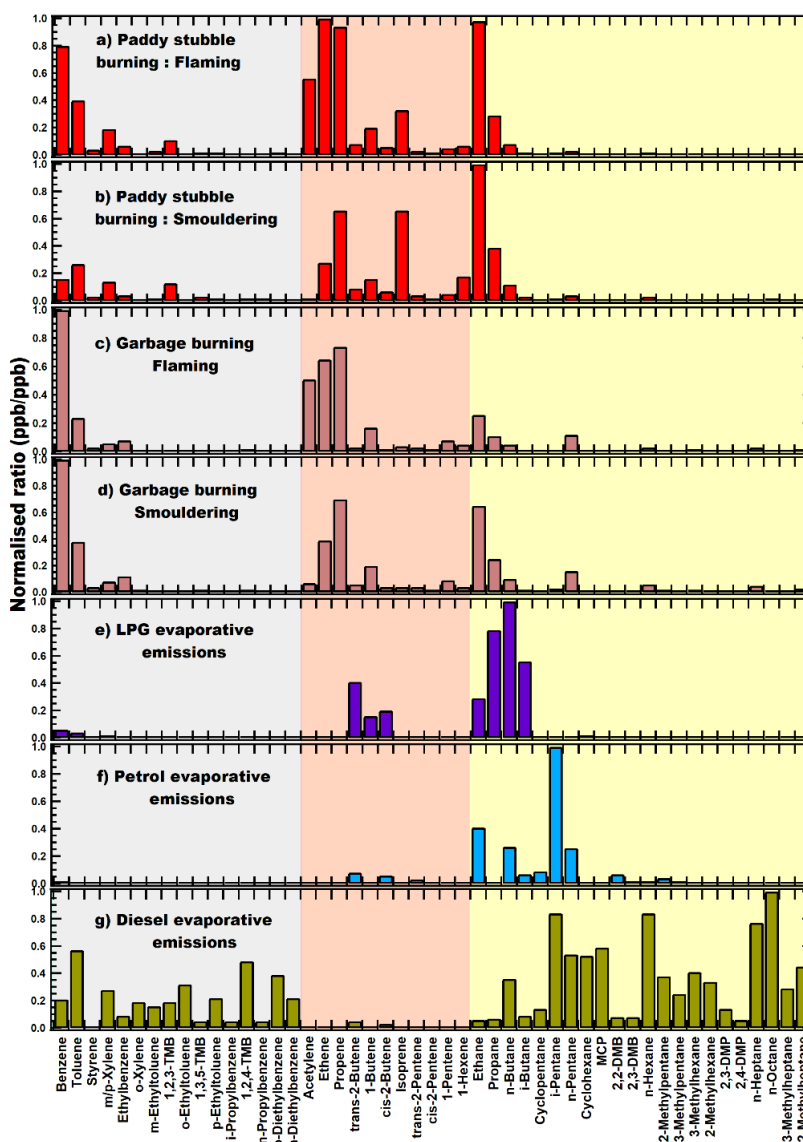

TMB: Trimethylbenzene; DMB: Dimethylbutane; DMP: Dimethylpentane; MCP: Methylcyclopentane

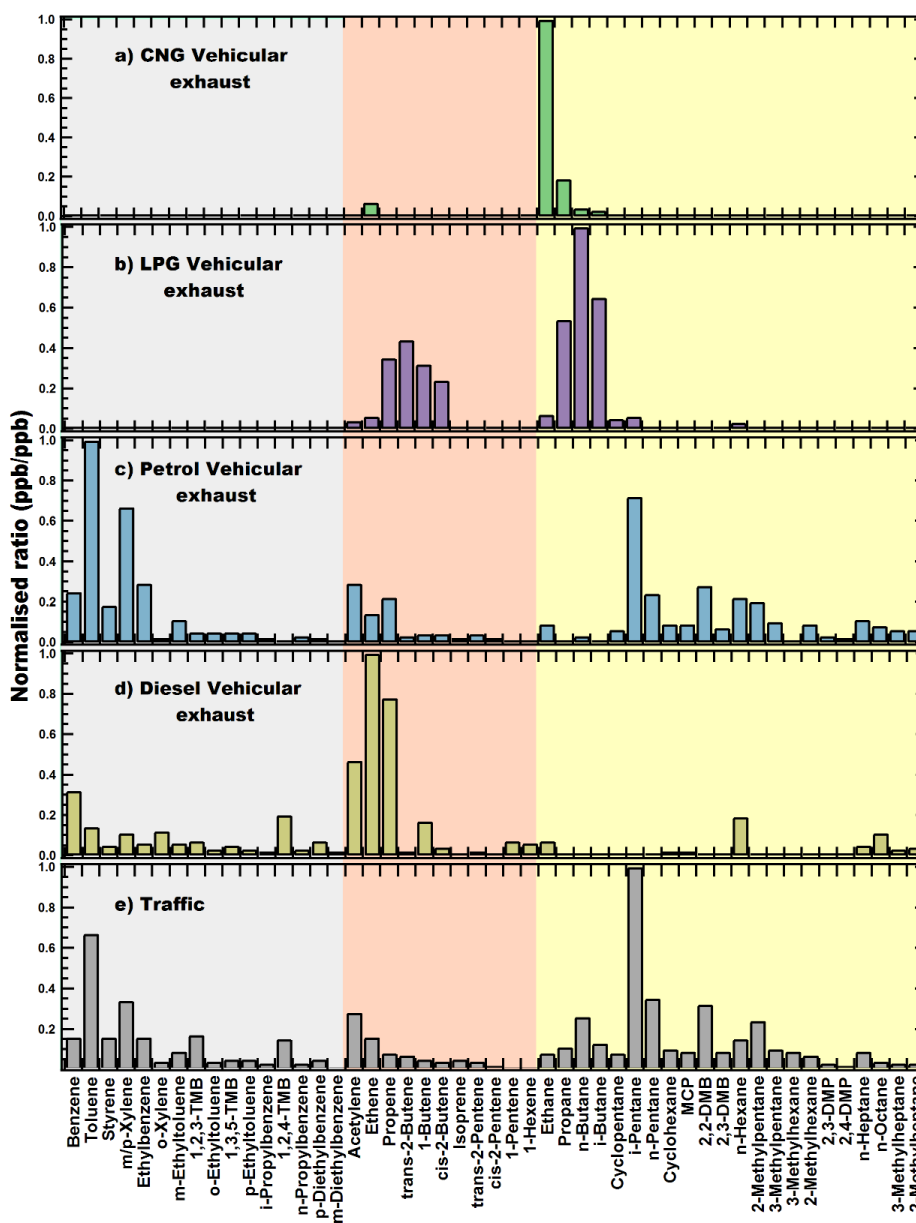
Figure 1: Normalized source profiles of **a)** Paddy stubble burning: Flaming; **b)** Paddy stubble burning: Smouldering; **c)** Garbage burning: Flaming; **d)** Garbage burning: Smouldering; **e)** LPG evaporative emissions; **f)** Petrol evaporative emissions; **g)** Diesel evaporative emissions, derived from the TD-GC-FID measurements.

TMB: Trimethylbenzene; DMB: Dimethylbutane; DMP: Dimethylpentane; MCP: Methylcyclopentane

Figure 2: Normalized source profiles of **a)** CNG vehicular exhaust; **b)** LPG vehicular exhaust; **c)**
Petrol vehicular exhaust; **d)** Diesel vehicular exhaust; **e)** Traffic, derived from the TD-GC-FID
measurements.

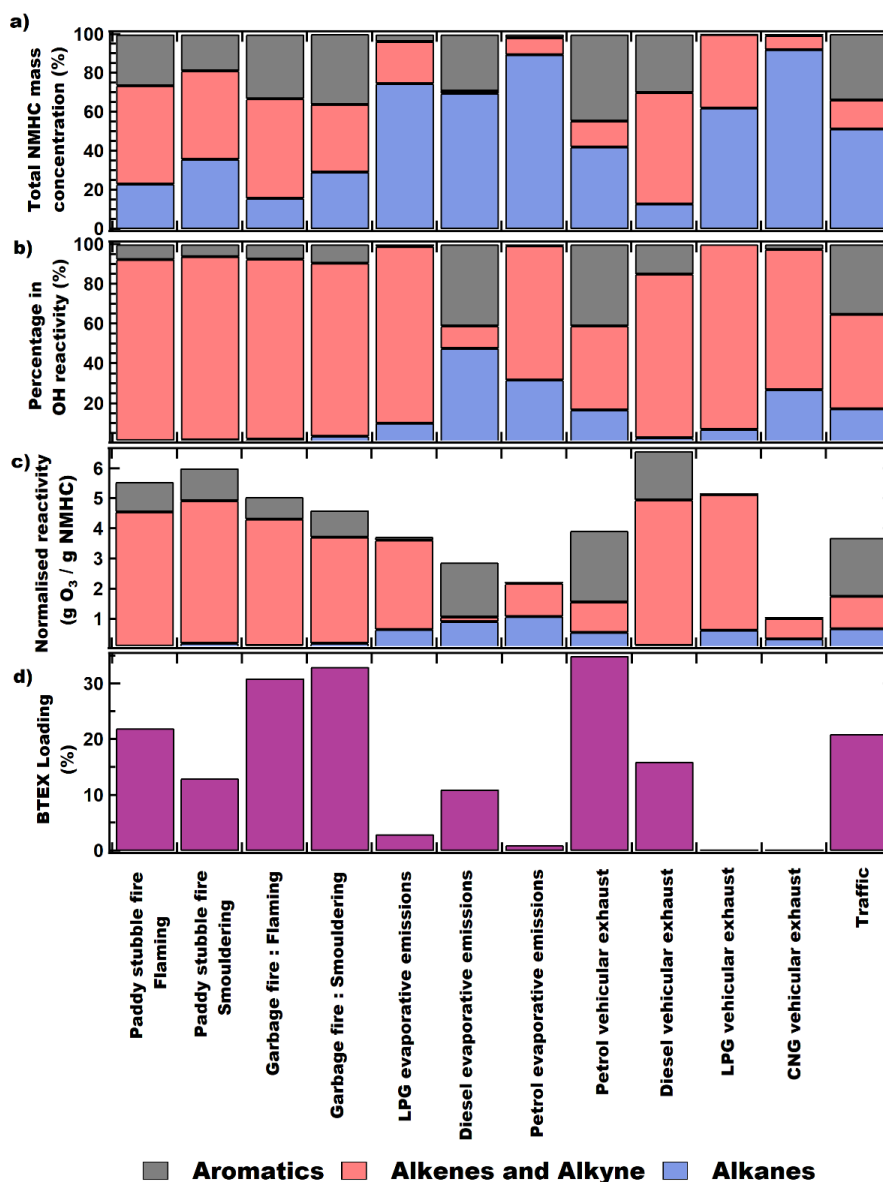



Figure 3: Comparison of contribution of chemical compositions in groups (aromatics, alkene and alkyne and alkanes) to **a)** NMHCs mass concentrations, **b)** OH reactivity (s^{-1}), and **c)** Normalised reactivity ($gO_3/gNMHC$) and **d)** BTEX loading (%) from various emission sources.

Table 1: Number of samples investigated per source for the measurements of NMHCs source profiles

Sources	Description	No. of samples
Paddy stubble burning (Flaming stage)	Agricultural field in Kurari, Mohali (30.605º N, 76.744º E) on 4 Nov 2017	3
Paddy stubble burning (Smouldering stage)	Agricultural field in Kurari, Mohali (30.605º N, 76.744º E) on 4 Nov 2017	3
Garbage burning (Flaming stage)	Waste sorting and disposing stations in Mohali and surrounding villages (30.642-30.699ºN, 76.713-76.729ºE) in February 2017	5
Garbage burning (Smouldering stage)	Waste sorting and disposing stations in Mohali and surrounding villages (30.642-30.699ºN, 76.713-76.729ºE) in February 2017	5
Traffic	Busy traffic junctions in Chandigarh and Mohali (30.691º N, 76.698º E; 30.678º N, 76.721º E and 30.717º N, 76.812º E) in March 2017	3
Petrol vehicular exhaust	Petrol LDV and 2 wheelers in idling stage in Chandigarh and Mohali (30.660-30.750ºN,76.700-76.840ºE) between Mar 2017- Oct 2018	23
Diesel vehicular exhaust	Diesel LDV 4 wheelers and 3 wheelers and HDV in idling stage in Chandigarh and Mohali (30.660-30.750ºN,76.700-76.840ºE) between Mar 2017- Oct 2018	33
LPG vehicular exhaust	LPG 3 wheelers in idling stage in Chandigarh and Mohali (30.660-30.750ºN,76.700-76.840ºE) between Mar 2017- Oct 2018	9
CNG vehicular exhaust	CNG 3 wheelers and LDV 4 wheelers in idling stage in Chandigarh and Mohali (30.660-30.750ºN,76.700-76.840ºE) between Mar 2017- Oct 2018	7

Table 2: Compound specific Precision errors (%), Limit of Detection (LOD) (in ppt) and Total measurement uncertainties (%).

Compounds	Precision (%)	LOD (ppt)	Uncertainty (%)	Compounds	Precision (%)	LOD (ppt)	Uncertainty (%)
Benzene	0.2	21	5.9	*o*-Xylene	0.2	24	5.8
Cyclohexane	0.2	2	5.8	*m/p*-Xylene	0.2	64	5.9
m-Diethylbenzene	0.1	5	12.3	Acetylene	0.1	3	5.8
p-Diethylbenzene	0.1	17	14.7	*n*-Butane	0.2	3	5.8
2,3-Dimethylpentane	0.1	1	5.8	1-Butene	0.2	8	5.8
2,4-Dimethylpentane	0.2	11	5.8	*cis*-2-Butene	0.3	18	6.0
Ethylbenzene	0.3	41	6.5	*trans*-2-Butene	0.2	3	6.3
m-Ethyltoluene	0.4	9	8.8	Cyclopentane	0.2	4	5.8
o-Ethyltoluene	0.3	9	8.9	2,2-Dimethylbutane	0.1	2	5.8
p-Ethyltoluene	0.3	9	9.3	2,3-Dimethylbutane	0.3	15	7.3
n-Heptane	0.3	15	5.9	Ethane	0.3	103	5.9
i-Propylbenzene	0.3	7	6.6	Ethene	0.5	3	5.8
Methylcyclopentane	0.3	13	5.8	1-Hexene	0.2	6	5.8
2-Methylheptane	0.2	85	5.8	*i*-Butane	0.2	4	7.3
3-Methylheptane	0.2	81	5.8	*i*-Pentane	0.3	4	5.8
2-Methylhexane	0.2	15	5.8	*n*-Hexane	0.2	2	5.8
3-Methylhexane	0.3	7	5.8	2-Methylpentane	0.2	3	5.8
n-Octane	0.2	103	5.8	3-Methylpentane	0.1	4	5.8
n-Propylbenzene	0.2	8	8.0	*n*-Pentane	0.1	2	5.8
Styrene	0.4	19	7.0	*cis*-2-Pentene	0.2	2	5.8
Toluene	0.3	87	6.2	*trans*-2-Pentene	0.2	4	5.8
1,2,3-Trimethylbenzene	0.2	104	11.3	Propane	0.2	20	5.8
1,2,4-Trimethylbenzene	0.2	56	9.0	Propene	0.3	47	5.8
1,3,5-Trimethylbenzene	0.2	14	9.0	Isoprene	0.2	4	6.0

Table 3: Characteristic **i**nter-NMHC molar ratios (ppb/ppb) for the whole air samples collected from Paddy stubble fires, Garbage fires, evaporative fuel emissions (Petrol, Diesel and LPG), Traffic and vehicular exhaust from different fuel types (Petrol, Diesel, LPG and CNG).

Emission ratio (ppb/ppb)	Paddy stubble burning (F)	Paddy stubble burning (S)	Garbage burning (F)	Garbage burning (S)	Evaporative emissions			Traffic	Vehicular exhaust emissions			
					Petrol	Diesel	LPG		Petrol	Diesel	LPG	CNG
Toluene/Benzene	0.42	1.39	0.21	0.32	0.45	2.28	0.60	3.54	3.41	0.37	0.97	6.99
i-Butane/n-Butane	0.28	0.26	0.25	0.21	0.25	0.24	0.56	0.48	0.30	0.36	0.65	0.84
i-Pentane/n-Pentane	0.70	0.53	0.09	0.16	3.87	1.55	8.77	2.83	2.99	1.34	8.68	3.27
Propane/n-Butane	4.94	4.41	2.85	3.22	0.01	0.24	1.05	0.58	0.32	3.68	0.71	6.66
Propene/Ethene	0.94	2.39	0.84	1.48	0	0.60	0.56	0.38	1.05	0.52	3.98	0.08
$trans$-2-Butene/cis-2-Butene	1.31	1.33	1.34	1.40	1.33	2.02	2.04	1.80	0.73	0.57	1.82	1.70
$trans$-2-Pentene/cis-2-Pentene	1.57	1.82	1.74	1.72	1.96	2.12	0	2.04	2.07	1.62	1.68	2.79
Styrene/1,3,5-TMB	1.98	1.36	2.22	2.54	0	0.12	0	3.73	4.34	1.02	3.27	1.88
1,2,3-TMB/1,2,4-TMB	10.15	8.20	0.81	0.43	0	0.39	0	1.78	9.22	0.34	0.25	0.15

TMB: Trimethylbenzene, F: Flaming, S: Smoldering