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## Overview of VOC emissions and chemistry from PTR-TOF-MS measurements during the SusKat-ABC campaign: high acetaldehyde, isoprene and isocyanic acid in wintertime air of the Kathmandu Valley

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#### Abstract

The Kathmandu Valley in Nepal suffers from severe wintertime air pollution. Volatile organic compounds (VOCs) are key constituents of air pollution, though their specific role in the Valley is poorly understood due to insufficient data. During the SusKat-

- ABC (Sustainable Atmosphere for the Kathmandu Valley-Atmospheric Brown Clouds) field campaign conducted in Nepal in the winter of 2012–2013, a comprehensive study was carried out to characterize the chemical composition of ambient Kathmandu air, including the determination of speciated VOCs by deploying a Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR-TOF-MS)–the first such deployment in
- <sup>10</sup> South Asia. 71 ion peaks (for which measured ambient concentrations exceeded the  $2\sigma$  detection limit) were detected in the PTR-TOF-MS mass scan data, highlighting the chemical complexity of ambient air in the Valley. Of the 71 species, 37 were found to have campaign average concentrations greater than 200 ppt and were identified based on their spectral characteristics, ambient diel profiles and correlation with specific emis-
- <sup>15</sup> sion tracers as a result of the high mass resolution ( $m/\Delta m > 4200$ ) and temporal resolution (1 min) of the PTR-TOF-MS. The highest average VOC mixing ratios during the measurement period were (in rank order): acetaldehyde (8.8 ppb), methanol (7.4 ppb), acetone (4.2 ppb), benzene (2.7 ppb), toluene (1.5 ppb), isoprene (1.1 ppb), acetonitrile (1.1 ppb), C8-aromatics (~ 1 ppb), furan (~ 0.5 ppb), and C9-aromatics (0.4 ppb).
- <sup>20</sup> Distinct diel profiles were observed for the nominal isobaric compounds isoprene (m/z = 69.070) and furan (m/z = 69.033). Comparison with wintertime measurements from several locations elsewhere in the world showed mixing ratios of acetaldehyde (~ 9 ppb), acetonitrile (~ 1 ppb) and isoprene (~ 1 ppb) to be among the highest reported till date. Two "new" ambient compounds namely, formamide (m/z = 46.029)<sup>25</sup> and acetamide (m/z = 60.051), which can photochemically produce isocyanic acid
- in the atmosphere, are reported in this study along with nitromethane (a tracer for diesel exhaust) which has only recently been detected in ambient studies. Two distinct periods were selected during the campaign for detailed analysis: the first was





associated with high wintertime emissions of biogenic isoprene, and the second with elevated levels of ambient acetonitrile, benzene and isocyanic acid from biomass burning activities. Emissions from biomass burning and biomass co-fired brick kilns were found to be the dominant sources for compounds such as propyne, propene, ben-

- <sup>5</sup> zene and propanenitrile which correlated strongly with acetonitrile ( $r^2 > 0.7$ ), a chemical tracer for biomass burning. The calculated total VOC OH reactivity was dominated by acetaldehyde (24.0%), isoprene (20.2%) and propene (18.7%), while oxygenated VOCs and isoprene collectively contributed to more than 68% of the total ozone production potential. Based on known SOA yields and measured ambi-
- ent concentrations in the Kathmandu Valley, the relative SOA production potential of VOCs were: benzene > naphthalene > toluene > xylenes > monoterpenes > trimethylbenzenes > styrene > isoprene. The first ambient measurements from any site in South Asia of compounds with significant health effects such as isocyanic acid, formamide, acetamide, naphthalene and nitromethane have been reported in this study. Our re-
- <sup>15</sup> sults suggest that mitigation of intense wintertime biomass burning activities, in particular point sources such biomass co-fired brick kilns, would be important to reduce the emission and formation of toxic VOCs (such as benzene and isocyanic acid) in the Kathmandu Valley and improve its air quality.

#### 1 Introduction

- <sup>20</sup> The Kathmandu Valley is a bowl-shaped basin at an altitude of ~ 1300 m that is surrounded by the Shivapuri, Phulchowki, Nagarjun and Chandragiri mountains which have an altitude range of 2000–2800 m above mean sea level and is prone to poor air quality and air pollution episodes (Panday et al., 2009). In particular during the winter mornings, due to the combination of suppressed mixing, katabatic wind flows and
- the topography of the basin, pollutants remain trapped under an inversion layer close to the surface of the Valley (Kitada et al., 2003; Regmi et al., 2003). Previous studies in similar Valley sites such as Santiago de Chile and Mexico City have investigated the





coupling of topography, meteorology, atmospheric dynamics, emissions and chemical processes in exacerbating air pollution episodes and suggested ways to mitigate the air pollution and improve air quality (Molina et al., 2007; de Foy et al., 2006; Schmitz, 2005; Rappenglück et al., 2005). In contrast, only few such studies have been carried 5 out within the Kathmandu Valley. Previous studies in the Kathmandu Valley have examined pollution in relation to carbon monoxide (CO), nitrogen oxides (NO<sub>v</sub>), sulfur dioxide (SO<sub>2</sub>), ozone (O<sub>3</sub>) (Panday and Prinn, 2009; Larssen et al., 1997; Yu et al., 2009; Ramana et al., 2004; Pudasainee et al., 2006) and particulate matter (Gurung and Bell, 2012; Sharma et al., 2012). An early study by Davidson et al. (1986) reported ambient average concentrations of 2 ppm CO during the winter season of 1982–1983. 10 Offline measurements of nitrogen dioxide  $(NO_2)$  and sulphur dioxide  $(SO_2)$  performed by Larssen et al. (1997) examined the average pollution exposure in different regions of the Valley and found that the brick kiln region south-east of the Valley and cities were most severely affected. With regard to quantification of volatile organic compounds in downtown Kathmandu and a rural site in Nagarkot, data pertaining to light C2-C6 com-15 pounds was obtained in a study in November 1998 using thirty-eight whole air samples analyzed offline with a GC-FID (Sharma et al., 2000). Subsequently Yu et al. (2008)

measured mixing ratios of seven monocyclic aromatic hydrocarbons, using long path differential optical absorption spectroscopy (DOAS) at a suburban site in Kathmandu

- <sup>20</sup> during January–February 2003. All these initial studies highlighted that traffic sources were major contributors to air pollution in the Kathmandu Valley (Yu et al., 2008). In the time since these studies, due to rapid urbanization and population growth over the last decade, the wintertime air quality has deteriorated severely. Yet very little information is currently available with regard to the emissions and chemistry of volatile organic com-
- pounds in the Kathmandu Valley. Except for a handful of species, most of which were measured only periodically using offline sampling methods, virtually no in-situ data is available from the region with regard to the concentration and speciation of several important volatile organic compounds.





Volatile organic compounds (VOCs), in particular the reactive ones, have atmospheric lifetimes ranging from few hours to few days (Atkinson, 2000) and exert a profound influence on regional air quality through their participation in chemical reactions leading to the formation of secondary pollutants such as tropospheric ozone and secondary organic aerosol (SOA). Both tropospheric ozone and secondary organic aerosol are important from the standpoint of air quality and climate due to their impact

- on health and the radiative forcing of the atmosphere (IPCC, 2013). Further, through reactions with the hydroxyl radicals (the detergent of the atmosphere Lelieveld et al., 2004), photodissociation reactions and radical recycling reactions, VOCs strongly in-
- <sup>10</sup> fluence ambient OH reactivity and the budget of  $HO_x$  (OH,  $HO_2$ ) radicals which control the removal rates of gaseous pollutants, including most greenhouse gases from the atmosphere. Inhalation of certain VOCs present in air also produces direct adverse health effects. For example benzene and nitromethane are reported to be human carcinogens by the World Health Organization (WHO, 2010) and isocyanic acid, which
- has only recently been quantified in ambient studies (Roberts et al., 2011) can cause cataracts, cardiovascular diseases and rheumatoid arthritis via protein carbamylation on exposure to concentrations as low as 1 ppb (Wang et al., 2007).

In order to address gaps in our scientific understanding of the air pollution in the Kathmandu Valley, a large scale scientific experiment called the Sustainable Atmosphere for

- the Kathmandu Valley-Atmospheric Brown Clouds (SusKat-ABC) campaign was carried out in the winter of 2012–2013 by an international team of scientists. An overview of the campaign objectives, measurement suite and sites will be presented in the overview paper (Rupakheti et al., 2015) while an overview of the meteorology and pollution transport processes will be presented in a second overview paper (Panday et al., 2015). We
- present here results derived from the in-situ measurements of speciated VOCs using a proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS), the first such deployment in South Asia. Another version of this type of instrument, which has lower mass resolution, namely a proton transfer reaction quadrupole mass spectrome-





ter (PTR-Q-MS) has been previously deployed in the North-West Indo-Gangetic Plain in Mohali, India (Sarkar et al., 2013; Sinha et al., 2014).

With a mass resolving power  $(m/\Delta m)$  of more than 4200, PTR-TOF-MS measurements enable identification of several compounds based on their exact monoisotopic

- <sup>5</sup> mass (molecular formula) and have fast time response (~ 1 min). These attributes were leveraged to quantify a suite of ambient VOCs at a suburban site (Bode; 27.689° N, 85.395° E, 1345 ma.m.s.l.) in the Kathmandu Valley during December 2012–January 2013. Oxygenated VOCs such as methanol, acetaldehyde, sum of acetone and propanal, aromatic VOCs such as benzene, toluene, sum of C8-aromatics and sum
- <sup>10</sup> of C9-aromatics, isoprene, furan and acetonitrile were quantified every minute and their diel emission profiles analyzed to constrain major sources. Careful analysis of the ambient mass spectra from 21–210 Th was undertaken to identify several "new" or rarely quantified VOCs based on their monoisotopic masses (and therefore molecular formula), spectral characteristics observed at a particular m/z in a 0.005 amu bin rela-
- tive to the ion peak, ambient diel profiles and correlation with specific emission tracer molecules such as acetonitrile (a tracer for biomass burning). By contrasting periods in the chemical dataset based on the dominance of biogenic emission sources and emissions from brick kilns co-fired with biomass, respectively, VOCs emitted from brick kilns and biomass burning sources were identified. The measured VOC concentrations
- in the Kathmandu Valley were compared with previous wintertime measurements from other urban/suburban sites and megacities. The diel profiles of rarely detected and measured VOCs such as nitromethane and isocyanic acid were correlated with tracer VOCs. The major VOC contributors to the total measured reactive carbon, the VOC OH reactivity, ozone production potential and secondary organic aerosol formation poten-
- tial were elucidated through detailed analyses. Finally, information pertaining to direct health impacts of some of the quantified VOCs detected in this complex chemical environment are discussed with conclusions and outlook for future VOC studies in the region.





### 2 Experimental

### 2.1 Site description and prevalent meteorology

The Kathmandu Valley is a bowl-shaped basin in the Himalayan foothills. The average altitude of the Valley is 1300 m above mean sea level (a.m.s.l.). It is encircled by a ring of mountains that range from 2000–2800 m a.m.s.l., with about five mountain passes approximately 1500–1550 m a.m.s.l. (Panday et al., 2009), that enable winds to blow across the Valley from west to east during the afternoon hours. VOC measurements during this study were performed in the winter season from 19 December 2012 till 30 January 2013 at Bode (27.689° N, 85.395° E; 1345 m a.m.s.l.), which is a suburban site located in the westerly outflow of Kathmandu city.

Figure 1 shows a zoomed view of the land use in the vicinity of the measurement site (Bode; red circle; image derived using Google Earth on 22 May 2015 at 14:55 LT) in relation to the surrounding cities – Kathmandu (~ 10 km to the west; brown circle), Patan (~ 12 km south-west of the site; blue circle) and Bhaktapur (~ 5 km south-east of

- <sup>15</sup> the site; pink circle), major point sources and forested areas. In 2011, the total population of Kathmandu, Patan and Bhaktapur cities were: 1 003 285 (population density: 20 289 km<sup>-2</sup>), 226 728 (population density: 14 966 km<sup>-2</sup>) and 83 658 (population density: 12 753 km<sup>-2</sup>), respectively according to Central Bureau of Statistics (2011). The region east of the site was usually downwind but it is important to note that several
- <sup>20</sup> brick kilns (white marker in Fig. 1; around 10 brick kilns) were located south-east of the site at about 1 km distance. Major industries (yellow triangles in Fig. 1) were concentrated primarily in the cities of Kathmandu (Balaju industrial area) and Patan (Patan industrial area), while Bhaktapur industrial area was located in the south-east direction within 2 km of the measurement site. About 20 small industries, mainly pharmaceuti-
- cals, plastic, tin, electronics and fabrics were located in this industrial area. Also few plastic, electronics, wood, aluminium and iron industries were located within 3 km from the Bode site in the south-east direction. The Tribhuvan international airport was located west of the site (~ 4 km from Bode).



The region north of the site has a small forested area (Nilbarahi Jungle in Fig. 1;  $\sim 0.5 \text{ km}^2$  area) and a reserve forest (Gokarna Reserve Forest in Fig. 1;  $\sim 1.8 \text{ km}^2$  area) at approximately 1.5 and 7 km from the measurement site, respectively. Other nearby forest areas were located adjacent to the international airport (Mrigasthali and

- <sup>5</sup> Bhandarkhal Jungle; 8–10 km from the site). The forests in the Kathmandu Valley consist of broad-leaved evergreen mixed forest of *Schima castanopsis* at the base (up to 1800 m a.m.s.l.), oak-laurel forest in the middle (1800 to 2400 m a.m.s.l.), and oak forest at the top, while the conifer tree species *Pinus roxiburghii* (Khote Salla) and *Pinus wallichianna* (Gobre Salla) are also found (Department of Plant Resources, Nepal, Nepa
- <sup>10</sup> 2015). Other major tree species are *Melia azedarach* (Bakaino), *Schima wallichii* (Chilaune), *Castanopsis indica* (Dhale Katus), *Piptanthus nepalensis* (Suga Phul), *Persia bombycina* (Kaulo), *Madhuca longifolia* (Mauwa), textitCeltis textitaustralis (Khari), *Quercus semecarpifolia* (Khasru), and *Cryptomeria japonica* (Dhupi salla) (Department of Plant Resources, Nepal, 2015).
- The wind flow pattern observed during our study was typical of wintertime meteorology in the Kathmandu Valley and similar to meteorological observations reported in previous studies carried out in the Kathmandu Valley during the winter season (Kitada et al., 2003; Panday et al., 2009; Regmi et al., 2003). Figure 2a presents a schematic of the wind flow pattern observed during the study and its interaction with surface emissions. The afternoon flow, as indicated by the local meteorological observations,
- was characterized by westerly winds with moderate speed which aided ventilation of daytime emissions (typical average speed at Bode:  $4 \text{ m s}^{-1}$ ). On the other hand, night-time and early morning periods were associated with weak easterlies (typical average speed:  $< 1 \text{ m s}^{-1}$ ). Thus, during afternoon hours pollutants emitted in the Kath-
- <sup>25</sup> mandu Valley moved towards the eastern mountain passes due to the strong westerlies whereas in the evening, the flow was mildly reversed and a part of the pollutants transported to the eastern mountain passes moved back to the Kathmandu Valley due to the development of downslope winds. At night, "pooling" of cold air from the mountain slopes caused the warmer surface air to rise resulting in upward transport of pollutants





under the nocturnal inversion (Panday and Prinn, 2009). After sunrise, the morning hours were characterized by convective mixing of the accumulated pollutants due the nocturnal inversion, with surface emissions.

- Figure 2b shows the box and whisker plots for the meteorological parameters meas sured at Bode from 16–30 January 2013 derived from the one minute temporal resolution data acquired using meteorological sensors (Campbell Scientific Loghborough, UK) installed on the rooftop ( $\sim 25 \,\mathrm{m}$  above ground and  $\sim 5 \,\mathrm{m}$  away from the instrument inlet). Daytime (08:00–17:00 LT) average ambient temperature for the measurement period was observed to be  $12.2 \pm 4.5$  °C. It is worth mentioning that most mornings were associated with dense fog (average ambient RH > 90% with visibility < 100 m) 10 whereas the afternoons were associated with high speed westerly winds (>  $4 \text{ m s}^{-1}$ ). Wind speeds from other wind sectors were generally lower (average wind speeds  $\sim 1 \text{ m s}^{-1}$ ). The early morning wind flow was normally from the south-east wind sector which comprised of several brick kilns and Bhaktapur city. Evening hours were also associated with dense fog and the relative humidity (RH) was generally greater than 15 90% throughout the night. Minimum RH levels (~ 35%) were observed during midday. The sunrise typically occurred between 07:00-08:00 and sunset timings were around
  - 17:00 Nepal Standard Time (NST), respectively.

### 2.2 VOC measurements using PTR-TOF-MS

- Volatile organic compounds (VOCs) over the mass range (21–210 amu) were measured using a commercial high sensitivity proton transfer reaction time of flight mass spectrometer (Model PTR-TOF-MS 8000; Ionicon Analytic GmbH, Innsbruck, Austria). This instrument has been described in detail by Jordan et al. (2009) and is a more recent development of the PTR technique (Lindinger et al., 1998) that enables higher mass resolution at not protected in details (2004).
- <sup>25</sup> mass resolution at ppt level detection limit (Ruuskanen et al., 2011; Müller et al., 2010; Park et al., 2013; Stockwell et al., 2015). Briefly, the instrument consists of a hollow cathode ion source which produces a pure flow of the H<sub>3</sub>O<sup>+</sup> reagent ions, a drift tube where analyte VOCs undergo ionization and an orthogonal acceleration





reflectron time of flight mass analyzer and multi-channel plate detector. The instrument was operated at a drift tube pressure of 2.2 mbar, drift tube temperature of 600 °C and drift tube voltage of 600 V, resulting in an operating *E/N* ratio of ~ 135 Td (1 Td =  $10^{-17}$  V cm<sup>-2</sup>; de Gouw and Warneke, 2007). The high mass resolution of the instrument (*m*/ $\Delta m$  > 4200 at *m*/*z* 21.022 and > 4800 at *m*/*z* 205.195) and detection limit of few tens of ppt permitted identification of several rarely measured or previously unmeasured compounds based on their monoisotopic masses.

The PTR-TOF-MS 8000 used in this work was installed in a room on the second floor of a building at the suburban measurement site at Bode, Kathmandu. Ambient air was sampled continuously from the rooftop (~ 20 m above ground) through a Teflon inlet line that was protected with a Teflon membrane particle filter to ensure that dust and

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debris did not enter the sampling inlet. The filters were changed on seven occasions during the 40 day long deployment from 19 December 2012 to 30 January 2013. The total inlet residence and sampling time was less than 25 s as determined by spiking the inlet with sesquiterpenes emitted from an orange peel.

Data acquisition of mass spectra was accomplished using the TofDaq software (version 1.89; Tofwerk AG, Switzerland). This software controls the timing of the pulser (used to pulse the ions produced in the drift tube and channel them into the time-offlight region) and stores the raw data as a series of mass spectra in HDF5 format along with relevant instrumental metadata. The raw mass spectral data was then analyzed us-

- ing the PTRMS-viewer software (version 3.1; Ionicon Analytic GmbH, Innsbruck, Austria) enabling peak search, peak fits and mass assignments. Mass axis calibration was accomplished using the following intrinsic ions:  $H_3^{18}O^+$  (monoisotopic mass 21.022) and  $H_3^{18}O^+$ . $H_2O$  (monoisotopic mass 39.033). In addition the transmission values of
- <sup>25</sup> benzene (m/z = 79.054), toluene (m/z = 93.070), xylenes (m/z = 107.086), trimethylbenzenes (m/z = 121.101), dichlorobenzene (m/z = 146.976) and trichlorobenzene (m/z = 180.937) were employed. Further analysis of the dataset was carried out using the IGOR Pro software (version 6.0; WaveMetrics, Inc.).





The instrument was calibrated twice (10 January 2013 and 15 January 2013) during the field deployment by dynamic dilution of VOCs using a 17-component VOC gas standard (Ionimed Analytik GmbH, Austria at ~ 1 ppm; stated accuracy better than 8 %). Calibration for these seventeen VOCs namely formaldehyde, methanol, acetonitrile, acetaldehyde, ethanol, acrolein, acetone, isoprene, methacrolein, 2-butanone, benzene, toluene, o-xylene, chlorobenzene,  $\alpha$ -pinene, 1, 2-dichlorobenzene and 1, 2, 4trichlorobenzene were carried out in the range of 2–10 ppb at various relative humidities (RH = 60, 75 and 90 %). In order to determine the instrumental background at all relevant m/z channels, VOC free zero air was produced by passing ambient air through an activated charcoal scrubber (Supelpure HC, Supelco, Bellemonte, USA) and a VOC scrubber catalyst maintained at 350 °C (GCU-s 0703, Ionimed Analytik GmbH, Innsbruck, Austria). Following the procedure of Stockwell et al. (2015), the measured ion signals were normalized to H<sub>3</sub>O<sup>+</sup> (m/z = 19) primary ions according to the following equation:

<sup>15</sup> ncps = 
$$\frac{/(RH^+) \times 10^6}{/(H_3O^+)} \times \frac{2}{P_{drift}} \times \frac{T_{drift}}{298.15}$$

Large changes in ambient humidity are known to affect the sensitivity of some VOCs (e.g. benzene, methanol). This occurs due to a change in the abundance and ratio of the primary reagent ions ( $H_3O^+$ ; m/z = 19) and the hydrated hydronium ions ( $H_3O^+$ . $H_2O$ ; m/z = 37) within the drift tube (de Gouw et al., 2003). It assumes importance when ambient RH has large variability (e.g. very dry < 20% RH to very humid > 80% RH) during the measurements (e.g. during airborne measurements) and when the ratio of m19/m37 in the drift tube is typically more than 10%. For the measurements reported in this study, the ratio of the hydrated hydronium ions ( $H_3O^+$ . $H_2O$ ; nominal m/z = 37) to the primary ions ( $H_3O^+$ ; nominal m/z = 19) was lower than 10%,

<sup>25</sup> for more than 92 % of the dataset and the ratio never exceeded 16 %. For the conditions during the campaign, our calibration experiments did not reveal significant humidity dependence for the VOC sensitivities (ncpsppb<sup>-1</sup>). Figure 3 shows the sensitivities



(1)



(ncps ppb<sup>-1</sup>) for acetonitrile (a biomass burning tracer), acetaldehyde (an oxygenated compound), isoprene (a biogenic tracer) and benzene (an aromatic compound) at different RH regimes (60, 75 and 90%) during the calibration experiments. In all cases an excellent linearity ( $r^2 = 0.99$ ) was observed. Hence the sensitivity (ncps ppb<sup>-1</sup>) derived at 90% RH was applied for converting the measured normalized counts per second

to ppb and no further humidity corrections were deemed necessary.

In order to derive the sensitivity for the sum of monoterpenes, which have a molecular ion peak at m/z = 137.132 and for which fragmentation results in ion signals at m/z 81.070 and m/z 137.132, the signal measured at m/z 137.132 was scaled by 2.63, as

- <sup>10</sup> calibrations at the instrumental settings employed in the study clearly showed that 38 % of the total molecular ion signal for monoterpene was detected at m/z = 137.132, consistent with fragmentation patterns reported previously by Tani et al. (2004) for similar reaction conditions in the drift tube.
- Variable background concentrations were observed for both formaldehyde and <sup>15</sup> methanol while sampling zero air during the calibration experiments. Hence for these two compounds and all the other compounds not present in the 17 component VOC gas standard but reported in this work, sensitivity factors were determined following the example of Stockwell et al. (2015), wherein calculated mass-dependent calibration factors based on linearly approximated transmission curve fits for oxygenated VOCs
- and hydrocarbons were employed. Figure S1a in the Supplement shows the linearly fitted mass-dependent transmission curve (black markers and dotted line) overlaid with the sensitivity factors of the calibrated compounds. Using linear approximations, mass-dependent calibration factors were determined separately for oxygenates (Fig. S1b) and hydrocarbons (Fig. S1c) in keeping with their different mass dependent behavior.
- For masses with heteroatoms other than oxygen, mass-dependent sensitivity factors were determined based on approximations used for the oxygenated compounds. For acetic acid, the sum of the signals at m/z 61.207 (parent ion peak) and m/z 43.018 (fragment of the parent ion), were used to derive an upper limit for its ambient concentration.



The limit of detection was defined to be 2  $\sigma$  of the measured normalized signal (ncps) while measuring VOC free zero air divided by the sensitivity expressed in ncps ppb<sup>-1</sup> (Sinha et al., 2014). The total uncertainty for calibrated compounds was calculated using the root mean square propagation of the accuracy error of the VOC standard, the mass flow controller's flow fluctuations during the calibration and the instrumental precision error (2  $\sigma$  while measuring 2 ppb of the compound). Using this approach, all calibrated VOCs had a total uncertainty of < 20% (e.g., acetaldehyde 9.9%, acetone 9.6%, isoprene 15.4%, benzene 9.4% and toluene 8.9%) whereas for the other compounds reported in this work that could not be calibrated, we estimate an over-all uncertainty of ~ 50% as also proposed by Stockwell et al. (2015) using a similar approach for quantification.

### 3 Results and discussion

# 3.1 Identification of VOCs present in ambient air using PTR-TOF-MS mass scans

- <sup>15</sup> The PTR-TOF-MS deployed in this study was operated over the range of 21–210 Th, with a mass resolution ( $m/\Delta m > 4200$  at m/z = 21.022 and > 4800 at m/z = 205.195) sufficient to identify several compounds based on their monoisotopic masses. A maximum of 71 ion peaks (m/z) were observed in the mass spectra during the measurement period for which the measured ambient concentrations exceeded the detection
- <sup>20</sup> limit. Among these 71 species, 37 compounds/species had an average concentration greater than or equal to 200 ppt during the study period. The molecular formula of compounds/species corresponding to these 37 ion peaks are listed in Table S1 in the Supplement. Additionally Table S1 also provides: (1) identity of plausible organic/fragment ions (e.g.  $NO_2^+$  due to C1–C5 alkyl nitrates), (2) sensitivity, (3) limit of detection, and (4) average ±1  $\sigma$  variability of ambient mixing ratios observed during the study period.





In order to minimize ambiguity arising due to multiple species or fragment ions contributing to ion peaks at a given m/z ratio, the following quality control measures were employed for attribution of mass identifications to the observed ion peaks: (1) Ion peaks for which the observed mass spectra had competing/major shoulder peaks in a mass

- bin width of 0.005 amu centred at the relevant monoisotopic ion peak were excluded from exclusive mass assignments (2) Next, the ambient time series of the observed ion peak assigned after step 1, was carefully examined and cases where the concentration profile was completely flat/showed no ambient variability were also excluded from mass assignments (3) Thirdly, the concentration profiles of the ion peaks ascribed to rarely
- reported or new compounds after step 1 and step 2, were compared to the ambient time series and diel profiles of more frequently/regularly quantified VOCs, such as acetonitrile, isoprene, benzene, toluene, acetone and acetaldehyde as their diel profiles would likely indicate the driving processes and emission sources of the compounds.

In cases, where the contributions of isotopologues were significant (e.g., acetic

- acid m/z = 61.027 and nitromethane m/z = 62.026), the signal at the concerned m/zwas duly corrected (Inomata et al., 2014). Out of these 37 ions which were identified with reasonable confidence, 8 contained nitrogen, 15 were oxygenated compounds, 13 were hydrocarbons and one contained sulfur. Two ion peaks (m/z = 51.044and m/z = 56.060) could not be identified based on the exact protonated monoiso-
- <sup>20</sup> topic *m*/*z* and for these, the closest contenders namely 1,3-butadiyne (*m*/*z* = 51.023) and propanenitrile (*m*/*z* = 56.050), were tentatively assigned. Two "new" compounds, which to the best of our knowledge have not been reported in any previous study, namely formamide (CH<sub>3</sub>NO; protonated *m*/*z* = 46.029) and acetamide (C<sub>2</sub>H<sub>5</sub>NO; protonated *m*/*z* = 60.051) were also detected. We discuss their diel variability and poten-
- tial sources in Sect. 3.5 along with some of the other rarely reported compounds in ambient air. Figure S2 in the Supplement shows illustrative mass spectra for isocyanic acid which demonstrates that it is the major contributor in the relevant mass bin.

To highlight the complexity of ambient chemical composition on specific periods/activity during the day, in Fig. 4 we show the hourly averaged mass scan data





for a selected day (15 January 2013; not influenced by any anomalous events) during morning (06:00-07:00 LT), afternoon (15:00-16:00 LT) and evening (18:00-19:00 LT). It can be seen that the maximum number of ion peaks were observed during evening hours (total 61 peaks) when primary emissions from wintertime biomass combustion and evening traffic dominated the ambient chemical composition. In contrast, fewer ion peaks were observed during morning (52) and afternoon hours (51), respectively. 18 compounds had a mixing ratio  $\geq$  1 ppb either in the morning, afternoon or in the evening. Distinct peaks were observed for the nominal isobars: isoprene (m/z = 69.070) and furan (m/z = 69.033), which are shown in the inset of Fig. 4. The occurrence of high concentrations of isoprene in wintertime was surprising and we 10 investigate its major source in Sect. 3.6. To the best of our knowledge, formamide (m/z = 46.029) and acetamide (m/z = 60.051) were identified for the first time in ambient air using the PTRMS technique and both of these compounds were present at average ambient concentrations greater than 200 ppt during the study period with clear daytime maxima (details are described in Sect. 3.5). 15

The total reactive carbon calculated as the sum of the average mixing ratios of all the 37 compounds reported in this study was 175.8 ppbC, of which fifteen compounds alone contributed 145.4 ppbC (83% of the total) and are listed in Table S2 in the Supplement. Propyne, acetaldehyde, benzene, acetic acid, acetone, propene and toluene collectively comprised more than 60% of the measured reactive carbon. Although the average O/C ratios for morning (06:00–07:00 LT), afternoon (15:00–16:00 LT) and evening (18:00–19:00 LT) were 0.57, 0.68 and 0.60, the O/C ratio for the entire period

- of deployment was found to be 0.33 which is within the O/C ratio of 0.3–0.4 observed for laboratory produced primary biomass burning organic aerosol (Aiken et al., 2008).
- <sup>25</sup> No significant change was noted for the N/C ratios on a diel basis which were always close to 0.08.

In Sects. 3.2 and 3.4, we examine the general trends and diel concentration profiles of the most abundant VOCs to gain more detailed insights into the emission sources and chemistry of VOCs in wintertime air of the Kathmandu Valley.



### 3.2 General trends in VOC concentrations during the SusKat-ABC campaign

Figure 5 shows the general trends in VOC mixing ratios (as 1 min temporal resolution data) during the period of study from 19 December 2012–30 January 2013. While the top panel represents the time series in mixing ratios of oxygenated VOCs namely
<sup>5</sup> methanol, acetaldehyde and the sum of acetone and propanal, the second and third panels show mixing ratios of isoprene, acetonitrile and furan, respectively. The bottom panel shows the mixing ratios of benzene, toluene, sum of C8-aromatics (xylenes and ethylbenzene), and sum of C9-aromatics (trimethylbenzenes and propylbenzenes). All these compounds collectively accounted for about 50% (total 85.4 ppbC) of the total
<sup>10</sup> reactive carbon and are amongst the most abundant VOCs known to be present in the air influenced by urban emissions.

It can be seen that the time series was characterized by two contrasting periods in terms of chemical emission signatures: Period 1 (shaded in pale yellow in Fig. 5; 19 December 2012–2 January 2013) and Period 2 (shaded in grey in Fig. 5; 4–18 Jan-

- <sup>15</sup> uary 2013). Period 1 was characterized by high mixing ratios of isoprene (> 3 ppb) during daytime and low acetonitrile mixing ratios relative to the remainder of the measurement period (generally < 2 ppb except for a plume on 28 December 2015 which was suspected to be due to garbage burning in the local vicinity), while Period 2 was marked by a decrease in the amplitude of daytime isoprene and a significant increase</p>
- in mixing ratios of acetonitrile (typically > 3 ppb) and benzene (typically > 10 ppb). The global budget of isoprene is dominated by emission from vegetation (500 Tg a<sup>-1</sup>; Guenther et al., 2006), in most cases as a function of photosynthetic active radiation (PAR) and temperature. Clearly, in the early part of this winter campaign, conditions were favourable for significant isoprene emissions from vegetation. It is worth mentioning
- that oak and *Melia azedarach* were present in the forested regions upwind of the site and are high isoprene emitters (Geron et al., 2001). As the ambient temperature and radiation decreased and early morning fog became frequent during the first half of January, biogenic emissions reduced in intensity (< 2 ppb). Leaf fall in deciduous trees by</p>





the end of December and more frequent leaf litter burning were likely important contributors to reduced isoprene and increased acetonitrile emission in the second half of the campaign. While the highest isoprene concentrations were driven by biogenic sources, biomass burning sources also emitted isoprene, a finding consistent with re-

- <sup>5</sup> ports from another South Asian site at Mohali, India (Sinha et al., 2014). The Federation of Nepalese Brick Industries (FNBI) provided information on operation of brick factories in the Valley. According to the FNBI, most brick kilns were closed for the season until the first week of January. Thereafter over the next 12–14 days (4–20 January 2013) all 110 plus brick kilns in the Valley were restarted and became fully operational. Thus,
- Period 2 represents the time when they were fired up again while the last part of the January represents a period when they were up and running and emissions from the brick kilns were no longer as high as during the firing up stage. The survey of 82 brick factories in the Valley showed that in addition to coal, a large amount of biomass such as sawmill dust, wood and other biomass are co-combusted in the brick kilns, con-
- tributing, on average, nearly 20% to the total energy used in firing bricks (Rupakheti et al., 2015). This emission activity appears to have been captured quite well in the time series profile of acetonitrile, for which the major emission source is biomass burning (Holzinger et al., 1999; Sarkar et al., 2013; Sinha et al., 2014). It was also interesting to note the similarities in the time series of furan (~ 1 ppb), another combustion tracer,
- with acetonitrile. Biomass burning and biofuel use contribute to half of the global budget of benzene (Henze et al., 2008; Andreae and Merlet, 2001; Sarkar et al., 2013) and it appears that brick kilns in Kathmandu being co-fired with biomass as fuel were a major source of benzene. We analyze the diel profiles for the two contrasting Periods and some of these aspects in detail in Sects. 3.4 and 3.6.
- <sup>25</sup> In the time series it can also be seen that 19 January 2013 was characterized by the lowest VOC concentrations because of an intense rain event during the previous night. For the oxygenated VOCs (OVOCs), high concentrations were typically observed in the early morning hours between 08:00–10:00 LT and surprisingly acetaldehyde, which is the most reactive VOC among the OVOCs, frequently reached



concentrations as high as 40 ppb. In contrast methanol and the sum of acetone and propanal were generally below 20 and 10 ppb, respectively. Acetaldehyde concentrations of about 30–40 ppb during several plume like episodes (e.g. 24 December 2012–26 December 2012; 11 January 2013–18 January 2013), were characterized by

- <sup>5</sup> co-synchronous peaks in isoprene until 28 December 2012 and peaks in the combustion tracers acetonitrile and furan from 4 January 2013 till 30 January 2013. Biomass burning sources and photo oxidation of precursor compounds co-emitted from the biomass burning appear to contribute significantly to the high concentrations of oxygenated VOCs. This points to the fact that the major sources of oxygenated VOCs
- <sup>10</sup> during wintertime in Kathmandu are different from what are generally considered to be the most important sources based on studies conducted in several other regions of the world, where photo oxidation and industrial sources dominate and has large implications for wintertime oxidation chemistry in the Valley, as these species play a key role in radical chemistry (Singh et al., 1995). For example, the observed ranking in oxy-
- <sup>15</sup> genated VOCs is different from the ranking observed during wintertime in megacities like Paris and London (methanol > acetaldehyde > acetone) (Dolgorouky et al., 2012; Langford et al., 2010). Furthermore the ranking observed for aromatic VOCs during this study (benzene > toluene > C8-aromatics > C9-aromatics) was in contrast to the ranking (toluene > benzene > C8-aromatics > C9-aromatics) observed in several urban
- sites such as Paris, London and Tokyo (Dolgorouky et al., 2012; Langford et al., 2010; Yoshino et al., 2012). This exemplifies that the nature and strength of emission sources for oxygenated and aromatic VOCs in the Kathmandu Valley differ from several urban areas in other parts of the world. Biomass burning sources and the manner in which regulation of benzene occurs, are likely the major causes for the observed differences.

#### 25 3.3 Comparison with wintertime VOC mixing ratios elsewhere

Figure 6 provides a comparison of average VOC mixing ratios measured in the Kathmandu Valley with VOC mixing ratios reported at other urban or urban influenced environments including megacities, during winter season. The





concentration ranking in the average VOC mixing ratios during our wintertime deployment was acetaldehyde (8.8 ppb) > methanol (7.4 ppb) > acetone + propanal (4.2 ppb) > benzene (2.7 ppb) > toluene (1.5 ppb) > isoprene (1.1 ppb) > acetonitrile (1.1 ppb) > C8-aromatics (~ 1 ppb) > furan (~ 0.5 ppb) > C9-aromatics (0.4 ppb). As

- <sup>5</sup> can be seen from Fig. 6, when compared to average wintertime mixing ratios reported from several sites elsewhere in the world, the mixing ratios of acetaldehyde (~ 9 ppb), acetonitrile (~ 1 ppb) and isoprene (~ 1 ppb) in the Kathmandu Valley are among the highest measured anywhere in the world. In contrast, Kathmandu had lower methanol mixing ratios than measured in London and Tokyo (Langford et al., 2010; Yoshino et al.,
- <sup>10</sup> 2012) during winter 2006 and 2007 (19.4 and 12.4 ppb, respectively) as well as lower acetone mixing ratios than what was measured in Barcelona (8 ppb) (Filella and Peńue-las, 2006). Apart from the contribution of biogenic sources during daytime, which was major, isoprene was also emitted by biomass combustion sources in the Kathmandu Valley. Borbon et al. (2001) have previously reported that due to traffic emissions alone,
- <sup>15</sup> isoprene mixing ratios can reach as high as 1.8 ppb in urban areas. The Bode site was located in the outflow of Kathmandu metropolitan city and Lalitpur sub-metropolitan city and therefore the evening time increase in isoprene can also be partially due to traffic emissions during the evening rush hour. The average benzene concentrations in Kathmandu (~ 3 ppb) were notably higher than those reported in other cities except for the
- city of Karachi (Barletta et al., 2002). The average toluene and sum of C8-aromatics mixing ratios, however were lower than in other urban areas like Tokyo (Yoshino et al., 2012), Barcelona (Filella and Peńuelas, 2006), Karachi (Barletta et al., 2002), Hong Kong (Guo et al., 2007) and Guangzhou (Liu et al., 2008), where industrial and traffic sources are much larger than in Kathmandu. Whereas benzene is emitted in almost
- equal proportion from fossil fuel and biomass combustion sources (Henze et al., 2008), fossil fuel combustion and industrial processes contribute a much larger fraction to the global budgets of toluene and sum of C8 and C9-aromatics. The observed trend in concentrations of some of the aromatic compounds measured using PTR-TOF-MS in this study differs from the trend reported in a previous study by Yu et al. (2008) who





employed the long path differential optical absorption spectroscopy (DOAS) technique to make measurements of monoaromatic VOCs in Kathmandu during winter 2003. In that study, xylene (a C8-aromatic compound) concentrations were reported to be the highest followed by toluene and benzene respectively. We think two reasons are re-

- <sup>5</sup> sponsible for differences from that study. The first reason is that the measurements by Yu et al. (2008) were carried out near a fairly busy road (Chabahil-Bouddha-Jorpati road) and a traffic intersection (Chabahil-Ringroad intersection) and consequently the aromatic VOC concentrations were primarily influenced by traffic sources. Secondly, VOC measurements using the long path DOAS technique are reported to have potentially large interferences due to ambient ozone and suspended particles (Yu et al.,
- 2008).

Despite much larger population and industries compared to Kathmandu, wintertime measurements in the megacities of London (Langford et al., 2010) and Paris (Dolgorouky et al., 2012) suggest that the air is much cleaner for many of the VOCs shown in

- Fig. 6. While the studies in other cities were conducted in different years, it is unlikely that inter annual variability would be the sole reason for lower concentrations in the megacities. As a city located in a developing country it is more likely that even with a population that is less than one tenth of these megacities, Kathmandu air has higher concentrations of carcinogens like benzene due to inadequate access to efficient and clean technologies and limited controls on emissions from existing industries.
- <sup>20</sup> clean technologies and limited controls on emissions from existing industries.

# 3.4 Diel profiles as a tool to constrain emission sources: VOCs emitted from biomass burning activities in the Kathmandu Valley

In order to contrast the role of diverse emission sources during Period 1 (19 December 2012–2 January 2013; shaded yellow in Fig. 5; marked by high daytime emissions of isoprene and only a couple of operational brick kilns) and Period 2 (4 January 2013–18 January 2013; shaded in grey in Fig. 5; coldest period of the year and marked by high acetonitrile emissions and almost all brick kilns in the Valley becoming operational), we analyzed the diel profiles of a number of VOCs. These are shown in





Fig. 7 as box and whisker plots for Period 1 (derived from total number of measurements > 20 500) and Period 2 (derived from total number of measurements > 21 500) for methanol, acetaldehyde, sum of acetone and propanal, isoprene, furan, isocyanic acid, acetonitrile, benzene and toluene. The time stamp is the start time of respective hourly data bin (e.g. 9 for data averaged between 9 and 10).

We note that the concentrations of acetonitrile (a chemical tracer for biomass combustion), methanol, benzene and isocyanic acid are significantly higher in Period 2 relative to Period 1, indicating that for all of them, the biomass co-fired brick kilns and burning of leaves and branches were major contributory sources. In contrast, isoprene and toluene concentrations were markedly higher during Period 1 as compared to Pe-

- and toluene concentrations were markedly higher during Period 1 as compared to Period 2. Acetaldehyde and furan did not differ much between Period 1 and Period 2. Except for isoprene, isocyanic acid and acetaldehyde, which did not show a marked bimodal profile (morning and evening maxima), all the other VOCs shown in Fig. 7 exhibited bimodal diel profiles to some degree, indicating the common influence of urban
- emission activities and biomass combustion sources for these compounds. Bimodal profiles for VOCs have previously been reported from several sites influenced by urban emissions (Staehelin et al., 1998; Stemmler et al., 2005), including our recent work in Mohali, India (Sinha et al., 2014), another site in South Asia that is somewhat closer to Kathmandu in terms of emission sources. Such bimodal profiles typically arise be-
- cause morning and evening emissions get mixed into a shallow boundary layer, while the afternoon emissions are diluted under a rapidly growing boundary layer due to the surface heat flux, giving rise to a daytime minima in the diel profile. This holds for VOCs which are not formed photochemically or emitted anomalously during the daytime in large measure. Thus, bimodal diel profiles were not observed for isoprene which
- is emitted by terrestrial vegetation during daytime and acetaldehyde and isocyanic acid which are known to be emitted from biomass fires and produced photochemically from precursor compounds (Millet et al., 2010; Roberts et al., 2014). In general, for both Period 1 and Period 2, the features of diel profiles in terms of rise and fall of concentrations are largely conserved for all the VOCs shown in Fig. 7. The diel profiles of all





VOCs also reveal at about 06:00 local time (LT), emission activities pertaining to cooking (use of biofuel and fossil fuel such as LPG), traffic and brick kilns pick up and the diel peaks for almost all VOCs occur at around 08:00–09:00 LT.

In addition to the typical boundary layer dynamics and emissions driving concentration profiles, the mountain meteorology appears to play a key role in the concentration peaks observed after sunrise around 08:00–09:00 LT. If one examines the diel pattern for wind speed, wind direction, temperature and solar radiation data (available for part of the study and shown in Fig. 2 b), it is clear that the diel meteorological conditions (e.g. surface wind flow, direction, temperature, RH) were very consistent even

- <sup>10</sup> on different days as there is a very narrow spread in the values for each hour and the average and median always converged. The wind speeds were typically lower than  $1 \text{ m s}^{-1}$  for almost all hours of the day except between 10:00–16:00 LT, when westerly winds from the mountain passes lying west of the site swept across the Valley attaining wind speeds of upto 3–4 m s<sup>-1</sup>, causing rapid venting and dilution. The wind direction
- <sup>15</sup> was very consistent on daily timescales. During the evening and at night, the horizontal wind flow was mainly from the south-east direction, which changed to a westerly flow during the day. Down-slope Mountain winds during nighttime result in pooling of cleaner cold air. Then shortly after sunrise, convective mixing of surface air with residual air commences the growth of the well mixed daytime boundary layer (Panday and Prinn, 2009).

The highest mixing ratios for acetaldehyde (average value of ~ 25 ppb for both Period 1 and Period 2) and acetone (average value of ~ 7 ppb for both Period 1 and Period 2) and indeed for most of the other VOCs were observed during morning hours about one hour after sunrise (09:00–10:00 LT). The breaking of the nocturnal bound-

ary layer and entrainment of air masses rich in accumulated oxygenated VOCs, which were displaced by cold air from the mountain slopes after midnight contribute towards the peaks observed in all VOCs between 09:00–10:00 LT. In mountain basins such as the Kathmandu Valley, at nighttime, katabatic winds are generated due to radiative cooling of mountains that lead to pooling of cold air to the Valley bottom (Fig. 2a). Due





to this katabatic flow, less cold and less dense air parcels in the Valley bottom containing the entire Valley's surface emissions rise upward during nighttime, while relatively clean cold air parcels flow underneath. After sunrise, downward mixing of the uplifted accumulated VOCs occurs with new surface emissions, as a growing mixed layer en-

- trains the elevated layers of the polluted air. Therefore during morning hours, mixing of oxygenated VOCs and their precursors that had accumulated during nighttime and a kick start to their photochemical production after sunrise, contributes to sharp peaks (e.g. for acetaldehyde and acetone). It should also be noted that the majority of the population in Kathmandu Valley cook their major meals in the morning and evening
   hours using fuel such as liquefied petroleum gas (LPG), kerosene and firewood (Pan
  - day et al., 2009).

Contributions from biogenic sources and oxidation of alkenes to acetaldehyde are also important. Reaction of oxygenated VOCs like ethanol and methyl ethyl ketone (MEK) with hydroxyl (OH) radicals and the reaction of tropospheric ozone ( $O_3$ ) with

- <sup>15</sup> alkenes can significantly contribute to photochemical formation of acetaldehyde (Sommariva et al., 2011; Grosjean et al., 1994). After the morning peak (09:00–10:00 LT), a sharp decrease was observed in the average acetaldehyde mixing ratios (from ~ 25 to ~ 8 ppb during 10:00–13:00 LT) relative to methanol and acetone, which is not surprising considering its much higher OH reactivity.
- The highest isoprene concentrations were observed during daytime for both Period 1 and Period 2 but the average concentrations were much higher during Period 1 when ambient temperature and solar radiation were comparatively higher and deciduous trees had not shed much of their leaves. This clearly points to daytime biogenic emission sources of isoprene in the Kathmandu Valley. In Sect. 3.6 we investigate the
- spatial and temporal location of the biogenic sources. We note that while the isoprene emission profile was dominated by biogenic sources, biomass burning (Christian et al., 2003; Andreae and Merlet, 2001; Warneke et al., 2011) and traffic (Borbon et al., 2001) also contributed to the ambient isoprene as can be seen from the nighttime peaks and discussed in previous sections. Thus, the contribution of both biogenic and an-





thropogenic sources resulted in high isoprene even in winter in the Kathmandu Valley which is different from what has been observed at high latitude sites in winter (Seco et al., 2011).

Apart from the biomass burning practices typical of developing regions of the world,
the brick kilns in the Kathmandu Valley do not only burn coal, but also burn large quantities of wood and crop residues, ca. 90 t per month per brick factory (Stone et al., 2010; Rupakheti et al., 2015), which can emit acetonitrile and benzene (Sarkar et al., 2013). Both acetonitrile and benzene levels were much higher during nighttime and morning hours in Period 2 as compared to Period 1 due to more intense biomass
burning in Period 2. During 08:00–09:00 LT (when highest ambient acetonitrile and benzene were observed) average mixing ratios were approximately 1 and 2 ppb higher for acetonitrile and benzene, respectively during Period 2 relative to Period 1.

Unlike acetonitrile and benzene, toluene concentrations were higher during Period 1 in comparison to Period 2. Despite the dilution effect of cold air descending from

- the mountain slopes, benzene concentrations increased during the night in Period 2, whereas toluene concentrations did not show any increase during the night in both Period 1 and Period 2, suggesting that biofuel and biomass burning sources (including the brick kilns co-fired with biomass) and not traffic were the driving factors responsible for nighttime increase in benzene during Period 2. The emission ratios of
- <sup>20</sup> benzene/toluene for key emission periods of the day are discussed further in Sect. 3.6 to constrain source signatures. The use of large number of diesel generators as an alternative power source in the Kathmandu Valley which suffers from scheduled daily power outages in some quarter of the city, could also have significant contributions to the observed high mixing ratios for aromatic VOCs.
- To our knowledge, this paper reports the first measurements of isocyanic acid from any site in South Asia. Isocyanic acid has only recently been measured in ambient air using novel mass spectrometric methods (Roberts et al., 2011), and much remains to be understood regarding its sources and sinks in different environments. The high isocyanic acid concentrations observed during the daytime suggest a strong photo-





chemical source from hydroxyl radical initiated oxidation of alkyl amines and amides with hydroxyl radicals (Roberts et al., 2011, 2014; Zhao et al., 2014). Isocyanic acid has also been detected in diesel exhaust (Wentzell et al., 2013), tobacco smoke and wild fires and in emissions from low temperature combustion of coal (Nelson et al.,

- 1996). From the diel profile, it is clear that around evening time there are primary emissions too but overall the secondary source dominates the ambient concentrations of isocyanic acid in this environment. Currently, global models of isocyanic acid (Young et al., 2012) do not incorporate a photochemical source. Our in-situ field data from the Kathmandu Valley suggests that inclusions of isocyanic acid's photochemical sources
- are necessary for deriving better estimates of the global isocyanic acid budget, as these 10 are likely to be significant over South Asia where biomass burning and agricultural activities can emit alkyl amines. Serious health impairments can occur upon exposure to isocyanic acid at concentrations greater than 1 ppb, which occurred during our study for several hours during Period 2. These health impacts have been previously mentioned in Roberts et al. (2011) and are also discussed in Sect. 3.9. 15

#### Diel profiles of rarely measured VOCs and correlation with emission tracer 3.5 VOC compounds for constraining their sources

Figure 8a–c shows the diel profiles of propyne (m/z = 41.039), propene (m/z = 43.055) and propanenitrile (m/z = 56.060) alongside acetonitrile (an excellent tracer for biomass combustion), respectively. These diel profiles correspond to data for the entire 20 measurement period. Strong correlation ( $r^2 \ge 0.7$  for the hourly averages) with acetonitrile clearly indicates that during our wintertime study in the Kathmandu Valley, all these compounds were primarily emitted from biomass burning. This inference is consistent with previous studies (Hao et al., 1996; Akagi et al., 2011; Andreae and Merlet, 2001) that reported propyne and propene in plumes sampled from biomass burning. Average 25 concentrations as high as 7.7 ppb propyne (maximum  $\sim$  46 ppb) and 4 ppb propene







trations of > 100 ppb were measured using the PTR-MS technique (Karl et al., 2003). These were attributed to industrial sources related to oil refining. Both propene and propyne participate in important chemical reactions in the troposphere. While propene is a source of OH radicals when it undergoes ozonolysis, propyne has been reported to produce methylglyoxal, formic acid and acetic acid in multistep reactions (Lockhart

- et al., 2013; Warneck and Williams, 2012). Propanenitrile has been previously detected in biomass smoke during laboratory studies (Akagi et al., 2011, 2013; Yokelson et al., 2013; Karl et al., 2003, 2007). Average propanenitrile mixing ratios observed during the measurement period were ~ 0.21 ppb. Propanenitrile reacts very slowly with hydroxyl radicals in the atmosphere ( $k_{OH}$  is of the order of 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) but the ox-
- idation of propanenitrile with OH radicals can produce long-lived nitrogen compounds in the troposphere and hence could contribute to the reactive nitrogen budget.

Figure 8d-f shows the diel profiles for nitromethane, dimethyl sulfide (DMS) and styrene alongside methanol, acetaldehyde and acetonitrile. Nitromethane (measured

- at m/z ratio 62.026) concentrations correlated strongly with the hourly average concentrations of methanol ( $r^2 = 0.81$ ). Nitromethane is known to be present in diesel exhaust (Inomata et al., 2013, 2014; Sekimoto et al., 2013) and biomass burning plumes (Akagi et al., 2013). The maximum nitromethane mixing ratios observed in the Kathmandu Valley were ~ 1.2 ppb which falls within the range of ambient nitromethane mix-
- ing ratios (1–9 ppb) reported previously in urban environments (Grosjean et al., 1998; Yassaa et al., 2001; Inomata et al., 2014). In the Kathmandu Valley, a large number of diesel power generators are used to supplement the main power supply. Ambient nitromethane observed in the Kathmandu Valley is therefore also likely from a combination of biomass burning sources and diesel exhaust emissions. The correlation with
- <sup>25</sup> methanol also suggests that diesel exhaust may be a contributory source for methanol. The major sink of nitromethane in the atmosphere is its photodissociation (photodissociation lifetime of ~ 10 h), which produces methyl radicals and NO<sub>2</sub> (Taylor et al., 1980). Therefore nitromethane can act as a NO<sub>x</sub> source in the atmosphere and could contribute to surface ozone production.





Dimethyl sulfide measured (at m/z ratio 63.026) in the Kathmandu Valley showed good correlation with the diel profile of acetaldehyde (correlation of hourly averages:  $r^2 = 0.8$ ). Average concentrations in the morning (09:00–10:00 LT) reached 0.4 ppb. Although marine phytoplankton emissions are known to be the major source of DMS in the atmosphere (Andreae and Raemdonck, 1983; Sinha et al., 2007), ambient mixing ratios up to 160 ppt have been recently reported in the Amazon rainforest, which were attributed to biogenic soil emissions (Jardine et al., 2015). Certain lichens, mosses, grasses and plant leaves can emit acetaldehyde (Kesselmeier et al., 1997; Kesselmeier and Staudt, 1999). Therefore the possibility of such vegetation on the mountain slopes

and the soil acting as sources of DMS and acetaldehyde, respectively, is plausible. Inefficient combustion of sulfur rich biofuel/biomass are also potential sources of DMS (Jardine et al., 2015).

Figure 8g and h shows the diel profiles of formamide and acetamide alongside isoprene while Fig. 8i shows the diel profile of naphthalene and benzene. During the <sup>15</sup> measurement period, daytime maximum average values of ~ 1 and ~ 0.5 ppb were observed for formamide and acetamide, respectively. Although formamide and acetamide correlate strongly with isoprene (hourly average  $r^2 \ge 0.8$ ), to our knowledge, biogenic sources of formamide and acetamide have not been reported previously. On the other hand short chain amides such as formamide and acetamide can be produced as a re-

- <sup>20</sup> sult of photochemical oxidation of alkyl amines with hydroxyl radicals and nitrogen oxides  $(NO_x)$  (Roberts et al., 2014). The presence of formamide in ambient air at concentrations as high as 1 ppb is consistent with the photochemical source of isocyanic acid discussed in the previous section. Also it is reported that both formamide and acetamide could be emitted from tobacco smoke and hence likely from pyrolsis of
- <sup>25</sup> biomass (Ge et al., 2011). The good correlation of formamide and acetamide with isoprene's diel concentration profile suggests that the photochemical source arising from oxidation of amines dominates over any primary emission sources of amides.

The ion peak detected at m/z ratio of 129.070 in the PTR-TOF-MS spectra was attributed to naphthalene. Naphthalene is the most volatile and abundant polycyclic





aromatic hydrocarbon (PAH) present in the atmosphere. Previously Martinez et al. (2004) have reported vehicle exhaust and residential heating in the urban environments as major sources of naphthalene. The similarity in diel profiles of naphthalene and benzene and their strong correlation with each other (hourly average  $r^2 = 0.79$ ),

- <sup>5</sup> suggests that biomass burning and traffic sources dominated emissions of naphthalene in the Kathmandu Valley. Average morning (08:00–10:00 LT) ambient concentrations of ~ 0.6 ppb naphthalene observed during this study were much higher than the maximum concentrations of ~ 0.35 ppb reported by Jordan et al. (2009) in ambient air previously at Innsbruck, which is one more indicator of the profound influence on at <sup>10</sup> mospheric composition exerted by biomass burning sources in the Kathmandu Valley
- during wintertime.

# 3.6 A detailed investigation of benzene from biomass co-fired brick kilns and isoprene from vegetation

The observed benzene to toluene ratios for the prime emission hours in the morning (06:00–08:00 LT) and in the evening (17:00–19:00 LT) were 1.08 and 0.44 for Period 1 (19 December 2012–2 January 2013) and 2.35 and 0.70 for Period 2 (4 January 2013–18 January 2013) respectively. The evening hour benzene to toluene ratio for both Period 1 and Period 2 were comparable to the ratio for vehicle exhaust emissions (0.41–0.83) reported in other cities (Langford et al., 2009). The morning period benzene to toluene ratio (06:00–08:00 LT) were somewhat high in Period 1 for traffic sources but in Period 2 considerably higher than values reported for traffic sources which suggests strong contribution from sources other than traffic to the ambient benzene levels. Stockwell et al. (2015) have reported benzene/toluene ratios greater than 1 from a large number of diverse biomass burning sources (e.g. crop residue, garbage fires), and the

observed emission ratios in the morning clearly indicate substantial biomass/biofuel emissions sources. As mentioned earlier, in Period 2 several biomass co-fired brick kilns were operational within a distance of 1 km from the site. Brick kilns in the Kathmandu Valley burn coal, wood, crop residues, and municipal solid waste (Stone et al.,



2010) which can produce large amount of aromatic compounds (Tsai et al., 2003; Sarkar et al., 2013). Therefore higher morning hour benzene to toluene ratios in Period 2 likely had strong contribution from the biomass co-fired brick kilns along with other typical biomass burning, domestic heating and cooking activities. While influence
of the morning traffic emissions at the site was still minimal, the evening hour peaks at the site were dominated mainly by vehicular emissions and diesel exhaust advected

from the cities. Along with benzene and acetonitrile, VOCs s

Along with benzene and acetonitrile, VOCs such as isocyanic acid, formamide, acetamide, nitromethane and naphthalene were present at higher concentrations during

- Period 2, which indicates biomass co-fired brick kiln emissions are also a potent source for these compounds in the Kathmandu Valley. In order to highlight how dominant a role this source can have on the ambient air quality, in Fig. 9 we show a 24 h period on 18–19 January 2013 containing high temporal resolution data (1 min) of benzene and acetonitrile. The red markers represent ambient acetonitrile mixing ratios while
- <sup>15</sup> the black markers represent ambient benzene mixing ratios. Peak concentrations of ~ 6 ppb acetonitrile and ~ 12 ppb benzene were observed during early morning hours (05:00–08:00 LT). The correlation of benzene with acetonitrile for the data as shown in the inset of Fig. 9 was excellent ( $r^2 = 0.97$ ). This suggests that equipping the existing brick kilns with cleaner brick kiln technology and scrubbers in the Kathmandu Valley would certainly help to lower concentrations of carcinogenic compounds like benzene
- and a suite of co-emitted VOCs, which also fuel formation of secondary organic aerosol in winter aggravating fog episodes.

Figure 10 shows a polar annulus plot of the hourly mean isoprene mixing ratio during the period 16–30 January 2013 (unfortunately, meteorological data for other pe-<sup>25</sup> riods of the study are unavailable). The polar annulus plot is a method of visualizing the temporal aspects of a specie's concentration with respect to wind direction. In the polar annulus plots, measured concentrations are averaged in separate time and wind direction bins and then further interpolation using Kriging technique are applied for conversion to polar coordinates (Ropkins and Carslaw, 2012). Such plots reveal im-





portant spatio-temporal information regarding emission sources. In Fig. 10 it can be seen that isoprene had highest ambient mixing ratios ( $\sim$  1 ppb isoprene) during the daytime (07:00–14:00 LT) which is an indication of biogenic sources. Significant isoprene concentrations ( $\sim$  0.5 ppb) could also be observed during evening and nighttime

- <sup>5</sup> which are likely from biomass combustion and traffic emission sources. Furan contributed a maximum of only ~ 40% (during nighttime) to the sum of ambient isoprene and furan. This is a very important finding as previous studies using proton transfer reaction mass spectrometers equipped with quadrupole mass analyzers, which cannot distinguish between furan and isoprene peaks due to their lower mass resolution and
- <sup>10</sup> detect the two compounds collectively at m/z = 69, tend to attribute the evening and nighttime concentrations to furan and not isoprene. Using a novel VOC-OHM chemical kinetics reactor (Kumar and Sinha, 2014), which constrained the rate coefficient of the isobaric contributor at m/z = 69, it has been demonstrated at another South Asian site in the north-west Indo Gangetic Plain (Mohali), that isoprene is the major contributor to
- m/z = 69. Thus it appears that isoprene has significant contributions from both vegetation and biomass/biofuel burning sources in South Asia, which has large implications for the atmospheric oxidation in this part of the world, as discussed also in Sinha et al. (2014). While several previous studies have reported significant contributions from anthropogenic sources to isoprene in urban areas elsewhere, especially in winter (Borbon
- et al., 2001; Barletta et al., 2005; Hellèn et al., 2012), the in-situ measurements from Mohali and Kathmandu suggest that the magnitude of the isoprene source from anthropogenic sources may be quite important regionally in South Asia.

High values of isoprene were generally observed from the west and northern sector (N.N.E where Nilbarahi Jungle and Gokarna Reserve Forest are located) and at <sup>25</sup> appreciable wind speeds (> 3 m s<sup>-1</sup>). The advection of air across the Valley in the afternoon as they flow through the mountain passes from west to east due to the high speed westerly winds has been previously described by Panday and Prinn (2009). The forest areas on the mountain slopes appear to contribute to the high ambient isoprene concentrations measured during the afternoon hours. The average daytime (08:00–





17:00 LT) isoprene concentrations observed during SusKat-ABC campaign (1.35 ppb) are comparable to the concentrations measured in south-east Asian tropical rainforest sites (Bryan et al., 2012; Jones et al., 2011). As mentioned in the site description section, the forested areas contained tree species like oak and *Melia azedarach*which have very high isoprene emission potentials (upto 350 µgg<sup>-1</sup> dry leaf h<sup>-1</sup> and 4.7 µgg<sup>-1</sup> dry leaf h<sup>-1</sup> respectively (Simon et al., 2005; Padhy and Varshney, 2005). The mixing of isoprene rich air with nitrogen oxides and anthropogenic emissions likely plays a profound role on the regional ozone formation potential and oxidizing capacity. In the Sect. 3.7 we examine the importance of VOCs measured during this study in terms of their OH reactivity contributions and ozone formation potential.

### 3.7 OH reactivity and ozone production potential of VOCs

The hydroxyl radical reactivity of an air mass reflects the total reactive pollutant loading of the air mass and can be used to infer its ozone formation potential (Sinha et al., 2012). While direct total OH reactivity measurements were not performed during the SusKat-ABC campaign, it is still instructive to examine the diel profile of the OH reactivity due to the suite of measured VOCs and assess the relative contributions of individual VOCs. For this analysis, we considered thirty three out of the thirty seven species that were observed at average ambient concentrations greater than 200 ppt, for which the rate coefficients with the hydroxyl radical are known. Thus, out of the thirty

seven species, four namely, the nitronium ion (m/z = 45.990), isocyanic acid, and assorted hydrocarbons detected at m/z ratios of 83.085 and 97.102, respectively, were excluded from this analysis.

The total VOC OH Reactivity was calculated as follows (Sinha et al., 2012):

Total VOC OH reactivity =  $\sum k_{VOC_i+OH}[VOC_i]$ 

15

<sup>25</sup> where  $k_{\text{VOC}_i+\text{OH}}$  is the first order rate coefficient for the reaction of VOC<sub>i</sub> with OH radicals and [VOC<sub>i</sub>] is the measured concentration of VOC<sub>i</sub>. The rate coefficients were



(2)

taken from Atkinson et al. (2006), and from the NIST chemical kinetics database (kinetics.nist.gov/kinetics) and Barnes et al. (2010) when they were unavailable in Atkinson et al. (2006).

Figure 11 shows the diel profile of the average sum of VOC OH reactivity due to 33 ambient VOCs, along with the diel profiles of the hourly averaged OH reactivity due to the top three contributors. The grey shaded region in Fig. 11 represents the 10th and 90th percentiles of the sum of VOC OH reactivities due to the 33 ambient VOCs. The average diel profile is bimodal in nature with peaks of ca.  $21 \text{ s}^{-1}$  at 09:00 LT and ca. 13 s<sup>-1</sup> at 18:00 LT. Interestingly, the nighttime value (22:00–06:00 LT) remains rather constant at ca.  $12 \, \text{s}^{-1}$ . The top four contributing compounds to the total calculated 10 VOC OH reactivity due to all 33 compounds were: acetaldehyde (24.0%) > isoprene (20.2%) > propene (18.7%). These three VOCs collectively accounted for ca. 63% of the campaign averaged total VOC OH reactivity of 12.3 s<sup>-1</sup>. Table S3 in the Supplement lists the top ten VOC contributors to the total VOC OH reactivity, many of which are emitted strongly from biomass combustion sources. The influence of south easterly 15 winds advecting primary emissions from biomass co-fired brick kilns in the morning hours is clearly discernible on the ambient OH reactivity profile.

VOCs significantly influence formation of tropospheric ozone in polluted environments. Tropospheric ozone in turn has strong impacts on air quality (as a key ingredient of photochemical smog), climate (due to its radiative forcing), human health (due to its ability to act as a pulmonary irritant) and in causing crop yield losses. The crop effect is particularly important for wintertime wheat crops grown in the Indo Gangetic Plain (Jerrett et al., 2009; Patton and Garraway, 1986; Sinha et al., 2015). In order to devise mitigation strategies for the control of ozone, VOCs are typically ranked in terms of

their ozone formation potential. Here, we applied the method proposed by Sinha et al. (2012) for calculating ozone production potential of VOCs described by the following equation:

Ozone production potential = 
$$\left(\sum k_{(VOC_i+OH)}[VOC_i]\right) \times [OH] \times n$$

Discussion Paper **ACPD** 15, 25021–25087, 2015 Wintertime high acetaldehyde, isoprene and **Discussion** Paper isocyanic acid in **Kathmandu Valley** C. Sarkar et al. **Title Page** Abstract Introduction **Discussion** Paper Conclusions References **Figures** Tables Close Back **Discussion** Pape Full Screen / Esc **Printer-friendly Version** Interactive Discussion

(3)

For the ozone production potential calculation, the average hydroxyl radical concentration was assumed to be  $[OH] = 1 \times 10^6$  molecules cm<sup>-3</sup> with n = 2 and only data pertaining to the mid-daytime period was considered (11:00–14:00 LT). Figure 12a and b summarizes the results in the form of pie charts for Period 1 (when most brick kilns were inactive but daytime biogenic emissions of isoprene dominated) and Period 2 (when brick kilns became operational, isoprene emissions were lower and biomass burning was stronger in intensity). To ascertain the contribution of different chemical classes of compounds (e.g. OVOCs, benzenoids, isoprene) to total ozone formation potential, the 33 compounds were further divided into 5 chemical subgroups as shown.

- <sup>10</sup> It was found that for both Period 1 and Period 2, oxygenated VOCs and isoprene collectively accounted for more than 68% (72% for Period 1 and 68% for Period 2) of the total ozone production potential. This is not surprising given that acetaldehyde and isoprene were among the highest contributors to the VOC OH reactivity. Interestingly, the contribution of nitriles, furans and benzenoids was much lower (< 12% for both pe-
- riods), whereas other VOCs (mainly alkenes) collectively contributed between 18 % (for Period 1) to 21 % (Period 2). Ozone production potential of xylenes, trimethylbenzenes, naphthalene and toluene were found to be highest among benzenoids. Nitriles did not have substantial contribution while some furan compounds such as 2-furaldehyde and furan made minor contributions to the total (< 3 %). Some of the alkene compounds</p>
- <sup>20</sup> such as propene and 1,3-cyclopentadiene along with propyne were found to be the major contributors for other class of compounds to total ozone production potential. The importance of alkenes in urban environments to ozone formation potentials is well established (Shao et al., 2009; Yoshino et al., 2012) but the stronger contribution of acetaldehyde and isoprene in the wintertime in Kathmandu in relation to the measured
- <sup>25</sup> alkenes suggests differences in atmospheric chemical processes for this environment compared to the other environments. The calculated total ozone production potential due to the 33 VOCs considered was found to be 4.93 ppbh<sup>-1</sup> for Period 1 and 3.79 ppbh<sup>-1</sup> for Period 2. The difference was mainly due to the higher isoprene mixing ratios observed during Period 1 (ozone production potential for isoprene alone was





1.68 ppb h<sup>-1</sup> for Period 1 and 0.81 ppb h<sup>-1</sup> for Period 2). Therefore biogenic isoprene emission is important for surface ozone formation even during the polluted conditions observed during the winter season in the Kathmandu Valley. This analysis puts in perspective the relative ranking of individual VOCs and classes of VOCs to the ozone production potential in the Kathmandu Valley for potential mitigation efforts.

### 3.8 SOA formation potential of VOCs in the Kathmandu Valley

Apart from ground level ozone formation, secondary organic aerosols (SOA) can also be formed as a result of atmospheric oxidation of VOCs. These secondary organic aerosols significantly affect air quality, visibility, cloud properties and climate (Rosenfeld et al., 2008). Previously isoprene was believed to be unimportant as a SOA precursor due to the high volatility of its reaction products (Kroll et al., 2006). However recent studies have highlighted that isoprene can also contribute to SOA formation along with aromatics and monoterpenes (Claeys et al., 2004; Capes et al., 2009; Lee et al., 2006; Ng et al., 2007). The SOA yield of individual VOCs depends on the ambient NO<sub>x</sub> contentrations. Under low NO<sub>x</sub>, the SOA yield is typically higher for aromatics, isoprene and monoterpenes whereas under high NO<sub>x</sub>, SOA yields of VOCs can get significantly reduced (Kroll et al., 2005; Henze et al., 2008; Presto et al., 2005). Pudasainee et al. (2006) reported NO<sub>x</sub> rich conditions in Kathmandu Valley and based on SOA yields

- reported in the literature (e.g., 5–10 % for toluene and xylenes and ~ 28 % for benzene; Ng et al., 2007) and the ambient concentrations of these VOCs measured during the period of study, we estimate the order of SOA production potential for these VOCs to be benzene > naphthalene > toluene > xylenes > monoterpenes > trimethylbenzenes > styrene > isoprene. Although the average ambient concentrations of the sum of monoterpenes (0.17 ± 0.16 ppb) were below 200 ppt, it contributed significantly to the total SOA formation due to its higher SOA yield under high NO<sub>x</sub> conditions (Lee
- the total SOA formation due to its higher SOA yield under high  $NO_x$  conditions (Lee et al., 2006). Apart from air quality and climate, SOA can substantially contribute to daily mortality and morbidity (Nawrot et al., 2007). As the major source of aromatics



appears to be biofuel/biomass combustion and traffic and diesel exhaust, cleaner energy use practices in these sectors will aid in reduction of secondary organic aerosol which is very important from a health and climate perspective due to its contribution to fine mode aerosol mass concentrations (PM<sub>1</sub>).

### **5 3.9 VOCs with direct health implications for exposed population**

Some of the VOCs in the Kathmandu Valley were detected at concentrations (refer to column 7; Table S1 in the Supplement) that can pose direct health risks to the exposed population. Benzene which is a human carcinogen and mutagen was present at an average concentration of ca. 3 ppb during this wintertime study. It may be noted that no safe level of exposure for benzene can be recommended (WHO, 2010). Formaldehyde (average observed concentration ~ 2 ppb during this wintertime study) is regarded as a probable human carcinogen as exposure to it can increase the possibility of lung and nasopharyngeal cancer (WHO, 2010). Other than its possible carcinogenic effects, formaldehyde exposure can also cause eye, nose and throat irritation and contribute

- to diseases like bronchitis (www.epa.gov). Among the other rarely quantified ambient VOCs, nitromethane is reported to be a possible carcinogen to humans and is classified as a Group 2B carcinogen (Inomata et al., 2014). Nitromethane was present at an average concentration of 240 ppt during this study. Several other species can result in formation of toxic secondary VOCs. For example, naphthalene is not considered
- to be a human carcinogen, but it can form mutagenic nitronaphthalenes by OH and NO<sub>3</sub> initiated reactions (Sasaki et al., 1997; Zhang et al., 2012). Short-chain amides, such as formamide and acetamide can have several health effects including irritation of eyes, skin, nose, throat and respiratory system, drowsiness and headache, dyspnea (breathing difficulty), conjunctivitis, corneal necrosis, abdominal pain, nausea, vomiting,
- <sup>25</sup> diarrhea, and shock or collapse (Ge et al., 2011). Also cumulative liver, lung and kidney damage can occur due to exposure to formamide and acetamide. The exposure generally occurs through inhalation, ingestion and absorption through skin. Acetamide is also considered to be a Group 2B human carcinogen by International Agency for Research





on Cancer (www.iarc.fr). It is noteworthy that for some of these species the ambient concentrations measured at the measurement site may not be serious but exposure closer to the point sources (where concentrations are much higher) for longer time periods may pose a serious health risk. Atmospheric oxidation of amide compounds such

- as formamide and acetamide with OH radicals can also lead to the formation of isocyanic acid (HNCO) that has adverse impacts on human health (Barnes et al., 2010). The average concentration of isocyanic acid measured during this study was ~ 1 ppb. It has been reported that exposure to > 1 ppb of isocyanic acid can cause cataracts, cardiovascular diseases and rheumatoid arthritis via protein carbamylation (Roberts et al.,
- <sup>10</sup> 2011). The exposure concentration of 1 ppb is based on the study of Wang et al. (2007) who reported that the conjugate anion NCO<sup>-</sup> can cause carbamylation of protein via post-translational protein modification initiating an inflammatory response that causes health effects similar to smoking, at NCO<sup>-</sup> concentrations corresponding to 1 ppb of isocyanic acid. Isocyanic acid had both photochemical and primary emission sources in Kathmandu Vallau and its ambient concentrations were highest during the period.
- <sup>15</sup> in Kathmandu Valley and its ambient concentrations were highest during the period when the biomass co-fired brick kilns were active. Thus, providing cleaner and more efficient brick kiln technology would help to reduce the manifold health risks posed to the population due to exposure to isocyanic acid.

### 4 Conclusions

- <sup>20</sup> This study has comprehensively characterized the chemical composition of air in the Kathmandu Valley in terms of speciated volatile organic compounds during the SusKat-ABC wintertime campaign. The measurements performed at high time resolution (every minute) and high mass resolution ( $m/\Delta m > 4200$ ) enabled us to identify a multitude of compounds based on their monoisotopic masses and hence exact molecular for-<sup>25</sup> mula. Novel insights could be acquired regarding chemical processes related to ozone
- and secondary organic aerosol formation in a complex chemical environment affected





by mountain meteorology and both anthropogenic and biogenic sources (even in winter).

A total of 71 ion peaks were observed in the mass spectra of PTR-TOF-MS that were above the detection limit of the instrument. Out of these, 37 species that had average ambient concentrations greater than 200 ppt during the campaign could be identified with reasonable confidence based on (1) spectral characteristics observed at a particular *m*/*z* in a 0.005 amu bin relative to the ion peak, (2) ambient diel profiles and (3) correlation with specific emission tracer molecules such as acetonitrile (a biomass burning tracer). Among these 37 species, 8 contained nitrogen, 15 contained oxygen, 13 were hydrocarbons and one contained sulfur. Based on chemical signatures of tracer compounds such as acetonitrile and isoprene, two periods with contrasting emission influences were identified during the campaign and investigated in detail. Period 1 (19 December 2012–2 January 2013) was characterized by high

daytime biogenic emissions of isoprene (average isoprene concentrations in Period 1
and Period 2 were 1.66 and 0.97 ppb, respectively) and the absence of operational brick kilns (and hence their emissions); while Period 2 (4 January 2013–18 January 2013) was marked by high acetonitrile (average concentration during this Period was 1.34 ppb), benzene (3.46 ppb) and isocyanic acid (1.03 ppb) due to emissions from the biomass co-fired brick kilns and other biofuel/biomass burning activities. A clear distinction of isoprene from furan, which had distinct emission profiles, highlighted the importance of deploying a PTR-TOF-MS for VOC measurements in the Kathmandu

Valley.

Two "new" compounds which have not been reported in any previous ambient study namely, formamide (CH<sub>3</sub>NO; protonated m/z = 46.029; campaign average 0.76 ppb) and acetamide (C<sub>2</sub>H<sub>5</sub>NO; protonated m/z = 60.051; campaign average 0.39 ppb) and are involved in photochemical formation of isocyanic acid were also detected. The average total reactive carbon (sum of the average mixing ratios of all the 37 species reported in this study) was 175.8 ppbC to which propyne, acetaldehyde, benzene, acetic acid, acetone, propene and toluene collectively contributed more than 60%. Isoprene





concentrations as high as 3 ppb were observed frequently during the daytime, in the early part of the campaign (December 2012) and could be traced to biogenic emissions from vegetation in fetch regions upwind of the site.

- The highest average VOC mixing ratios during our wintertime deployment were (in
  rank order): acetaldehyde (8.8 ppb), methanol (7.4 ppb), acetone (4.2 ppb), benzene (2.7 ppb), toluene (1.5 ppb), isoprene (1.1 ppb), acetonitrile (1.1 ppb), C8-aromatics (~ 1 ppb), furan (~ 0.5 ppb), and C9-aromatics (0.4 ppb). The results suggest that the emission sources of oxygenated and aromatic VOCs in the Kathmandu Valley are different compared to several cities such as Paris and London, likely due to the emission sources of original different burning of biomass (e.g. garden waste, agro-residue burning and garbage burning) and extensive use of diesel generators. In comparison to wintertime mixing ratios reported from several sites elsewhere in the world, the mixing ratios of acetaldehyde (~ 9 ppb), acetonitrile (~ 1 ppb) and isoprene (~ 1 ppb ppb) in the Kathmandu Valley are among the highest measured anywhere in the world. The major sources of propyne, propene, benzene, and propanenitrile in the
- Valley appeared to be biomass burning as concentrations of all these compounds correlated well with the biomass burning tracer acetonitrile ( $r^2 > 0.7$ ) and had diel emission profiles similar to that of acetonitrile. Nitromethane (a tracer for diesel exhaust) correlated with methanol while dimethyl sulfide (DMS) correlated strongly with acetaldehyde, indicating commonality of sources.

The top three contributing compounds to the total calculated VOC OH reactivity due to 33 compounds were: acetaldehyde (24.0%), isoprene (20.2%), and propene (18.7%), which collectively accounted for ca. 63% of the campaign averaged total VOC OH reactivity of  $12.3 \text{ s}^{-1}$ . Oxygenated VOCs and isoprene collectively accounted for more than 68% (72% for Period 1 and 68% for Period 2) of the total ozone production potential. Based on known SOA yields of compounds and the ambient concentrations measured in the Kathmandu Valley, it was estimated that the relative SOA production potential of VOCs was in the following order: benzene > naphthalene > toluene > xylenes > monoterpenes > trimethylbenze-



nes > styrene > isoprene. Several VOCs known to enhance health risks for cancer, cataract and pulmonary diseases were detected in the ambient air. The synergistic effect of these VOCs on air toxicity is difficult to quantify but likely significant. The prominent ones were: isocyanic acid, formamide, acetamide, naphthalene and nitromethane for which this study presents the first measurements in ambient air from South Asia

along with benzene, a human carcinogen.

A major conclusion of this study is that the wintertime air pollution in the Kathmandu Valley can be significantly reduced by replacing the existing brick kiln technology with cleaner and more efficient brick kiln technology. To reduce the emission and formation

- of toxic VOCs (such as carcinogenic benzene and isocyanic acid) it is important to mitigate the intense biomass burning activities (agro-residue, garden waste, leaf litter burning) in the Kathmandu Valley, in particular biomass co-fired brick kilns, which appear to combust the fuel inefficiently (as evidenced by the reduced carbon compounds). While measures like introduction of better quality catalytic scrubbers in the traffic fleet
- and cleaner diesel generators are generic for urban sites in developing countries the world over, the inefficient biomass co-fired brick kilns seem to be specific point sources that are particularly important in the Kathmandu Valley.

While this first study has quantified several important gaseous emission tracers and reactive VOCs and revealed several new insights related to wintertime emissions and

- chemistry in the Kathmandu Valley, future studies need to focus on what happens in the Valley on seasonal and inter-annual timescales. Of particular interest would be assessing the concentrations of isoprene and acetaldehyde in summer and their atmospheric chemistry. Assessment of source specific emission ratios (inter VOC and VOC/CO) for the major sources (brick kilns, diesel generator exhaust, leaf litter fires etc.) and im-
- <sup>25</sup> provement of existing emission inventories using the in-situ data should be undertaken. Some of these aspects will be presented in a companion paper (Sarkar et al., 2015) to this special issue. While much has been learnt about wintertime VOC speciation in this study, and the first comprehensive dataset has been acquired, the differences in emissions sources and chemical composition of the air call for long term measurements



and further field intensives to unravel some of the new chemical processes identified in this part of the world.

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All the data reported in this article can be obtained from the corresponding author by sending an email to vsinha@iisermohali.ac.in.

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 Table 1. Principal operational settings for PTR-TOF-MS parameters.

Parameter	Value
Overall drift voltage ( $U_{drift}$ )	600 V
Temperature at drift tube ( $T_{drift}$ )	60 °C
Pressure at drift tube (P <sub>drift</sub> )	2.2 mbar
Length of the drift tube $(L_{drift})$	9.3 cm
Reaction Time (t)	92 µs
Field strength of the drift tube $(E/N)^*$	135 Td

\* *E* is the electric field strength (V cm<sup>-1</sup>) and *N* is the gas number density (molecule cm<sup>-3</sup>).  $1 \text{ Td} = 10^{-17} \text{ V cm}^2 \text{ molecule}^{-1}$ .

Discussion Pap	<b>AC</b> 15, 25021–	<b>ACPD</b> 15, 25021–25087, 2015		
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**Figure 1.** Location of the measurement site (Bode; red circle) along with surrounding cities (Kathmandu, brown circle; Patan, blue circle and Bhaktapur, pink circle), brick kilns (white markers), major industries (yellow triangles), forest areas (green tree symbols), airport (blue marker) and major river path (sky blue path) in the Google Earth image of the Kathmandu Valley (obtained on 22 May 2015 at 14:55 LT).







**Figure 2. (a)** Schematic of wind flow during different times of the day in the Kathmandu Valley. **(b)** Box and whisker plots of the measured meteorological parameters (wind speed, wind direction, solar radiation, relative humidity and ambient temperature) at the Bode site (16–30 January 2013).







**Figure 3.** Compound specific normalized sensitivities at different relative humidities (RH 60, 75 and 90%) for acetonitrile, acetaldehyde, isoprene and benzene during the calibration experiment performed on 10 January 2013. Horizontal bars reflect the error due to the MFC flows and the accuracy of the VOC gas standard whereas vertical bars reflect the precision error (2  $\sigma$ ) of the measurements.







**Figure 4.** Ion peaks observed during ambient air mass scans (hourly averages) on 15 January 2013. Zoom-in of the isobaric species furan and isoprene is shown in the inset.







**Figure 5.** Time series of one minute time resolution data for the mixing ratios of methanol, acetaldehyde, and the sum of acetone and propanal (top panel); isoprene (second panel from top); acetonitrile and furan (second panel from bottom); benzene, toluene, the sum of C8-aromatics (xylene isomers and ethyl benzene) and the sum of C9-aromatics (isomers of trimethyl benzenes and propyl benzenes) (bottom panel) during SusKat-ABC campaign.







**Figure 6.** Comparison of wintertime VOC mixing ratios measured in the Kathmandu Valley with wintertime VOC mixing ratios at selected urban sites elsewhere in the world.







**Figure 7.** Box and whisker plots showing average, median and variability (10th, 25th, 75th and 90th percentile) for some major VOCs in the Kathmandu Valley during Period 1 and Period 2.







**Figure 8.** Comparison of diel box and whisker profiles of several rarely measured or previously unreported ambient VOCs with more frequently measured VOCs/emission tracers.







**Figure 9.** Time series of benzene and acetonitrile for an illustrative day (18 January 2013) that was influenced by biomass burning and biomass co-fired brick kiln emissions (correlation of benzene with acetonitrile for same data is shown in the inset).





**Figure 10.** Polar annulus plot of isoprene for the period 16–30 January 2013 highlighting the spatio-temporal variation of isoprene and its biogenic sources.





**Figure 11.** Diel profiles of the calculated total VOC OH reactivity (with 10th and 90th percentile contributions represented by the grey shaded region) and the major VOC contributors.



**Discussion** Paper



**Figure 12. (a)** Pie charts showing contribution of different class of compounds to total ozone formation potential for Period 1 (19 December 2012–2 January 2013). **(b)** Pie charts showing contribution of different class of compounds to total ozone formation potential for Period 2 (4 January 2013–18 January 2013).



