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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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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 South Asia. 71 ion peaks (for which measured ambient concentrations exceeded the 2σ 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 emission 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). 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 ($m/z = 46.029$) 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

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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 out within the Kathmandu Valley. Previous studies in the Kathmandu Valley have examined pollution in relation to carbon monoxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO₂), ozone (O₃) (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. Offline measurements of nitrogen dioxide (NO₂) and sulphur dioxide (SO₂) 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 compounds 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 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 compounds 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.

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 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 m.a.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 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 relative 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 potential 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.

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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 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⁻²), 226 728 (population density: 14 966 km⁻²) and 83 658 (population density: 12 753 km⁻²), 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 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 pharmaceuticals, 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).

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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 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 wallichiana* (Gobre Salla) are also found (Department of Plant Resources, Nepal, 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), *Celtis 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 m s^{-1}). On the other hand, nighttime 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 Kathmandu 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 measured at Bode from 16–30 January 2013 derived from the one minute temporal resolution data acquired using meteorological sensors (Campbell Scientific Loughborough, UK) installed on the rooftop (~ 25 m above ground and ~ 5 m away from the instrument inlet). Daytime (08:00–17:00 LT) average ambient temperature for the measurement period was observed to be $12.2 \pm 4.5^\circ\text{C}$. It is worth mentioning that most mornings were associated with dense fog (average ambient RH > 90 % with visibility < 100 m) 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 90 % throughout the night. Minimum RH levels ($\sim 35\%$) 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 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_3O^+ reagent ions, a drift tube where analyte VOCs undergo ionization and an orthogonal acceleration

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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 ($1 \text{ Td} = 10^{-17} \text{ V cm}^{-2}$; 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 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-of-flight 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 using 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: $\text{H}_3^{18}\text{O}^+$ (monoisotopic mass 21.022) and $\text{H}_3^{18}\text{O}^+ \cdot \text{H}_2\text{O}$ (monoisotopic mass 39.033). In addition the transmission values of 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.).

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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, α -pinene, 1, 2-dichlorobenzene and 1, 2, 4-trichlorobenzene 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, Bellefonte, 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_3O^+ ($m/z = 19$) primary ions according to the following equation:

$$\text{ncps} = \frac{I(\text{RH}^+) \times 10^6}{I(\text{H}_3\text{O}^+)} \times \frac{2}{P_{\text{drift}}} \times \frac{T_{\text{drift}}}{298.15} \quad (1)$$

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 ($\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$; $m/z = 37$) 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 ($\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$; nominal $m/z = 37$) to the primary ions (H_3O^+ ; nominal $m/z = 19$) was lower than 10 %, 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 (ncps ppb^{-1}). Figure 3 shows the sensitivities

(ncps ppb⁻¹) 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⁻¹) 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 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 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.

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The limit of detection was defined to be 2σ of the measured normalized signal (ncps) while measuring VOC free zero air divided by the sensitivity expressed in ncps ppb⁻¹ (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 (2σ 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 overall uncertainty of $\sim 50\%$ 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

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 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 $\pm 1\sigma$ variability of ambient mixing ratios observed during the study period.

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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/z was 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 ($m/z = 51.044$ and $m/z = 56.060$) could not be identified based on the exact protonated monoisotopic 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_3NO ; protonated $m/z = 46.029$) and acetamide ($\text{C}_2\text{H}_5\text{NO}$; protonated $m/z = 60.051$) were also detected. We discuss their diel variability and potential 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

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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 ≥ 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 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).

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). 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.

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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 reports 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, contributing, 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.

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

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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 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 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 oxygenated 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.

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

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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 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., 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 Peñuelas, 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, 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 Peñuelas, 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

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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 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 because 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

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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 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 ms^{-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 $3\text{--}4 \text{ ms}^{-1}$, causing rapid venting and dilution. The wind direction 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 boundary 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

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to this katabatic flow, less cold and less dense air parcels in the Valley bottom contain-
ing 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 (O₃) with
alkenes can significantly contribute to photochemical formation of acetaldehyde (Som-
mariva 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 sur-
prising considering its much higher OH reactivity.

The highest isoprene concentrations were observed during daytime for both Pe-
riod 1 and Period 2 but the average concentrations were much higher during Period 1
when ambient temperature and solar radiation were comparatively higher and decid-
uous 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 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-

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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 $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) but the oxidation 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 mixing 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 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_2 (Taylor et al., 1980). Therefore nitromethane can act as a NO_x source in the atmosphere and could contribute to surface ozone production.

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 s^{-1} at 09:00 LT and ca. 13 s^{-1} at 18:00 LT. Interestingly, the nighttime value (22:00–06:00 LT) remains rather constant at ca. 12 s^{-1} . The top four contributing compounds to the total calculated 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^{-1} . 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 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:

$$\text{Ozone production potential} = \left(\sum k_{(\text{VOC}_i + \text{OH})} [\text{VOC}_i] \right) \times [\text{OH}] \times n \quad (3)$$

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For the ozone production potential calculation, the average hydroxyl radical concentration was assumed to be $[\text{OH}] = 1 \times 10^6 \text{ molecules cm}^{-3}$ 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. 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 periods), 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 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 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^{-1} for Period 1 and 3.79 ppbh^{-1} 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 ppbh⁻¹ for Period 1 and 0.81 ppbh⁻¹ 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_x concentrations. Under low NO_x, the SOA yield is typically higher for aromatics, isoprene and monoterpenes whereas under high NO_x, 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_x 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_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

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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 (PM₁).

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 NO₃ 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, 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

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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_3NO ; protonated $m/z = 46.029$; campaign average 0.76 ppb) and acetamide ($\text{C}_2\text{H}_5\text{NO}$; 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

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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 emissions from biomass co-fired brick kilns, open 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) 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 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-

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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 improvement 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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15 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_{drift})	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^{-1}) and N is the gas number density (molecule cm^{-3}).
 1 Td = $10^{-17} \text{ V cm}^2 \text{ molecule}^{-1}$.

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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).

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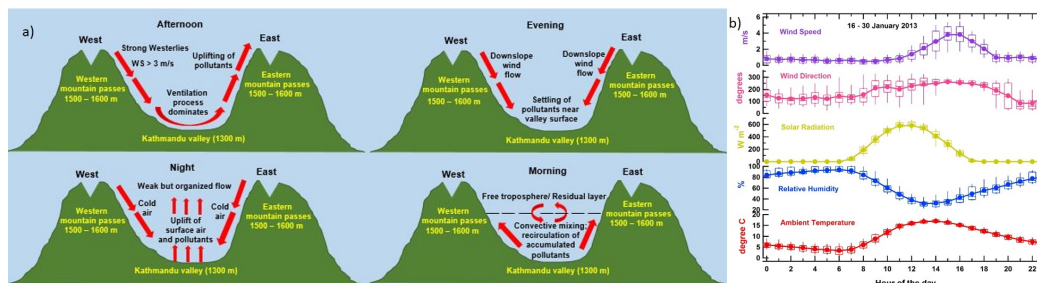


Figure 2. (a) Schematic of wind flow during different times of the day in the Kathmandu Valley. (b) Box and whisker plots of the measured meteorological parameters (wind speed, wind direction, solar radiation, relative humidity and ambient temperature) at the Bode site (16–30 January 2013).

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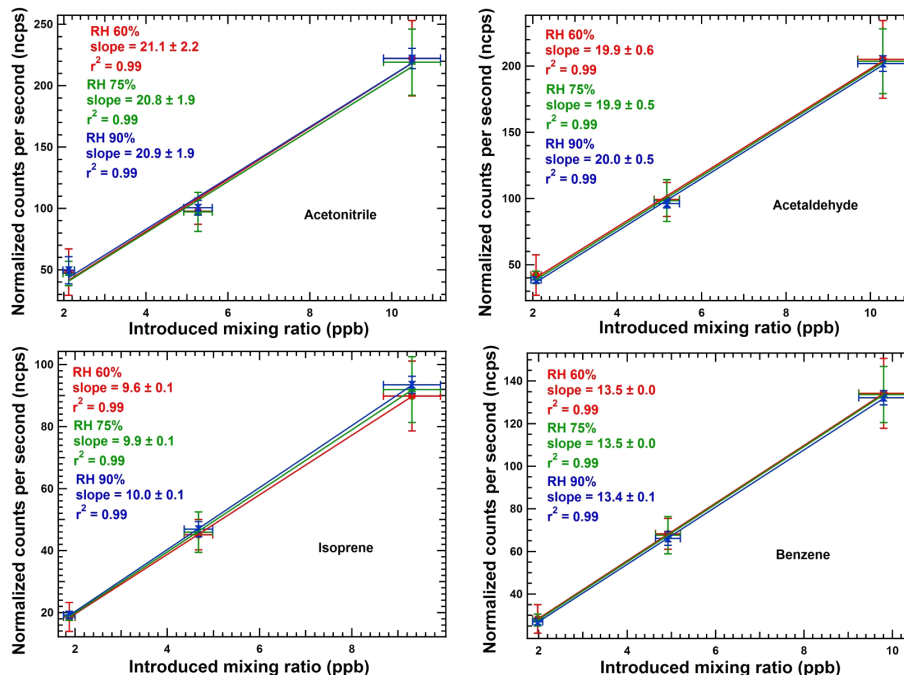


Figure 3. Compound specific normalized sensitivities at different relative humidities (RH 60, 75 and 90 %) for acetonitrile, acetaldehyde, isoprene and benzene during the calibration experiment performed on 10 January 2013. Horizontal bars reflect the error due to the MFC flows and the accuracy of the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

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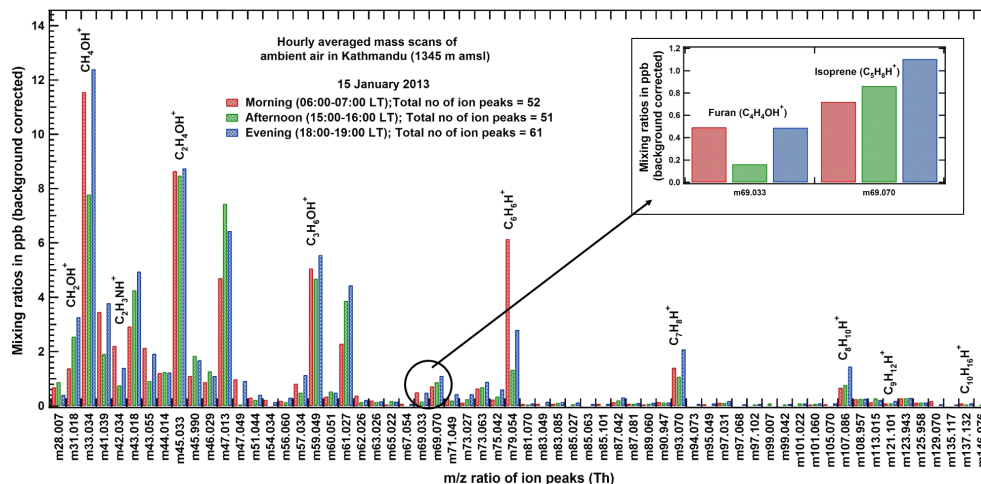


Figure 4. Ion peaks observed during ambient air mass scans (hourly averages) on 15 January 2013. Zoom-in of the isobaric species furan and isoprene is shown in the inset.

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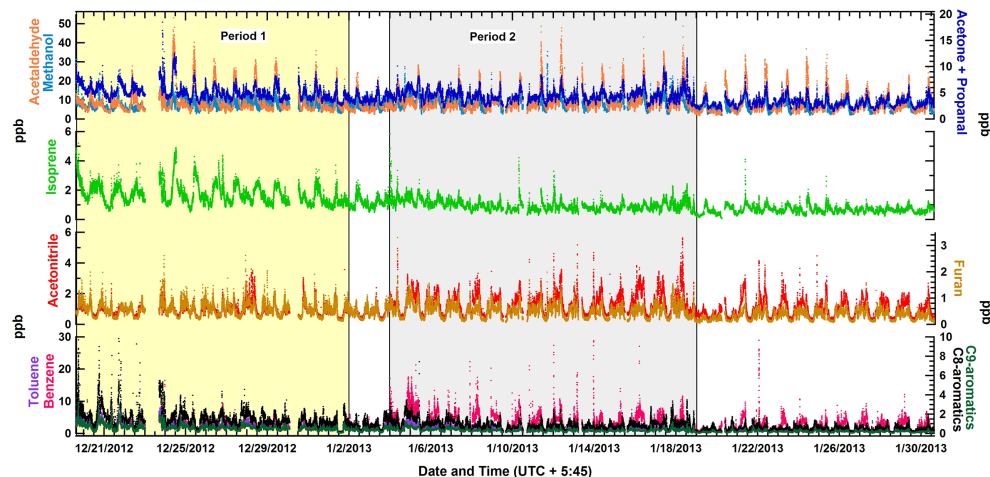


Figure 5. Time series of one minute time resolution data for the mixing ratios of methanol, acetaldehyde, and the sum of acetone and propanal (top panel); isoprene (second panel from top); acetonitrile and furan (second panel from bottom); benzene, toluene, the sum of C8-aromatics (xylene isomers and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

Wintertime high acetaldehyde, isoprene and isocyanic acid in Kathmandu Valley

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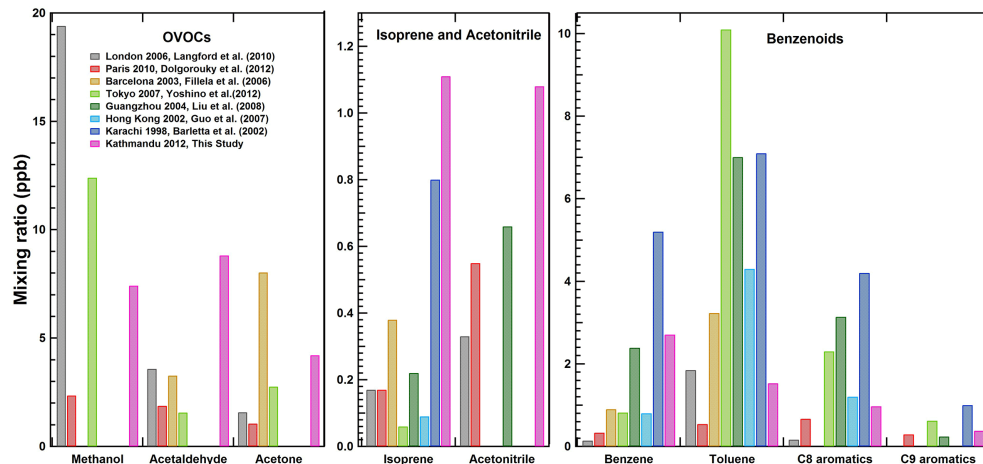


Figure 6. Comparison of wintertime VOC mixing ratios measured in the Kathmandu Valley with wintertime VOC mixing ratios at selected urban sites elsewhere in the world.

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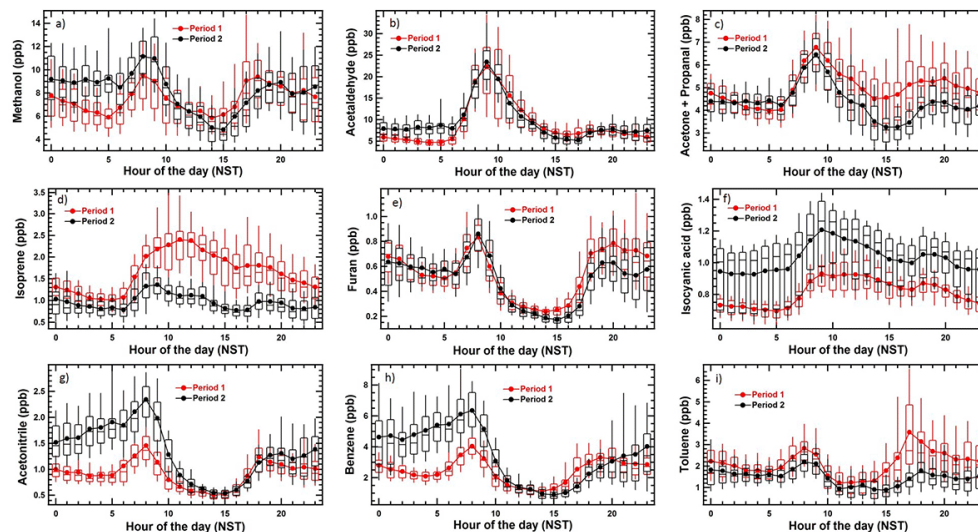


Figure 7. Box and whisker plots showing average, median and variability (10th, 25th, 75th and 90th percentile) for some major VOCs in the Kathmandu Valley during Period 1 and Period 2.

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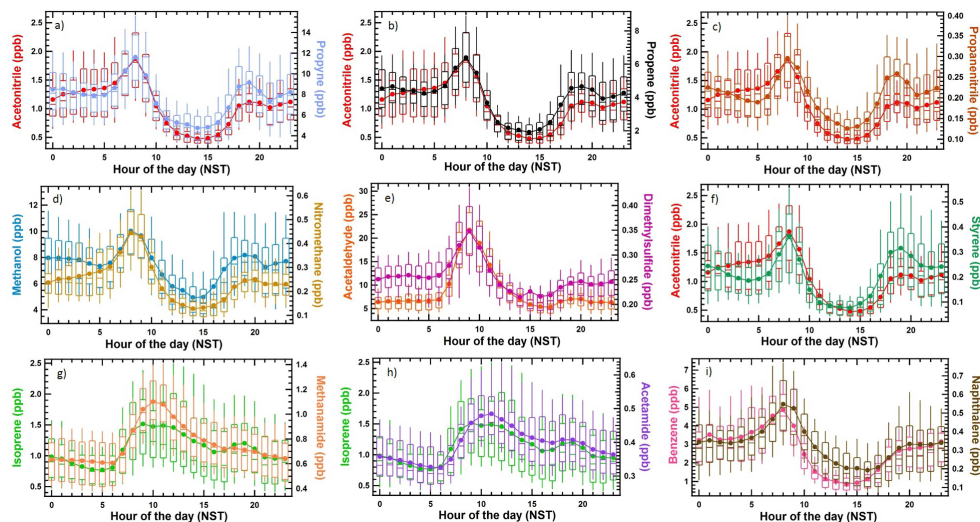


Figure 8. Comparison of diel box and whisker profiles of several rarely measured or previously unreported ambient VOCs with more frequently measured VOCs/emission tracers.

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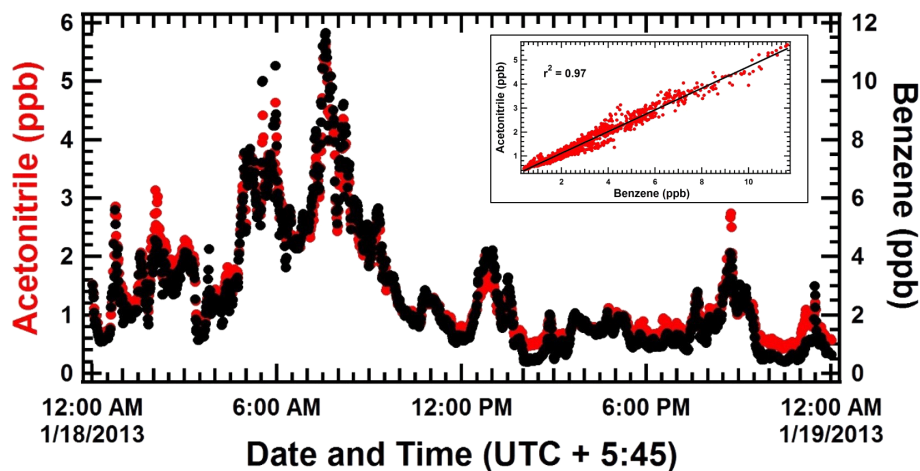


Figure 9. Time series of benzene and acetonitrile for an illustrative day (18 January 2013) that was influenced by biomass burning and biomass co-fired brick kiln emissions (correlation of benzene with acetonitrile for same data is shown in the inset).

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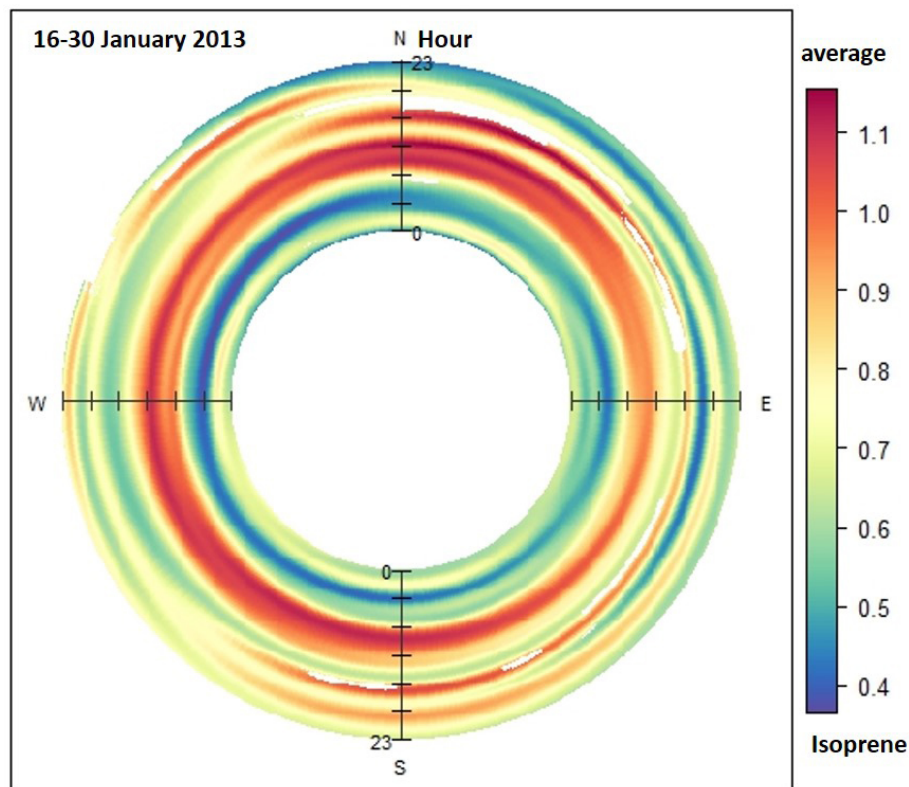


Figure 10. Polar annulus plot of isoprene for the period 16–30 January 2013 highlighting the spatio-temporal variation of isoprene and its biogenic sources.

Wintertime high acetaldehyde, isoprene and isocyanic acid in Kathmandu Valley

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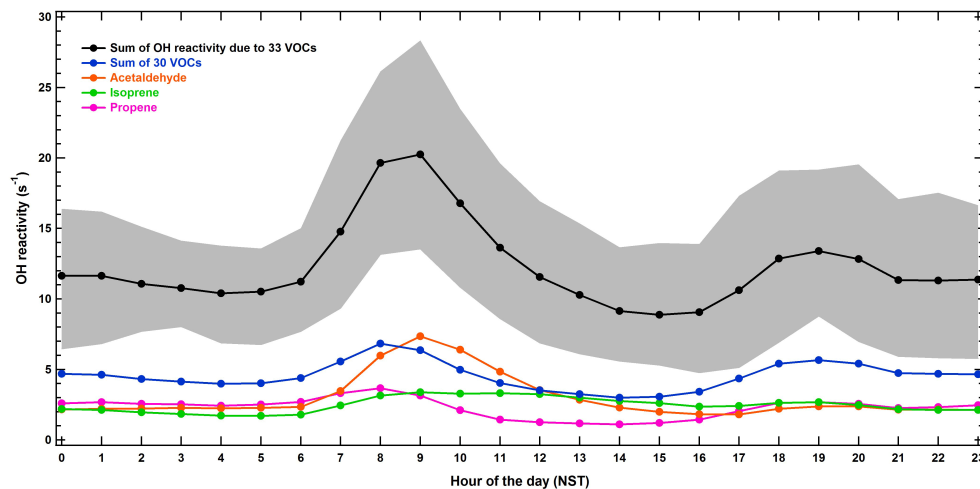


Figure 11. Diel profiles of the calculated total VOC OH reactivity (with 10th and 90th percentile contributions represented by the grey shaded region) and the major VOC contributors.

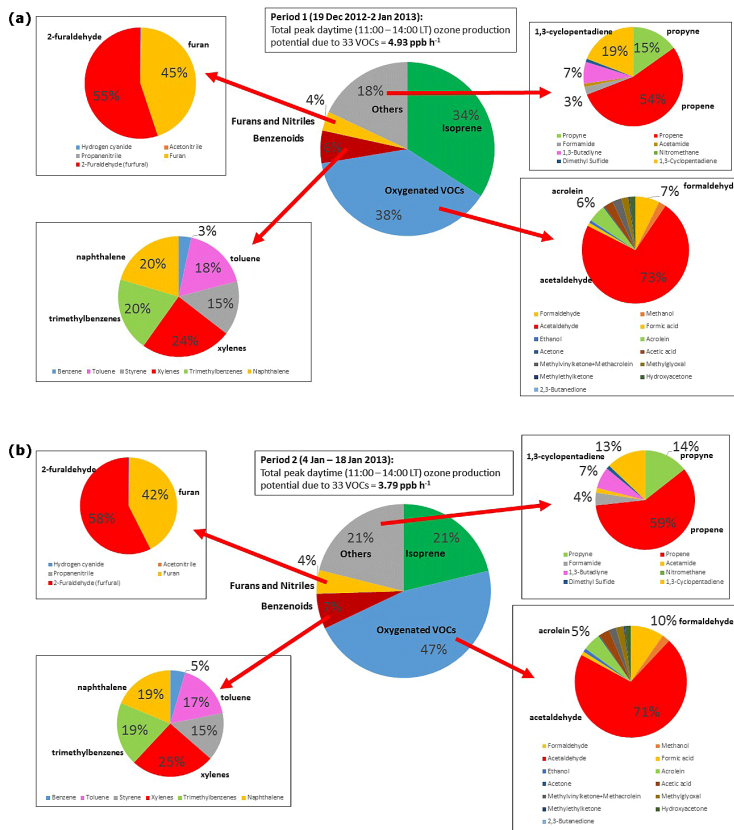


Figure 12. (a) Pie charts showing contribution of different class of compounds to total ozone formation potential for Period 1 (19 December 2012–2 January 2013). **(b)** Pie charts showing contribution of different class of compounds to total ozone formation potential for Period 2 (4 January 2013–18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

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