Variability of Anthropogenic Gases: Nitrogen Oxides, Sulfur Dioxide, Ozone and Ammonia in Kathmandu Valley, Nepal

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ABSTRACT

Kathmandu Valley is one of the largest and most polluted metropolitan regions in the Himalayan foothills. Rapidly expanding urban sprawl and a growing fleet of vehicles, and industrial facilities such as brick factories across the valley have led to conditions where ambient concentrations of key gaseous air pollutants are expected to exceed Nepal’s National Ambient Air Quality Standards (NAAQS) and World Health Organization (WHO) guidelines. In order to understand the spatial variation of the trace gases in the Kathmandu Valley, passive samples of SO2, NOx, NO2, NH3, and O3 were collected simultaneously from fifteen locations between March and May 2013. A follow-up study during two separate campaigns in 2014 sampled these gases, except ammonia, one site at a time from thirteen urban, suburban and rural stationary sites. In 2013, urban sites were observed to have higher weekly averaged NO2 and SO2 (22.4 ± 8.1 µg m–3 and 14.5 ± 11.1 µg m–3, respectively) than sub-urban sites (9.2 ± 3.9 µg m–3 and 7.6 ± 2.8 µg m–3, respectively). Regions located within 3 km of brick factories had higher SO2 concentrations (22.3 ± 14.7 µg m–3) than distant sites (5.8 ± 1.1 µg m–3). Higher O3 (108.5 ± 31.4 µg m–3) was observed in rural locations compared to urban sites (87.1 ± 9.2 µg m–3), emphasizing the importance of meteorological factors and precursor species for ozone production and titration. Parallel to previous studies, these results suggest that ground-level O3, as its levels frequently exceeded guidelines throughout the sampling periods, is an important concern throughout the valley. NH3 near polluted rivers and SO2 around brick factories are also important pollutants that need more intensive monitoring, primarily due to their importance in particulate matter formation chemistry.

Keywords: Nitrogen oxides; Sulfur dioxide; Tropospheric ozone; Passive sampling; Air quality.

INTRODUCTION

Deteriorating air quality has been observed in many cities in Asia, Europe and North America (Fang et al., 2009; Pascal et al., 2013; Parrish et al., 2011), and notably in rapidly developing regions or countries. High levels of air pollutants have been observed even in remote regions like the Himalayas and Tibetan Plateau (e.g., Marinoni et al., 2010; Lüthi et al., 2015) which are still relatively poorly sampled regions of the world. The primary reasons for poor air quality in fast growing cities are emissions from rapidly increasing yet poorly maintained vehicles (Rakowska et al., 2014), and industries with no or limited pollution control (Lim et al., 2010) to meet the needs of growing population and demands, as well as open burning of municipal waste and agro-residues which are common in developing countries (Shakya et al., 2010). This poses a significant threat to human health (Gurung and Bell, 2013), environmental degradation (Zhang et al., 2012), and economic stability (Dhimal, 2009).

Kathmandu Valley, where the capital of Nepal is located, is an example of a rapidly developing metropolitan area in South Asia. The valley has a population of 3 million and maintains a 4 percent per year population growth rate (Muzzini and Aparicio, 2013), and is the largest metropolitan area in the Himalayan foothills. The valley is surrounded by mountains creating a distinctive bowl shaped area of approximately

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340 km² (Gurung and Bell, 2012). This shape is conducive for physically limiting ventilation and vertical movement of air in the valley, as well as leading to wintertime thermal inversions trapping pollutants near the surface (Sapkota and Dhaubhadel, 2002; Regmi et al., 2003). Consequently, air pollutants emitted from natural and anthropogenic sources build up and remain within the valley with little to no exchange of low level cold air with warm air sitting above the valley (Sapkota and Dhaubhadel, 2002; Panday et al., 2009), making the valley one of the most polluted regions in Nepal. With summer time temperatures reaching up to 35°C (and dropping below 0°C during winter), the valley experiences sub tropical, temperate climate conditions with four distinct seasons (i.e., winter, pre-monsoon, monsoon and post-monsoon) (Giri et al., 2006).

Previous studies have identified Kathmandu’s urban sprawl, rapidly increasing vehicle fleet, and expanding industries as precursors of degrading air quality within the valley and boarder surrounding region in the Himalayan foothills (Shah and Naggal, 1997). Particulate pollution has been the main concern in Kathmandu Valley with PM$_{2.5}$ levels regularly exceeding the WHO guidelines in Kathmandu (Aryal et al., 2009). Trace gases, such as ozone, have also been observed to be at very high levels in Kathmandu Valley (Pudasainee et al., 2006). Previous studies (Byanju et al., 2012; Pradhan et al., 2012) have highlighted the trace gases related with anthropogenic emissions such as NO$_x$, SO$_2$, and O$_3$ in Kathmandu Valley.

Adverse health effects are often strongly associated with exposure to particulate matter (PM) (WHO, 2005), and it is the main health risk in the Kathmandu Valley (Regmi and Kitada, 2003). Sulfate, nitrate, and ammonium were also found to be the main inorganic constituent of PM at an urban location in Kathmandu (Shakya et al., 2010). Anthropogenic emission of gaseous air pollutants, such as nitrogen oxides (Chen et al., 2012), sulfur dioxide (Kan et al., 2010) and ozone (Jhun et al., 2014) also cause adverse health effects directly or through the formation of secondary aerosols. Similar to PM spatial profile, the concentration and dispersion of these gaseous pollutants depend on factors such as the presence of local and distant emission sources (Morawska et al., 2002), and topographic and meteorological conditions that cause spatial and temporal variations (Chai et al., 2014). Therefore, knowledge about the temporal and spatial distributions of these trace gases can help assess the emission sources of these gases and particulate matter, and improve the understanding of air quality and its health effects in Kathmandu Valley.

For their direct health effects and, more importantly, indirect health consequences as a result of particulate matter formation, WHO strongly recommends regular monitoring of these gases and their levels kept within permissible limits (WHO, 2005). Nepal has implemented a system of National Ambient Air Quality Standards (NAAQS) with 24 hour standards for NO$_2$ (80 µg m$^{-3}$) and SO$_2$ (70 µg m$^{-3}$), as well as the recommended World Health Organization (WHO) 8-hour guideline for O$_3$ (100 µg m$^{-3}$). Previous studies have noted exceedances of WHO guideline value for O$_3$ in the Kathmandu Valley in 2003–04 (Pudasainee et al., 2006), and NO$_2$ (Byanju et al., 2012) across weekly or 8-hour averaged data, though these studies are not directly comparable to the nationally adopted 24-hour NO$_2$ standards.

In the Kathmandu Valley, there are thought to be many unregulated sources of air pollutants such as extensive fossil fuel combustion in nearly 250,000 backup power generators of various sizes, coal used in more than 100 brick factories, open burning of municipal waste, landfill sites, unpaved roadways, poorly maintained motor vehicles, and other high-temperature combustion processes in industrial operations (Dhimal, 2009; Pradhan et al., 2012). Only a handful of emissions control strategies or regulations exist to ameliorate the air quality concerns in the Kathmandu Valley, but due to weak enforcement of the regulations, many of these sources continue to emit pollutants unabated.

A particular challenge in conducting measurements in Kathmandu is the lack of operational ambient air monitoring stations, which have been largely nonfunctional since 2008 (Dhimal, 2009). Routine online monitoring techniques for criteria gaseous pollutants are expensive and require regular maintenance which is often not available within the country. Distributed grid electricity is often interrupted – as much as 12-14 hours per day without electricity, particularly in the winter – which greatly restricts the measurement capacity of investigators. Because of these logistical limitations, adopting a passive sampling measurement method is a useful option for collecting samples in developing countries. This technique has proven reliable and effectively used in developing African (Adon et al., 2010) and south Asian countries (Byanju et al., 2012; Behera et al., 2015) to collect trace gaseous pollutants from ambient air because they are low cost, require little training and oversight, and need almost no research infrastructure support in the field.

In this paper, we present week-long measurements of nitrogen oxides (NO$_x$), nitrogen dioxide (NO$_2$), nitric oxide (NO), surface ozone (O$_3$), sulfur dioxide (SO$_2$), and ammonia (NH$_3$) using Ogawa passive samplers at multiple sites in the Kathmandu Valley during three discrete field campaigns in 2013 and 2014. Ogawa passive samplers have been widely used and validated for ambient trace gas monitoring (Meng et al., 2010; Roadman et al., 2003). The passive sampling was carried out as a part of a larger SusKat-ABC (Suskat: Sustainable Atmosphere for the Kathmandu Valley-Atmospheric Brown Cloud) international air pollution measurement campaign which aimed at understanding the dynamics of air pollution in the Himalayan foothills, including Kathmandu Valley (Rupakheti et al., 2016). Our objectives are: (1) to make a quantitative analysis of the distribution of gaseous pollutants across the valley characterized by different emission sources, and (2) to compare our findings with previous studies conducted in the valley and (3) to assess influence of meteorology in the region on the temporal variability and spatial distribution of these gases, including differences at sites upwind and/or downwind of three major cities - Kathmandu Metropolitan City, Lalitpur Sub-Metropolitan city, and Bhaktapur Municipality.

This paper hence provides a broad and comprehensive air quality analysis from many sites including rural, suburban, urban, and roadside sites across the Kathmandu Valley.
METHODS

Passive Sample Collection

Passive Sampling during 2013

During the 2013 sampling, 644 week-long passive samples of NOx, NO2, SO2, O3, and NH3 were collected using Ogawa diffusive samplers (Model PS-100, Ogawa USA, Inc.) for 8 consecutive weeks between March 23rd and May 18th, 2013. This study collected concurrent samples from fifteen locations across remote and urban regions of the Kathmandu Valley, each site representing a unique setting of that area (Table S-1, Fig. 1). Site selection was based on publically-available land-use type datasets retrieved from International Centre for Integrated Mountain Development.

Fig. 1. Location of sampling sites in the Kathmandu Valley, and respective pollutant concentrations (µg m⁻³). The figure also includes pollution-rose plot for real-time O3 measurement (µg m⁻³) at Bode, the SusKat supersite, during 2013.
Further classification was implemented based on an approximate distance of a given site from the 28 km circle-like Ring Road surrounding Kathmandu metropolitan city and the northern part of Lalitpur district, including Lalitpur sub-metropolitan city. The sites located within this Ring Road are defined as urban sites. The immediate neighborhood setting of the site and distance from the urban core (i.e., area enclosed by Kathmandu’s Ring Road) were also taken into account while classifying the sites.

All samplers in this study were deployed by trained individuals and affixed under rain shelters. The samplers were exposed to ambient air at each site for 5–7 days before being collected and replaced. In addition, field blanks were also collected in the same procedure for the same period. The passive samplers are normally exposed in pairs, one for actual sampling and another for field blank. In this study field blanks were not collected at each site, but were collected at four key representative sites. No duplicate samples were collected in this study. However, Ogawa passive samplers have been proven to yield reproducible results in the past (Roadman et al., 2003; Meng et al., 2010, 2011). As particulate matter loading is quite high in ambient air in the valley, the samplers were replaced every week before the sampling pads start getting clogged with deposition of particles, which could reduce diffusion of gases and hence introduce measurement artifacts. After the completion of the sampling, these samples were then shipped to our laboratory for chemical analysis. Meteorological parameters such as amount of rainfall, wind speed and direction were also monitored at 6 locations that overlapped with sampling sites (Bode, Pakanajol, Nagarkot, Naikhandi and Bhimdhunga).

During the same sampling period, ozone data were collected at a stationary site using online ozone monitor (Model-400E, Teledyne Technologies, Inc., USA) at one of the sampling sites, Bode, that served as the supersite for SusKat-ABC campaign (Naja et al., 2016). Among the 15 sampling sites, 5 were classified as urban, 4 as suburban, and 6 as rural sites (Table S-1). NO was calculated as the difference between NOx and NO2.

Passive Sampling during 2014

Additional passive samples collected in 2014 included measurements from two seasons: the cold and dry winter, and warm and wet monsoon season. During the first phase of sampling (February 23rd to April 4th, 2014), a total of 5 week-long samples of NO, NO2, SO2 and O3 were collected consecutively at one site at a time using Ogawa passive samplers from 5 on-road (i.e., busy intersections of major traffic roadways) urban locations within Kathmandu city. During the second phase (July 27th–September 21st, 2014), a total of 13 week-long samples of the same gases were collected consecutively at one site at a time using Ogawa passive samplers from 13 locations across remote and urban regions of Kathmandu Valley. Overall, among 2014 sampling sites, 5 were on-road urban sites (these sites are the five on-road urban locations from the winter season mentioned above), 4 were urban background sites (i.e., urban sites situated farther from busy roadways), 2 were classified as suburban and 2 were rural sites (Table S-1, Fig. 1). In each case, a set of passive samplers was attached under a rain shelter that was immediately adjacent to, or in the median of, roadways.

Laboratory Analysis

The samples, including field blanks, were digested in ultrapure water. Extracted NOx and NO2 samples were analyzed using a spectrophotometer (SpectraMax-M2, USA), while SO2, O3 and NH3 extracts were analyzed using Ion Chromatography (Dionex-ICS-1100, USA). During analysis, internal standards and laboratory blanks were analyzed in between every ten samples for quality control; field blanks were treated as unknowns. Using the equations in Ogawa sampling protocols (Ogawa & Company, Pompano Beach, USA), liquid concentrations were converted to ambient atmospheric concentrations by incorporating adjustments for corresponding lab blanks, temperature, relative humidity, vapor pressure, sample dilution, and gas-specific diffusion coefficients.

RESULTS AND DISCUSSION

Wide variability of trace gases was observed in the Kathmandu Valley across time, location, and measured species during the sampling periods. The weekly mean concentrations for each gaseous pollutant measured during these different sampling periods are presented in Table 1: measurements from 2013 and Table 2: measurements from 2014. Data collected during 2013 is also further classified by sampling week and presented in Table S-2. In addition, 8-week average concentrations from 2013 and one-week concentrations from 2014 are shown in Figs. 2 and 3 (a and b), respectively. Although the 2013 measurements are limited to the winter season only (Fig. 2), we observed a spatially diverse profile of trace gases in the valley. From the 2014 measurements, it is interesting to note that monsoonal on-road concentrations were no lower than compared to winter season trace gas levels (Fig. 3(a)), where it was expected concentrations would be higher. Pollutant levels were of the same order of magnitude in two cases (i.e., NO and NO2) and were higher in other two (i.e., O3 and SO2) during the monsoon season of 2014 (Fig. 3(a)). Although not particularly evident from 2014 sampling period due to limited samples size, urban areas of Kathmandu Valley had elevated levels of trace gases except O3, whereas intermediate levels of all gases are observed in prominently residential suburban areas of the valley. Rural outskirts have lowest trace gas levels with the exception of ozone, where it was often highest (Figs. 2 and 3(b)).

Variability across Sites

The overall average concentrations of trace gases for 2013 winter season and 2014 winter and monsoon seasons are shown in Fig. 2 and 3, respectively. In addition, 2013 measurements are further classified based on recognized emission sources such as traffic intensity and distance from brick factories (Fig. S-1). The measurements in 2013 indicated that for all trace gaseous pollutants except O3, the average concentrations are highest in urban sites followed...
Table 1. 8-week mean concentrations of NO$_2$, NO$_x$, NO, O$_3$ and SO$_2$ in µg m$^{-3}$ of 2013 measurements. Eight consecutive weeks beginning on March 23$^{rd}$ and ending on May 18$^{th}$, 2013.

<table>
<thead>
<tr>
<th>Site type</th>
<th>Site</th>
<th>NO$_2$ Mean ± Standard deviation (µg m$^{-3}$)</th>
<th>NO$_x$</th>
<th>NO</th>
<th>SO$_2$</th>
<th>O$_3$</th>
<th>NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban</td>
<td>Bode</td>
<td>15.4 ± 2.7</td>
<td>19.6 ± 3.1</td>
<td>7.4 ± 1.0</td>
<td>39.2 ± 21.6</td>
<td>99.6 ± 27.7</td>
<td>19.5 ± 6.8</td>
</tr>
<tr>
<td></td>
<td>Indrachowk</td>
<td>32.6 ± 7.3</td>
<td>36.7 ± 6.5</td>
<td>4.7 ± 4.0</td>
<td>8.5 ± 5.2</td>
<td>74.2 ± 12.1</td>
<td>30.8 ± 14.0</td>
</tr>
<tr>
<td></td>
<td>Maharajgunj</td>
<td>28.8 ± 3.4</td>
<td>35.2 ± 2.5</td>
<td>6.4 ± 2.7</td>
<td>9.7 ± 4.8</td>
<td>90.9 ± 23.6</td>
<td>22.4 ± 4.8</td>
</tr>
<tr>
<td></td>
<td>Mangal Bazaar</td>
<td>27.3 ± 5.3</td>
<td>32.3 ± 4.3</td>
<td>5.6 ± 3.7</td>
<td>9.9 ± 5.4</td>
<td>78.9 ± 15.7</td>
<td>27.8 ± 14.4</td>
</tr>
<tr>
<td></td>
<td>Suryabinayak</td>
<td>24.8 ± 6.6</td>
<td>28.7 ± 5.7</td>
<td>4.5 ± 2.2</td>
<td>15.8 ± 7.4</td>
<td>80.9 ± 10.5</td>
<td>35.2 ± 15.2</td>
</tr>
<tr>
<td>Suburban</td>
<td>Bhaisepati</td>
<td>10.9 ± 3.4</td>
<td>13.4 ± 3.0</td>
<td>2.9 ± 2.1</td>
<td>9.1 ± 3.1</td>
<td>93.5 ± 17.9</td>
<td>18.1 ± 5.6</td>
</tr>
<tr>
<td></td>
<td>Budhanilkantha</td>
<td>7.0 ± 3.3</td>
<td>9.2 ± 2.3</td>
<td>2.3 ± 1.7</td>
<td>6.8 ± 2.9</td>
<td>98.6 ± 22.1</td>
<td>18.9 ± 8.6</td>
</tr>
<tr>
<td></td>
<td>Kirtipur</td>
<td>16.7 ± 2.1</td>
<td>19.7 ± 2.2</td>
<td>3.5 ± 0.9</td>
<td>9.4 ± 7.2</td>
<td>92.0 ± 19.2</td>
<td>23.2 ± 7.5</td>
</tr>
<tr>
<td></td>
<td>Lubhu</td>
<td>8.6 ± 2.8</td>
<td>11.4 ± 0.9</td>
<td>3.2 ± 3.2</td>
<td>12.0 ± 5.1</td>
<td>99.3 ± 16.9</td>
<td>22.7 ± 8.1</td>
</tr>
<tr>
<td>Rural</td>
<td>Bhimdhunga</td>
<td>8.0 ± 1.6</td>
<td>9.3 ± 1.4</td>
<td>2.0 ± 1.0</td>
<td>4.7 ± 1.6</td>
<td>117.0 ± 23.4</td>
<td>17.4 ± 7.1</td>
</tr>
<tr>
<td></td>
<td>Nala Pass</td>
<td>14.2 ± 5.8</td>
<td>15.9 ± 5.4</td>
<td>1.9 ± 1.6</td>
<td>6.5 ± 2.3</td>
<td>85.4 ± 20.6</td>
<td>22.3 ± 4.7</td>
</tr>
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<td></td>
<td>Sankhu</td>
<td>15.7 ± 13.9</td>
<td>17.2 ± 13.1</td>
<td>2.6 ± 1.8</td>
<td>6.8 ± 2.9</td>
<td>112.8 ± 23.4</td>
<td>15.2 ± 10.0</td>
</tr>
<tr>
<td></td>
<td>Tinpiple</td>
<td>9.8 ± 4.8</td>
<td>12.9 ± 3.9</td>
<td>3.5 ± 2.8</td>
<td>5.1 ± 2.1</td>
<td>106.7 ± 26.3</td>
<td>23.1 ± 12.1</td>
</tr>
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</table>

Table 2. Weekly concentration of NO$_2$, NO$_x$, NO, O$_3$ and SO$_2$ in µg m$^{-3}$ of 2014 dry and monsoon season measurements.

<table>
<thead>
<tr>
<th>Season</th>
<th>Site type</th>
<th>Sampling Dates (2014)$^a$</th>
<th>Site One week concentrations (µg m$^{-3}$)</th>
<th>NO$_2$</th>
<th>NO$_x$</th>
<th>NO</th>
<th>SO$_2$</th>
<th>O$_3$</th>
</tr>
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<td>Dry</td>
<td>Urban</td>
<td>Feb 23$^{rd}$–28$^{th}$</td>
<td>Balaju</td>
<td>116</td>
<td>232.2</td>
<td>116.2</td>
<td>-</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mar 2$^{nd}$–7$^{th}$</td>
<td>Gaushala</td>
<td>85.6</td>
<td>275.3</td>
<td>189.7</td>
<td>7.0</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mar 9$^{th}$–14$^{th}$</td>
<td>Kotashwor</td>
<td>101</td>
<td>239.3</td>
<td>138.2</td>
<td>-</td>
<td>30.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mar 23$^{rd}$–28$^{th}$</td>
<td>Tripureshwor</td>
<td>93.6</td>
<td>185.3</td>
<td>92</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mar 30$^{th}$–Apr 4$^{th}$</td>
<td>Jawalakhel</td>
<td>123.5</td>
<td>123.5</td>
<td>-</td>
<td>6.5</td>
<td>14.4</td>
</tr>
<tr>
<td>Monsoon</td>
<td>Urban</td>
<td>Jul 27$^{th}$–Aug 1$^{st}$</td>
<td>Balaju</td>
<td>88</td>
<td>88</td>
<td>-</td>
<td>32.5</td>
<td>9.6</td>
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<td></td>
<td></td>
<td>Aug 6$^{th}$–10$^{th}$</td>
<td>Jawalakhal</td>
<td>184.4</td>
<td>184.4</td>
<td>-</td>
<td>31.1</td>
<td>26.4</td>
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<td></td>
<td></td>
<td>Aug 10$^{th}$–15$^{th}$</td>
<td>Koteshwor</td>
<td>58.2</td>
<td>184.5</td>
<td>126.3</td>
<td>12.8</td>
<td>17.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aug 18$^{th}$–22$^{nd}$</td>
<td>Gaushala</td>
<td>115.1</td>
<td>335.6</td>
<td>220.5</td>
<td>-</td>
<td>11.8</td>
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<td></td>
<td>Sep 13$^{rd}$–19$^{th}$</td>
<td>Tripureshwor</td>
<td>64.4</td>
<td>96.2</td>
<td>31.9</td>
<td>-</td>
<td>17.4</td>
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<td>Aug 31$^{st}$–Sep 7$^{th}$</td>
<td>Baneshwor</td>
<td>31.8</td>
<td>36.5</td>
<td>4.7</td>
<td>1.2</td>
<td>14.1</td>
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<td>Sep 6$^{th}$–13$^{th}$</td>
<td>Dadhikot</td>
<td>24.7</td>
<td>28.8</td>
<td>4.1</td>
<td>-</td>
<td>5.1</td>
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<td></td>
<td>Sep 13$^{rd}$–21$^{st}$</td>
<td>Lainchaur</td>
<td>17.1</td>
<td>17.12</td>
<td>-</td>
<td>0.3</td>
<td>20.1</td>
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<tr>
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<td></td>
<td>Aug 27$^{th}$–Sep 3$^{rd}$</td>
<td>Lokanthali</td>
<td>11.9</td>
<td>11.9</td>
<td>-</td>
<td>-</td>
<td>13.2</td>
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<td>Suburban</td>
<td>Aug 27$^{th}$–Sep 3$^{rd}$</td>
<td>Kirtipur</td>
<td>4.2</td>
<td>47</td>
<td>42.8</td>
<td>4.3</td>
<td>14</td>
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<td></td>
<td>Sep 4$^{th}$–12$^{th}$</td>
<td>Balkot</td>
<td>5.6</td>
<td>6.2</td>
<td>0.6</td>
<td>-</td>
<td>13.6</td>
<td></td>
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<tr>
<td>Rural</td>
<td>Sep 6$^{th}$–12$^{th}$</td>
<td>Thankot</td>
<td>6.7</td>
<td>6.9</td>
<td>0.2</td>
<td>5.0</td>
<td>23.5</td>
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<tr>
<td></td>
<td>Aug 23$^{rd}$–Sep 3$^{rd}$</td>
<td>Godavari</td>
<td>5.4</td>
<td>5.4</td>
<td>-</td>
<td>-</td>
<td>6.9</td>
<td></td>
</tr>
</tbody>
</table>

$^a$: Measurements conducted in consecutive weeks at one site at a time.

by suburban and rural sites. The reverse holds true for O$_3$ concentrations with the highest O$_3$ concentrations at rural sites in 2013 (Fig. 2) and 2014 (Fig. 3(b)). From measurements taken during 2013, NO$_x$, NO$_2$, NO and O$_3$ concentrations were statistically different among urban, suburban and rural site types (ANOVA test, p < 0.05).

Measurements from 2013

Oxides of Nitrogen: Mean weekly concentrations of nitrogen oxide species (NO$_x$, NO$_2$ and NO) were highest at urban sites (NO$_2$ 25.8 ± 6.5 µg m$^{-3}$, NO$_x$ 30.5 ± 6.8 µg m$^{-3}$, NO 5.7 ± 1.2 µg m$^{-3}$) and lowest in rural sites (NO$_2$ 9.6 ± 4.6 µg m$^{-3}$, NO$_x$ 11.5 ± 4.6 µg m$^{-3}$, NO 2.4 ± 0.6 µg m$^{-3}$) (Fig. 2). Concentrations of these gases were highly variable with observed weekly concentrations in the valley ranging from 0.4–12.4, 0.2–46.0, and 4.1–46.7 µg m$^{-3}$ for NO, NO$_2$, and NO$_x$, respectively. The measurements were statistically different among these three site types (ANOVA test, p < 0.05). However, intergroup comparison using an ANOVA post-hoc analysis (with Bonferroni correction) showed a statistically significant difference between urban and suburban, and urban and rural site types, but not between suburban and rural site types.

NO$_2$ forms quickly from on-and off-road vehicular
Fig. 2. 2013 pre-monsoon season mean concentrations (µg m\textsuperscript{-3}) of gases classified by site types. Log Scale; error bars = standard deviation. (*) ANOVA (p < 0.05) significance between urban and suburban site types. (**) ANOVA (p < 0.05) significance between urban and rural site types.

Fig. 3(a). One week concentrations (µg m\textsuperscript{-3}) of gases from on-road urban sites classified by season, winter and monsoon of 2014. Log Scale; error bars = standard deviation.

Fig. 3(b). One week concentrations (µg m\textsuperscript{-3}) of gases from monsoon season of 2014 classified by site type. Note: On-road urban sites not included. Log Scale; error bars = standard error.
emissions and is a good indicator for the larger group of oxides of nitrogen (Lippmann et al., 2003). Since automobiles are the major contributors of oxides of nitrogen to ambient air pollution (Rakowska et al., 2014), elevated levels of NO2 are typically observed in urban sites where there is high traffic activity in the valley. Shakya et al. (2010) found that vehicle emissions are expected to be the most important air pollution source, particularly for PM, in the valley. Using NO2 as an indicator, highly urbanized areas such as Indrachowk were observed with the highest mean concentrations (32.6 ± 7.4 µg m⁻³) (Table 1). This contrasts with much lower concentrations (3.9 ± 2.0 µg m⁻³) at Nagarkot, a hill top site downwind of the valley surrounded by forest and minimal traffic and anthropogenic activities.

Byanju et al. (2012) also found similar results in which urban sites had the highest NO2 levels due to traffic emission and rural sites had the lowest NO2 concentrations within the Kathmandu Valley. This study has shown that monthly NO2 levels, particularly during the winter season, were highly elevated. Our measurements of NO2 at urban sites (range: 19.3–32.3 µg m⁻³) are comparable to what Byanju et al. (2012) have found during the 2008 dry season (8.2–32.2 µg m⁻³). These levels are also comparable to passive sampling results from urban and suburban locations of two major cities, Delhi and Kanpur, in India (Behera et al., 2015). Week-long monitoring of NO2 (0.2–46.0 µg m⁻³) indicated that levels likely remained below the NAAQS 24-hr level (80 µg m⁻³) throughout the 2013 sampling, though this is based on week-long measurements and it is not possible to discern daily concentrations. However, sites located in urban areas within the Ring Road have been reported to exceed NO2 recommended levels, particularly during the winter season (Byanju et al., 2012).

Traffic is the main source of air pollution in Kathmandu Valley where the transport sector in the valley is responsible for 86% of total anthropogenic NO emissions compared to the next highest contribution from manufacturing industries sector (6%) such as petroleum and brick kiln factories (Pradhan et al., 2012). At 14% annual growth rate between 2000 and 2010, approximately 570,145 vehicles have been registered in Bagmati zone (one of fourteen administrative zones in Nepal where Kathmandu Valley is located) during the fiscal year 2009/10 (Shrestha et al., 2013). This fact provides the basis to further classify and investigate the spatial association shown in (Fig. S-1(a)). Sampling locations within 2 km of Ring Road have the statistically significant highest levels of NO2 (ANOVA test, p < 0.05). NO2 is emitted directly from the combustion processes and also results from oxidation of NO (Yao et al., 2005). At the urban sites, slightly elevated levels of NO2/NOx ratio were found (80.2 ± 8.7%) compared to that of suburban sites (78.8 ± 4.3%) and rural sites (76.2 ± 8.0%). Ratios reaching as high as 95% and 96% in Indrachowk and Suryabinayak, respectively, were measured while the lowest ratios were observed in Nagarkot (37%) and Lubhu (21%). The increased NO2/NOx ratios at urban sites indicate that there is a significant contribution of primary NO2 from on-road vehicle sources to ambient air pollution. Previous studies have found that, under normal driving conditions, the reported primary vehicular NO2/NO ratio of gasoline engines varied from 2–5% to approximately 30% (Yao et al., 2005). This volume ratio has been found to be substantially higher for diesel engines. Tang et al. (2004) report volume ratios as high as 50% for diesel buses.

It is interesting to note the observed NO2/NOX ratios in the Kathmandu Valley which were higher than what many previous studies have reported. Carslaw (2005) noted an increasing trend over time of NO2/NOx in London, UK, explained by an overall decrease in NOx emissions in the diesel fleets, and an increasing fraction of primary NO2 within this NOx. However, most work in this field is on modern diesel vehicles, typically in western countries, and is not entirely relevant to the observations made in Nepal. A few possible causes for this ratio enhancement include the unique fleet emission profile endemic to Nepal, the influence of upwind brick kilns which have poorly understood effect on regional NOx, and the widespread, daily reliance on diesel power generators to ameliorate power disruptions across the Kathmandu Valley. Motorcycles and diesel vehicles are also widely used in the valley. It is likely a combination of these effects that lead to high NO2/NOx ratios, though week-long passive samples as used in this work may not be directly comparable to previous tunnel studies with high time resolution and thus are unlikely to provide any better insight or evidence necessary to test these hypotheses. Thus, more work in this area is needed to explain this observation.

In the valley, alternative fuel sources such as batteries and LPG (Liquified Petroleum Gas) used in light duty vehicles such as vans and microbuses make up only a small share of transport fuel consumption, while gasoline and diesel-powered vehicles dominate the valley (Shrestha et al., 2013).

High NO levels and low O3 concentrations observed at urban sites during the winter season suggest that ground level ozone most likely undergoes rapid NO titration in urban areas. Studies have found that places in the valley located in the immediate vicinity of very large NO emission, such as high traffic intensity areas, experience O3 concentration depression through reaction with NO (Pudasainee et al., 2006, 2010). Thus, it is quite plausible that high intensity traffic sources explain the observed higher NO2 near urban core Ring Road. In contrast, vehicle emission might be of lesser importance in rural sites such as Nagarkot, Naikhandi and Bhimdhunga, however, rural sites located downwind from Kathmandu city and northeast section of the valley (i.e., Sankhu and Nala Pass) show surprisingly higher NO2 levels. Prevailing southwesterly winds were dominant during the winter sampling period (Fig. 1) indicating that these compounds are advected from the urban areas to downwind sites, even if there aren’t many local sources at downwind locations. Additional significant sources at these rural sites may be NOx emission from brick kiln factories and anthropogenic combustion from suburban residential sites located within 1 km of these rural sites.

Sulfur Dioxide: SO2 concentrations during 2013 varied from site to site as shown in Table 1. The weekly mean SO2 concentrations at urban sites (16.6 ± 12.9 µg m⁻³) were...
higher than suburban (9.3 ± 2.1 µg m⁻³) and rural sites (6.9 ± 2.5 µg m⁻³) (Fig. 2). However, the spatial variation of SO₂ did not show statistically significant differences among site categories when ANOVA test was performed. The average SO₂ concentrations between Bode, Suryabinayak and Lubhub were in the range of 12.0–39.2 µg m⁻³ with the highest weekly average SO₂ concentration observed at Bode (39.2 ± 21.6 µg m⁻³) and Suryabinayak (15.8 ± 7.4 µg m⁻³), both urban locations, and somewhat lower levels in Lubhub (12.0 ± 5.1 µg m⁻³), a suburban site. These three sites are located within 3 km of at least 10 brick factories (Fig. S-1(b)), which typically use high quantities of low grade coal in brick production (Raut, 2006; Pariyar et al., 2013).

In contrast, sampling sites located with similar proximity but to fewer brick kiln factories are observed with lower SO₂ levels. Such sites included Kirtipur and Naikhandi where highest weekly averages levels reached 9.4 ± 7.2 µg m⁻³ and 11.7 ± 7.7 µg m⁻³, respectively. Sub categorizing these site types based on proximity to brick kilns showed no statistical significance at p < 0.05 using ANOVA test. The lowest average concentration of SO₂ was measured at Bhimdhunga, a mountain pass on the western rim of the valley, with an overall average of 4.7 ± 1.6 µg m⁻³. Bhimdhunga is a rural location with no nearby brick kilns and other major SO₂ sources.

Coal combustion in brick factories are likely to contribute to elevated ambient levels of SO₂. More than 100 brick kilns throughout the valley produce over 350 million bricks per year, and they are a significant emission sources of SO₂ and PM in the Kathmandu Valley, contributing to over 60% of total SO₂ and particulate matter emissions (Joshi and Dudani, 2008; Pariyar et al., 2013). Moreover, 74% of total anthropogenic SO₂ emissions in the valley result from combustion in the manufacturing industry that is mainly comprised of brick factories and other petroleum products (Pradhan et al., 2012). On the other hand, commercial and residential sectors accounts for just 16% of total anthropogenic SO₂ emission in the valley (Pradhan et al., 2012), indicating that SO₂ sources are mainly point sources such as brick kilns. Apart from mandatory gravity settling chambers on brick kiln factories, no other pollution control devices are in operation on 111 known brick kilns, 89 known stone crushing factories and 70 industries with boilers (Dhimal, 2009). Brick kiln facilities are concentrated in the southern and southeastern regions of the valley (Raut, 2006; Joshi and Dudani, 2008), this suggests a plausible source of SO₂ observed in high concentrations at Bode, Suryabinayak and Lubhub, all of which are located in the south and southeastern regions of the valley and close to the brick kilns. High levels of SO₂ in Naikhandi (11.7 ± 7.7 µg m⁻³), one of the southern locations in the valley, might be attributed to 6 brick kiln factories located within 3 km of this sampling site. Other studies in Kathmandu have also found elevated SO₂ levels (3.3–23.4 µg m⁻³) in the southeastern region of the valley where several brick kilns are located (Byanju et al., 2012; Pradhan et al., 2012). Much higher SO₂ levels were also measured in the 2001 dry season (36.7–78.6 µg m⁻³) at sites surrounded by brick kilns (Regmi and Kitada, 2003).

**Ammonia:** The weekly mean concentrations of ammonia at urban sites (27.2 ± 6.3 µg m⁻³) were higher than suburban (20.7 ± 2.6 µg m⁻³) and rural sites (19.8 ± 4.9 µg m⁻³) (Fig. 2). NH₃ concentrations varied from site to site as shown in Table 1; however, the variation was not significantly different across site categories. This might be attributable to fewer emissions of NH₃ from industries such as coke and ammonia production factories (Pradhan et al., 2012), compared to SO₂ and NO₂. Weekly concentrations in the valley varied from 3.0–50.4 µg m⁻³, with highest weekly averages in Suryabinayak (35.2 ± 15.2 µg m⁻³) followed by Indrachowk (30.8 ± 14.0 µg m⁻³), while the lowest weekly mean concentrations are in Nagarkot (14.4 ± 5.8 µg m⁻³) and Sankhu (15.2 ± 10.0 µg m⁻³), mainly forested areas. NH₃ plays a key role in the formation and neutralization of acidic atmospheric pollutants such as nitrates and sulfates (Sharma et al., 2007). About 47% of anthropogenic NH₃ emission in the valley comes from agriculture residues, soil emission, burning and manure management (Pradhan et al., 2012). In addition, the waste sector, which includes municipal waste and incineration, contributes 36% to the anthropogenic NH₃ emissions (Pradhan et al., 2012).

High NH₃ concentrations in Suryabinayak are likely attributed to fertilizer use and ammonia emissions from animal manure and chemical fertilizer used in nearby agricultural fields. In urban locations like Indrachowk these agricultural sources are not likely important, and it is possible this NH₃ is linked to municipal waste disposal and incineration. Dahal et al. (2011) have indicated increasing levels of municipal waste contamination in rivers throughout Kathmandu. Indrachowk, for instance, is located approximately half a kilometer away from highly polluted Bismumati River that cuts through the urban core. Other urban locations, such as Budhanilkantha and Maharajgunj, which are away from such rivers had lower NH₃ concentrations, and tended to have more typical of regional background levels indicated by the rural sample locations. These levels were typically around 19–22 µg m⁻³ on average. Generally, regions located downstream of major rivers in the valley had elevated NH₃ levels (Fig. S-1(c)), although one-tailed t-test showed no significance (p = 0.09) compared to upstream sites. Additional sources of ammonia in the valley include emissions from ammonia-based refrigeration and ammonia-based solvent manufacturing factories, and naturally from microorganisms involved in decaying animal matter and also in sewage treatment (Pradhan et al., 2012), including highly polluted rivers themselves, though these emission sources are poorly documented.

**Ozone:** The weekly mean concentrations of ground level ozone at rural sites (110.7 ± 17.0 µg m⁻³) were higher than suburban (95.9 ± 3.7 µg m⁻³) and urban sites (84.9 ± 10.2 µg m⁻³) as shown in Fig. 2. Variations across site type are significantly different (p = 0.01) from one another as indicated by ANOVA test, however, post-hoc analysis showed that significance was detected only between urban and rural site types. Among 15 sites, the 8-weekly average O₃ concentrations in the valley varied from a minimum value of 74.2 ± 12.1 µg m⁻³ (at Indrachowk) to a maximum value of 137.5 ± 19.1 µg m⁻³ (at Nagarkot). The highest weekly concentration was reported in Nagarkot (160.9 µg m⁻³) followed by...
Tinpiple (155.7 µg m⁻³) and Naikhandi (150.9 µg m⁻³), all of which are classified as rural outskirts. Nagarkot (1895 m asl) and Tinpiple (1450 m asl) are at higher elevations and Naikhandi (1250 m asl) is in the southernmost end of the valley from where the Bagmati River exits the valley. The lowest weekly concentrations are reported in Maharajgunj (50.1 µg m⁻³), an urban location.

It is not surprising to see ozone at higher levels at sites downwind of urban outflows. In Kathmandu Valley, there are many unregulated sources of ozone precursor gases (Sapkota and Dhaubhadal, 2002) including a high number of vehicles (Gurung and Bell, 2012), and fossil fuel and biomass combustion in manufacturing industries such as brick factories (Raut, 2006). NOₓ and Volatile Organic Carbon (VOC) emissions from such sources in the valley, as indicated in our measurements and past studies in the valley (e.g., Pudasainee et al., 2006) are likely sufficient to support ozone formation. The proportional contribution of NOₓ and several VOCs to O₃ formation in the valley requires further investigation.

Higher altitude locations also had elevated O₃ concentrations. For instance, Nagarkot and Bhimanthunga, the two most elevated sampling sites located at an elevation of 1895 m and 1530 m above sea level had highest mean (8 week) concentration of 137.5 ± 19.1 µg m⁻³ and 117.0 ± 23.4 µg m⁻³, respectively. One possible explanation could be elevated levels due to in-situ or in-transport conversion of its precursors such as NOₓ and VOCs. Other studies have also found elevated ozone levels at high altitude rural sites, for example, in Spain (Sánchez et al., 2005) and in India (Naja et al., 2003). Simultaneous increase of O₃ concentrations in early March and April at almost all sites, especially rural sites within the valley and on the valley rim, is also an indication of increase in background level ozone as a result of increased agro-residue burning and forest fire in northern South Asia. Meteorological factors, such as wind, play an important role in the dispersion and transportation of pollutants such as ozone (Tu et al., 2007).

Polar plots (Fig. 1, Fig. S-1) for O₃ concentrations monitored with an online instrument at the Bode site, based on frequency of count by local wind direction and wind speed, suggests that lowest O₃ concentrations occur when easterly wind direction is accompanied by low wind speed. In contrast, highest ozone was observed with southwesterly winds with strong wind speed which normally occur in the afternoons in winter and pre-monsoon season. High ozone concentrations observed at Bode, Sankhu and Nagarkot, sites located in northeastern part of the valley (downwind from major urban centers in the valley) are thus likely due to formation of O₃ in the polluted urban outflows and transport to these rural sites.

**Measurements from 2014**

Concentration data from passive sampling of NOₓ, NO₂, NO, SO₂ and O₃ in 2014 is presented in Table 2. Urban sites during the winter season had very high concentrations of oxides of nitrogen, with weekly averages frequently exceeding the 24-hour NAAQS guideline for NO₂ (80 µg m⁻³). Though not directly comparable, more than 30% of total 2014 winter season weekly measurements exceeded the 24-hour NAAQS level. This is not surprising as these are roadside measurements taken from main traffic intersections with heavy traffic movement in the valley. Large primary NO₂ concentrations were observed from on-road vehicle sources with NO₂/NOₓ ratios reaching as high as 58% at urban on-road sites in both seasons (43 ± 9.0% during winter season, and 46 ± 17.0% during monsoon season). Lower O₃ levels measured in 2014 compared to 2013 levels, particularly in urban areas, attribute to high NO concentrations in 2014 suggesting that ground level ozone was scavenged by NO titration. Studies have found that sampling sites located in the immediate vicinity of very large NO emission, such as high traffic density areas, experience high removal of ozone through reaction with NO (Derwent et al., 2003; Pudasainee et al., 2010).

SO₂ levels remained low throughout the dry season (Fig. 3(a)). Although a large fraction of the data was below the detection limit, higher average SO₂ levels were observed during the rainy season (25.4 ± 11 µg m⁻³) compared to winter season (6.7 ± 0.4 µg m⁻³) at urban sites. As discussed earlier, the major source of SO₂ in suburban and rural locations is brick production, an industry which does not normally operate in rainy season and hence the SO₂ concentrations were expected to be lower in rainy season. Also, frequent rain events wash away the SO₂ from the atmosphere through acidic rain formation. Incomplete site type and missing data limits our spatial variability interpretation of the SO₂ concentrations observed during the winter season alone. In contrast, spatial variability is observed during the monsoon season (Fig. 3(b)). Mean SO₂ levels were lower in urban areas (0.7 ± 0.7 µg m⁻³) compared to suburban (4.3 µg m⁻³) and rural (5.0 µg m⁻³) sites. O₃ levels in the monsoon season (14.0 ± 1.1 µg m⁻³) remained similar among all site types and also were comparable to winter season (14.0 ± 9.6 µg m⁻³). Moreover, mean concentrations of NO₂ at urban sites (21.4 ± 8.7 µg m⁻³) in the monsoon season were higher than suburban sites (NO₂ 4.9 ± 1.0 µg m⁻³) while mean concentrations of NOₓ and NO at urban sites (NO₂ 23.6 ± 11.1 µg m⁻³, NO 4.4 ± 0.4 µg m⁻³) were lower than suburban sites (NOₓ 26.6 ± 28.8 µg m⁻³, NO 21.7 ± 29.8 µg m⁻³) during the same monsoon season. Large NOvariability observed in Fig. 3(b) indicates that one site in particular, Kirtipur (Table 2), was responsible for deriving the average levels of NO and NOₓ to much higher levels. It is possible that highly localized sources emitting high levels of NO existed near sampling location in Kirtipur—perhaps a momentary spike in traffic activity at Tribhuvan University—during the time of measurement. As expected, the lowest levels of NOₓ and NO (6.2 ± 1.1 µg m⁻³ and 1.0 µg m⁻³, respectively) were observed in rural sites; although rural NO levels were measured at one site only. NO₂ concentrations at rural sites (6.1 ± 0.9 µg m⁻³) were slightly higher than suburban sites (4.9 ± 1.0 µg m⁻³), however, this can be explained by NO₂ long range transport (Zien et al., 2014) or a highly localized source during the measurement week. The effect could have also been observed due to limited number of sampling sites used in the site type stratification.
**Temporal Variations**

**Measurements during 2013**

Week to week variation in the valley during 2013 is presented in Table S-2. In rural sites, NO\textsubscript{2} concentration variation between the first two sampling weeks (i.e., March 23\textsuperscript{rd}–April 6\textsuperscript{th}, 2013) and the last two sampling weeks (i.e., May 4\textsuperscript{th} to May 8\textsuperscript{th}, 2013) was found to be significant (ANOVA test, $p = 0.03$). NO\textsubscript{2} levels in urban and suburban regions showed higher concentration in May than March, although not statistically significant. NO\textsubscript{x} and NO levels showed higher concentrations in March than the late periods of the pre-monsoon season, and the temporal variations showed significance for NO at all sites ($p = 0.001$, $p = 0.003$, $p = 0.01$ at urban, suburban and rural, respectively).

Higher significance of NO change in urban areas indicate the high variability of this gas with respect to traffic intensity and meteorological conditions such as amount of solar radiation compared to suburban and rural areas. One possible explanation for the higher NO\textsubscript{x} levels in March could be the seasonal component of oxides of nitrogen species, where drier and colder conditions contribute to the presence of many other reactive nitrogen oxides, other than NO\textsubscript{2}. The mixing ratio of each component of nitrogen oxide species is observed being the highest during the driest seasons in Quebec, Canada, due to seasonal cycle partitioning of NO\textsubscript{x} (total odd nitrogen) that includes HNO\textsubscript{3}, NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} (Hayden, 2003).

Another interesting observation is that NH\textsubscript{3}, O\textsubscript{3} and SO\textsubscript{2} concentrations in the valley were higher during the relatively dry first half of the sampling duration, particularly during the third week of sampling (April 6\textsuperscript{th}–13\textsuperscript{th}, 2013) than rest of the sampling period. Winter and sunny days during late March and early April possibly attributed to these highest levels, compared to the lowest levels during the rainy weeks observed in the relatively wet second half of the sampling period (i.e., week 5–8). Also, brick factories, a major source of SO\textsubscript{2}, were operating from around 20\textsuperscript{th} Jan to 20\textsuperscript{th} April 2013 (personal communication with M. Chitrakar, President of the Federation of Nepalese Brick Industries). Although weekly average concentrations of these gases show temporal variations, all pollutants except O\textsubscript{3} remained within 24-hr NAAQS limits throughout the sampling period. The higher O\textsubscript{3} in March–April is also linked to regional scale enhancement in O\textsubscript{3} due to extensive forest fire and agro-residue burning in the region.

A total of 50 (42%) weekly O\textsubscript{3} measurements in the valley exceeded 100 µg m\textsuperscript{-3}. It can be inferred from the weekly average O\textsubscript{3} concentrations that O\textsubscript{3} levels in many parts of the valley likely exceed the WHO 8-hour guideline. It should be noted here that we cannot make direct comparison between weekly data and 8-hour permissible limits.

At the Bode site, where O\textsubscript{3} concentrations were monitored simultaneously with both passive and active sampling methods, it was found that five out of eight weekly measurements using passive sampling exceeded 100 µg m\textsuperscript{-3} (Fig. 4). Online continuous measures of ozone monitored at the same site shows that 8-hour running mean concentrations remained between 60–160 µg m\textsuperscript{-3} and exceeded the WHO 8-hour guideline for 60% of the days between March 23 and May 18, 2013. Comparison of these two sampling methods indicated that passive sample measurements of ozone were likely to be biased low, on the order of a factor of 20–30%, possibly due to deposition of particles on the sampling pad that might have reduced the diffusion process. However, passive samplers have been used extensively to monitor ambient O\textsubscript{3} in Europe (Bytnerowicz et al., 2002a) and North America (Bytnerowicz et al., 2002b). Nonetheless, this has important public health relevance as O\textsubscript{3} levels higher than 100 µg m\textsuperscript{-3} are associated with 1–2% increase in daily mortality (WHO, 2005). The highest monthly peaks were recorded in April, and the lowest in late March and May as shown in Fig. 4. Pudasainee and colleagues (2006) found that enhanced ozone concentrations were due in part to long sunshine hours during the spring season (i.e., March – May) in the valley, prior to the more frequent cloud cover prevalent during the rainy season. Ozone measurements collected in 2004 (Pudasainee et al., 2006) at Pulchowan (an urban site 7 km west of Bode) reported that the hourly levels of ozone during the same spring season peaked at a maximum of 120 µg m\textsuperscript{-3}. Our findings, on average, were observed to be somewhat higher than previous measurements with hourly maximums peaking up to 200 µg m\textsuperscript{-3} (Fig. 4). This suggests that ozone levels in the valley have increased over time over the past decade. Other studies in neighboring countries have also found high levels of ozone in Delhi, India (Jain et al., 2005) and increased background levels of ground ozone by 0.5% per year from 1950s to 1990 in Ahmedabad, India (Naja and Lal, 1996) indicating that this may be a regionally important issue.

**Measurements during 2014**

Dry winter and monsoon measurements of NO\textsubscript{2}, NO\textsubscript{x}, NO, SO\textsubscript{2} and O\textsubscript{3} were made at five on-road urban locations (Fig. 3(a)) in 2014. NO\textsubscript{2}, NO, and NO\textsubscript{x} concentrations showed higher levels in the winter season (NO\textsubscript{2} 103.9 ± 15.7 µg m\textsuperscript{-3}, NO 233.1 ± 36.8 µg m\textsuperscript{-3}, and NO\textsubscript{3} 134.1 ± 41.6 µg m\textsuperscript{-3}) compared to the monsoon season (NO\textsubscript{2} 102 ± 51.2 µg m\textsuperscript{-3}, NO 168.8 ± 25.8 µg m\textsuperscript{-3}, and NO\textsubscript{3} 126.2 ± 94.3 µg m\textsuperscript{-3}). Similar NO\textsubscript{x} levels were observed across the two seasons, likely because the focus of this study was on-road emissions in busy roadways. Our findings of NO\textsubscript{2} levels (103.9 ± 15.7 µg m\textsuperscript{-3} and 102 ± 51.2 µg m\textsuperscript{-3} during dry and wet season, respectively) are at least a factor of two higher than the urban site 7 km west of Bode) reported that the hourly levels of nitrogen oxides (including NO\textsubscript{x}) that includes HNO\textsubscript{3}, NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} (Hayden, 2003).

In contrast, SO\textsubscript{2} and O\textsubscript{3} levels were elevated in the monsoon season (SO\textsubscript{2} 25.4 ± 11 µg m\textsuperscript{-3} and O\textsubscript{3} 16.6 ± 6.5 µg m\textsuperscript{-3}) compared to the winter season (SO\textsubscript{2} 6.7 ± 0.4 µg m\textsuperscript{-3} and O\textsubscript{3} 14 ± 9.6 µg m\textsuperscript{-3}). This is contrary to the previous study (Byanju et al., 2012) that reported higher levels of SO\textsubscript{2} during the winter season. It should be noted that fewer samples of SO\textsubscript{2} are available in this study because 50% of collected on-road samples were below the detection limit (Table 2). Comparing SO\textsubscript{2} levels at Jawalakhel, where both monsoon and winter levels are available (Table 2), it is possible that an air pollution episode might have occurred during the second week of August 2014 causing levels of
pollutants to be elevated. At Jawalakhel, NO levels during monsoon season were below the detection limit possibly because of reaction with high O₃, suggesting high ozone levels (Table 2). In addition, lower O₃ levels during the winter season could be partly explained by the presence of higher NO levels in the winter season compared to the monsoon season; leading to enhanced O₃ titration by NO. These five on-road urban sites are in the immediate vicinity of very large NO emissions from high traffic intensity, and such levels are pronounced during the winter season where concurrent ozone concentration depression is often observed (Pudasainee et al., 2006, 2010). Thus, it is likely that high intensity traffic sources explain the temporal variations observed among NOx species and O₃ levels.

CONCLUSION

Measurements of NO₂, O₃, SO₂ and NH₃ at 28 sites in the Kathmandu Valley, Nepal during 2013 and 2014 using a passive sampling technique showed variations across the site types, locations, and seasons. Their concentrations showed large spatial and temporal variations, particularly for O₃. The data show a clear association of nitrogen oxides pollution in the valley with traffic activities, and sulfur dioxide pollution with fossil fuel combustion, most likely from low-quality coal combustion in brick kiln factories. An increasing rate of poorly maintained vehicles in the valley continues to indicate that traffic emission is one of the largest contributors to degrading air quality in the Kathmandu Valley. Substantial ammonia, thought to be linked to agricultural and municipal solid waste, particularly near rivers, was observed. This indicates that several highly polluted rivers in the valley, such as Bagmati and Bishnumati, could be a substantial source of air pollution. Lastly, evidence suggested that meteorology, particularly wind speed and direction, plays a decisive role in building up or ventilation of pollutants in
valley, where ozone was observed at lower levels within the urban regions and at high concentrations, often exceeding the WHO recommended guidelines, downwind of these urban centers. This work provides a broad analysis of anthropogenic gases by incorporating multiple sites over the wide range of the Kathmandu Valley, a region known for its notorious particulate matter pollution. It is still the main pollutant that pose serious health risks to 3.5 million residents of the valley, and thus requires priority mitigation actions. Our measurements from 28 sites across the valley clearly indicate that \( O_3 \), which is toxic to both human and plants, especially crops, is also an important pollutant of concern that requires immediate attention for its control through mitigation of its predecessors. These results could be useful to aid urban planning and pollution mitigation efforts that will encourage cleaner, healthier, more sustainable and livable cities across the Kathmandu Valley.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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