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

A Thesis Presented

By

FILIMON KIROS

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

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Public Health

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ACKNOWLEDGEMENTS

“To fear the Lord is the beginning of wisdom and knowledge!” Proverb 1:7. First and foremost, I would like to praise and thank God “Igziabethair Yimesgen; Emebaetae Mariam lezele’alem fikrish ayileyegn, Amen!” (in Amharic language), for I would not have accomplished my work without His guidance and protection.

Secondly, I would like to sincerely thank my advisor, Dr. Richard Peltier, for his sustained mentorship, guidance and encouragement. I would also like to mention my sincere appreciation for the financial support provided by the Institute for Advanced Sustainability Studies for the field campaign, and assistance of Dr. Maheswar Rupakheti and his team for passive sample collection during 2013 campaign, and the International Centre for Integrated Mountain Development for partial funding this work. I would also like to sincerely thank the Initiative for Maximizing Student Development/ Post-baccalaureate Research Education Program (IMSD/PREP) at the University of Massachusetts for providing me with partial financial and academic support throughout my graduate studies. Also, I would like to thank these people who have made valuable contribution to my work: Kabindra Shakya, Rashmi Maharjan, Rejina Byanju, Ram Regmi, Manish Naja, Khadak Mahata, and Bhogendra Kathayat. Last but not least, I would also like to recognize the continued support I received from my family and friends.
ABSTRACT

VARIABILITY OF ANTHROPOGENIC GASES: NITROGEN OXIDES, SULFUR DIOXIDE, OZONE AND AMMONIA IN KATHMANDU VALLEY, NEPAL
MAY 2017
FILIMON KIROS, B.S., UNIVERSITY OF MASSACHUSETTS AMHERST
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Background: Kathmandu Valley is one of the largest and most polluted metropolitan regions in the Himalayan foothills. Rapidly expanding urban sprawl and 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 and World Health Organization guidelines.

Objectives: The aim of this study is to quantify the distribution of gaseous pollutants across the valley characterized by different emission sources, and also 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 in the Kathmandu Valley.

Methods: In order to understand the spatial variation of the trace gases in the Kathmandu Valley, passive samples of SO$_2$, NOx, NO$_2$, NH$_3$, and O$_3$ were simultaneously collected 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.

Results: In 2013, urban sites were observed to have higher weekly averaged NO$_2$ and SO$_2$ (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/m³, respectively). Regions located within 3 km of brick factories exhibited higher SO₂ concentrations (22.3 ± 14.7 µg/m³) than sites at least than 3 km away (5.8 ± 1.1 µg/m³). Increased NH₃ levels were observed at sites downstream from polluted rivers (25.8 ± 5.5 µg/m³) compared to upstream sites (19.9 ± 3.6 µg/m³). Increased O₃ was observed in rural locations (108.5 ± 31.4 µg/m³) compared to urban sites (87.1 ± 9.2 µg/m³) (ANOVA, p<0.05), emphasizing the importance of meteorological factors and movement of precursor pollutants via urban outflow.

**Conclusions:** Parallel to previous studies that found O₃ levels that exceeded guideline, 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, NO₂ near high traffic activity and SO₂ around brick factories are also important pollutants that need more intensive monitoring, primarily due to their importance in particulate matter formation chemistry.
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CHAPTER 1
INTRODUCTION

1.1 Background

According to World Health Organization (WHO), approximately 3.7 million deaths out of total global mortality were attributed to outdoor air pollution in 2012 alone (WHO, 2014), and the mortality rates nearly double when taking into account impacts from indoor air pollution. In 2012, about 89% of the premature deaths due to the ambient air pollution occurred in low and middle income countries from illnesses such as stroke, heart disease, lung cancer and both chronic and acute respiratory diseases (WHO, 2014).

The United States Environmental Protection Agency (US EPA) reports that the major constituents of atmospheric air pollutants include particulate matter and anthropogenic gases (EPA, 2012). Among anthropogenic gases, the US EPA has designated tropospheric ozone, carbon monoxide, sulfur dioxide and oxides of nitrogen as criteria pollutants due to their significant potential to affect human health and the environment. Due to such pollutants, 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).

1.1.1 Air pollution in Kathmandu Valley

Kathmandu Valley is surrounded by mountains creating a distinctive bowl shaped area which 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 (Regmi et al., 2003; Sapkota and Dhaubhadel, 2002). 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 (Panday et al., 2009: Sapkota and Dhaubadel, 2002), making the valley one of the most polluted regions in Nepal.

Previous studies have identified Kathmandu’s urban sprawl, rapidly increasing vehicle fleet, and expanding industries as contributors to poor air quality within the valley and boarder surrounding region in the Himalayan foothills (Shah and Nagpal, 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 NOx, SO$_2$, and O$_3$ in Kathmandu Valley.

In the Kathmandu Valley, there are 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 small number of emissions control strategies or regulations exist to ameliorate the air quality concerns in the Kathmandu Valley, but due to weak enforcement of existing regulations, many of these sources continue to emit pollutants unabated.

1.1.2 Health effects of gaseous pollutants

Degraded air quality is linked to a variety of health effects, and that these exposures trigger both direct health end points (inflammation, toxic chemical accumulation) as well as act as triggers for longer term non communicable diseases (cardiovascular and pulmonary diseases). Several acute and chronic effects on human health have been associated with breathing NOx (Chen et al., 2012), SO₂ (Kan et al., 2010) and O₃ (Jhun et al., 2014). A wide range of health effects are observed ranging from upper respiratory irritation to chronic respiratory disease, aggravated asthma attacks, acute respiratory infections in children and chronic bronchitis in adults, heart disease and lung cancer, premature mortality and reduced life expectancy (WHO, 2005). Exposure to increased levels of NO₂ and O₃ can also induce oxidative stress that triggers a variety of health problems such as lung inflammation, shortness of breath and aggravated asthma, emphysema, and chronic bronchitis (EPA, 2012).

NO₂ has adverse health effects in both long and short term exposure timeframes, and asthmatics have been shown to be more sensitive to NO₂ exposure. NO₂ is strongly related to PM, as both are often emitted from the same combustion sources which makes it is difficult to differentiate the effects of NO₂ from those of other pollutants in epidemiology studies (WHO 2006). Studies have shown that a strong correlation exists between NO₂ and fine and ultrafine
particulate matter, inorganic acids, elemental and organic carbon and therefore this gas can be considered as a reasonable tracer of the complex gas-particle mixture that originates from traffic (Seaton and Dennekamp, 2003). A multi-city study in Europe has found that the effect of PM on daily mortality was greater in areas with high NO₂ levels (Samoli et al. 2003). Short term exposure studies have indicated that daily average concentrations of NO₂ are significantly associated with increased overall, cardiovascular, and respiratory mortality. For example, after adjusting for the effects of PM, a meta-analysis report shows a 0.9% increase per 24 ppb (45.9 µg/m³) of NO₂ (24hr mean) as an effect estimate for all-cause mortality (Stieb et. al., 2002). In addition, a 10 µg/m³ increase in 24hr mean NO₂ level has been found to increase hospital admissions due to respiratory causes by 0.4-0.5% (Bylin and Forsberg, 2009). Other studies have suggested that long-term exposure of oxides of nitrogen (i.e. NO₂ and NO) were associated with an increased risk of all-cause mortality (Felleul et. al, 2005, Hoek et. al., 2002), although most of the association was attributed to PM pollution. Other long-term effects of increased concentrations of NO₂ include an observed association with childhood cancer and lung cancer in adults, association with decreased lung function in children and in adults, and association with an increased incidence of asthma in children (WHO 2006).

Acute and chronic exposure to O₃ has been associated with several health outcomes such as inflammation and reduction of pulmonary function. For short-term exposure, WHO reports that there is a significant increase in mortality observed above 50-70µg/m³ of O₃ measured at 8 hour average (WHO, 2008). WHO also reports that, unlike NO₂, the health effects of O₃ occur independently without being masked by PM. at least in short term exposures. For example, Bell et al (2005) and Levy et al., (2005) showed a significant association between O₃ and short-term mortality that was not substantially altered by exposure to other pollutants (such as PM) and
factors such as meteorological parameters. Increases in total mortality have been observed at a concentration as low as 75 μg/m³ (1-hour mean) (Gryparis et al., 2004). Other studies have used hospital admission attributed to respiratory tract infections and exacerbation of chronic airway diseases as health end-points to find health effect associations to acute O₃ exposure. For example, an increase of 100 μg/m³ O₃ level was associated with admissions for pneumonia with a 2-day lag (RR = 1.14, 95% CI 0.94–1.38) and for COPD with a 1-day lag (RR = 1.17, 95% CI 0.86–1.60) amongst and elderly population in Alabama (Schwartz, 1994a), Michigan (Schwartz 1994b) and Minneapolis (Schwartz 1994c), U.S. Burnett et al. (2001) found a 35% increase (95% CI 19–52) in the daily hospitalization rate for respiratory problems associated with a 5-day moving average of the daily 1-hour maximum O₃ of 90 μg/m3. Studies have also used health end-points such as hospital admission and school absenteeism to provide evidence that acute exposure to O₃ increases morbidity rates. For example, by using school absenteeism due to respiratory events as an end-point, Chen et al (2000) conducted a study in an elementary school in Nevada and showed that a 100 μg/m³ increase in ambient O₃ levels was estimated to increase absence from school by 13%. Similarly, another study found that ambient levels of O₃ greater than 260 μg/m3 for two consecutive days resulted in a 20% increased absence from kindergarten schools in Mexico City, Mexico (Romieu et al 2002). And by using emergency department visits for asthma as a health end-point, a 100-μg/m3 increase in 1-hour O₃ was associated with 35% increased likelihood of wheeze among in asthmatic children in New Haven, Connecticut (Gent et al 2003). Similarly, for children 3–15 years of age, there was an increase of 5% in lower respiratory symptoms for a 50-μg/m3 increase in O₃ level (Ostro et al. 1999). Consistent results were observed in long term exposure studies, where Jerrett et al (2005) found a 2% estimated
increase in relative risk of death from respiratory causes that was associated with 10µg/m³ increment in O₃ concentration.

As a primary irritant, SO₂ can have severe health effects, both short-term and long-term. In general, chronic exposure to SO₂ is associated an overall increase in morbidity and mortality (Zhang et al 2000). Several health effects of chronic exposure include: wheezing, mild dyspnoea, persistent cough, and chronic obstructive pulmonary disease (COPD) (Wichmann and Heinrich 1995, and Jammes 1998). Exposure to SO₂ has also been associated with cardiovascular abnormalities including decrease in heart rate variability (Tunnicliffe et al. 2001). In two European cities (Paris and Milan), there was a significant 4% increase associated with hospital respiratory admissions in associated with annual mean SO₂ of 50 µg/m³ (Dab et al 1996). And the Harvard Six cities study showed that increased mortality was observed in cities with higher SO₂ levels (Dockery et al 1993). Increases in mortality have been associated with increased proportions of ambient SO₂ levels. The elevated death rate is due to respiratory and pulmonary diseases, along with cardiovascular and cerebrovascular diseases, including coronary and ischemic heart diseases and atherosclerotic diseases (Chang et al 2003). Short term (less than 24 hour) SO₂ exposure studies report that health effects such as reductions in Forced Expiratory Volume in 1 sec (FEV1), increases in specific airway resistance, and symptoms such as wheezing or shortness of breath (Linn et al. 1984). Long-term exposure to lower concentrations of SO₂ causes throat irritation and bronchoconstriction, particularly among individuals with asthma (Kampa & Castanas, 2008). Although the main target system for exposure and toxic action is the respiratory system, SO₂ can also cause severe irritation to other body parts such as the eye and skin from direct contact (Witek et al 1985).
In addition to their direct impact on health, such gaseous pollutants also cause harm to health by contributing to the formation of secondary aerosols such as sulfate, nitrate, and ammonium that were found to be the main inorganic constituent of PM at an urban location in Kathmandu (Shakya et al., 2010). Health effects of ammonia are often indirect through contribution to ammonium ion formation which increased the health burden attributed to particle matter formation. Adverse health effects are often strongly associated with exposure to particulate matter (PM) (WHO, 2005), and it is one of the main health risk in the Kathmandu Valley (Regmi and Kitada, 2003).

1.1.3 Sources of gaseous pollutants

The main anthropogenic sources of these gases are mobile and stationary combustion sources, such as fossil fuel combustion. Oxides of nitrogen, such as NO₂, are formed when NO (primary pollutant emitted from combustion activity) rapidly reacts with oxidizing agents such as O₃ or radicals in the surrounding atmosphere forming NO₂. Tropospheric ozone (i.e. ground-level ozone) is formed by a series of reactions involving NO₂ and Volatile Organic Compounds (VOCs), with the catalytic involvement of ultraviolet radiation from sun light (Venkataramani et al., 2010). Anthropogenic SO₂ emission results from the combustion of sulfur containing fossil fuels such as coal, heavy oils and the smelting of sulfur containing ores (Kampa & Castanas, 2008). Although NH₃ is most present from natural sources as it is emitted by microorganisms involved in the decay of animal matter and is often a byproduct of agricultural activities, it can be used as an indicator for poor sewage treatment systems that can pollute rivers and streams. Industries such as coke and ammonia production factories also contribute to anthropogenic emissions of NH₃ in the atmosphere (Pradhan et al., 2012)
1.1.4 Air quality standards in Nepal

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\(^3\)). 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).

1.2 Passive sampling

Air quality monitoring and sampling is often conducted by either passive or active sampling techniques. Unlike active sampling which requires the use of a pump to actively pull air through the collection media; passive sampling does not require active air movement from a pump. Rather, gases are captured by a diffusion process through a static air layer or permeation through membrane in accordance with Fick’s first law of diffusion (Salter, 2005). The basic principle on which passive samplers operates is of molecular diffusion, whereby the molecules of gas diffusing from the region of the high concentration (i.e. the surrounding atmosphere) to the region of the low concentration (i.e. absorbent pad of the sampler). With efficient reliability, the filters used in passive samplers are built for single-use application designed to absorb or attach to a specific pollutant over sampling time periods ranging from weeks to months depending on study timeframe.

Passive samplers can be used to monitor gaseous pollutants such as O\(_3\), NH\(_3\), SO\(_2\) and NO\(_2\). In recent years, various types of passives samplers such as Ivl-Sweden, Gradko-UK, and
Ogawa-Japan have been introduced into the global market. Ogawa passive samplers have been widely used and validated for ambient trace gas monitoring (Meng et al., 2010; Roadman et al., 2003). As a badge type passive sampler manufactured by the Ogawa Incorporated, Japan, the Ogawa sampler is comprised of two chambers (Ogawa & Co., 2014). In each chamber of the sampler, the setup of the sampler starts at the innermost position with the pad and pad retaining ring, stainless steel screen along with coated collection filter pads which progress outwards to the diffuser end cap (Figure 1.) The Ogawa filter pad’s impregnated with pollutant specific absorbing reagents was used for sampling the gases. The filter pads are coated with a different chemical absorbent depending upon which pollutants to be monitored were loaded on the sampler (Table 1).

![Figure 1: Ogawa passive sampler (a) assembled into a badge and (b) parts 1) End Cap; 2) Stainless Steel Screen; 3) Pre-Coated Collection Pad; 4) Retainer Ring; 5) Inner Base Pad; 5) Sampler Body. (Photos from: Ogawa & Co., 2014)](image)

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*PTIO: 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide
1.3 Rationale

Previous studies have noted exceedances of the WHO guideline value for O$_3$ in the Kathmandu Valley between 2003 and 2004 (Pudasainee et al., 2006), as well as NO$_2$ and SO$_2$ (CAI-Asia, 2010) across weekly or 8-hour averaged data. Though these studies are not directly comparable to 24-hour SO$_2$ and NO$_2$ standards or sampling methods, the data provides us with insight on the Valley’s degraded air quality during certain time periods. Beyond these few studies, little quantitative data has been published on gaseous air pollutants and air quality in general within the Kathmandu Valley and broader surrounding region in the Himalayan foothills, despite the apparent presence of high concentrations of these trace gases and particulate matter.

A particular challenge in conducting measurements in Kathmandu is the lack of operational ambient air monitoring stations, which have been largely nonfunctional since 2008 mainly due to frequent power outages and the lack of financial power to provide the necessary maintenance needed for the monitoring equipments (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 and financial limitations, adopting a passive sampling measurement method is a useful option for collecting samples in developing countries such as Nepal. Passive sampling technique 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. Therefore, these samplers can be effective for a developing country like Nepal which still lacks effective continuous monitoring (Pradhan et al., 2011). Furthermore, knowledge about the temporal and spatial distributions of these trace gases gained through such passive sampling techniques can help assess the emission sources of these gases, and hence improve the understanding of air quality and its health effects in Kathmandu Valley. By utilizing passive sampling techniques, this paper has attempted to provide a broad and comprehensive air quality analysis from many sites including rural, suburban, urban, and roadside sites across the Kathmandu Valley.

1.4 Research Question

a) What are the ambient concentrations of NO₂, NO, NOx, SO₂, NH₃ and O₃ in Kathmandu Valley?

b) Are there meteorological factors that may contribute to temporal and spatial patterns of these gaseous pollutants?

c) Are there any specific known sources to these gases near sampling regions?

1.5 Hypothesis Statement

Weeklong passive sampling in Kathmandu Valley will capture ambient levels of pollutants that exceed Nepal’s ambient standards and recommended levels that may have negative implications on the health outcomes of the population residing within the valley. In addition, the concentration and dispersion of these gaseous pollutants in the valley depends on factors such as the presence of local and distant emission sources, and topographic and meteorological conditions that will cause apparent spatial and temporal variations.
1.6 Objectives

My objective through this work is: (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.

As the scope of my master’s thesis work, I will present week-long measurements of nitrogen oxides (NOx), nitrogen dioxide (NO₂), nitric oxide (NO), surface ozone (O₃), sulfur dioxide (SO₂), and ammonia (NH₃) using Ogawa passive samplers at multiple sites in the Kathmandu Valley. The field study 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 during three discrete field campaigns: pre-monsoon season in 2013 and briefly presented data from winter and monsoon season of 2014, across 28 sampling sites. It is important to indicate, however, that I was not involved in the study planning and sample collection at field sites. I began my graduate studies post-SusKat-ABC in the Fall of 2015 and the extent of my involvement in this campaign does not go beyond laboratory measurements that I conducted during my post-baccalaureate fellowship and data analysis of already-collected samples during my graduate studies.

1.7 Limitations
• In this study field blanks were not collected at each site, other than at five key representative sites.

• No duplicate samples were collected in this study.

• There was 5-13 months lag period between end of sampling period and laboratory analysis due to shipment period and instrument malfunction.

• Samples were not kept in a cool environment (i.e. refrigerated) prior to being shipped to our laboratory

• Sensitivity of method for \( \text{SO}_2 \) analyte (i.e. sulfate ion). Elevated sulfate compound detected in laboratory blanks.
CHAPTER 2

METHODS AND MATERIALS

2.1 Study area and site selection

Located in Bagmati administrative zone in Nepal, the Kathmandu Valley consists of three major districts: Kathmandu (capital city), Lalitpur and Bhaktapur district (Figure 2). The selection of the passive sampling area 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). The field study was carried out during 2013 pre-monsoon season (March-May) across 15 sampling sites (Table 2). The stratification of sampling sites into urban, sub urban and rural was based on publically-available land-use type datasets retrieved from International Centre for Integrated Mountain Development (http://rds.icimod.org/).
Figure 2: Location of Kathmandu Valley. Black dots represent all 15 sampling locations.

Table 2: Description of passive sampling sites

<table>
<thead>
<tr>
<th>Season</th>
<th>Site</th>
<th>Site Type(^{(1)})</th>
<th>Land use type(^{(1)})</th>
<th>District/Region(^{(2)})</th>
<th>Geographic Location/Altitude (m)(^{(3)})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2013 Winter</strong></td>
<td><strong>Indrachowk</strong></td>
<td>Urban</td>
<td>Built-up/residential</td>
<td>Kathmandu/Central</td>
<td>27°42'44&quot;N, 85°18'36&quot;E 1311</td>
</tr>
<tr>
<td></td>
<td><strong>Maharajgunj</strong></td>
<td>Urban</td>
<td>Built-up/residential</td>
<td>Kathmandu/Central</td>
<td>27°44'12&quot;N, 85°19'50&quot;E 1341</td>
</tr>
<tr>
<td></td>
<td><strong>Mangal Bazaar</strong></td>
<td>Urban</td>
<td>Built-up/residential</td>
<td>Lalitpur/Central</td>
<td>27°40'25&quot;N, 85°19'36&quot;E 1324</td>
</tr>
<tr>
<td></td>
<td><strong>Bode</strong></td>
<td>Urban</td>
<td>Built-up/agriculture</td>
<td>Bhaktapur/East</td>
<td>27°41'27&quot;N, 85°23'19&quot;E 1344</td>
</tr>
<tr>
<td></td>
<td><strong>Suryabinayak</strong></td>
<td>Urban</td>
<td>Built-up/agriculture</td>
<td>Bhaktapur/Southeast</td>
<td>27°39'43&quot;N, 85°25'12&quot;E 1392</td>
</tr>
<tr>
<td></td>
<td><strong>Budhanikantha</strong></td>
<td>Suburban</td>
<td>Residential</td>
<td>Kathmandu/North</td>
<td>27°46'35&quot;N, 85°21'44&quot;E 1435</td>
</tr>
<tr>
<td></td>
<td><strong>Kirtipur</strong></td>
<td>Suburban</td>
<td>Residential</td>
<td>Kathmandu/West</td>
<td>27°40'37&quot;N, 85°16'42&quot;E 1410</td>
</tr>
<tr>
<td></td>
<td><strong>Lubhu</strong></td>
<td>Suburban</td>
<td>Residential/agriculture</td>
<td>Lalitpur/Southeast</td>
<td>27°38'33&quot;N, 85°22'10&quot;E 1335</td>
</tr>
<tr>
<td></td>
<td><strong>Bhaisepati</strong></td>
<td>Suburban</td>
<td>Residential</td>
<td>Kathmandu/South</td>
<td>27°38'56&quot;N, 85°18'25&quot;E 1355</td>
</tr>
<tr>
<td></td>
<td><strong>Sankhu</strong></td>
<td>Rural</td>
<td>Forest/agriculture</td>
<td>Kathmandu/Northeast</td>
<td>27°43'49&quot;N, 85°27'45&quot;E 1399</td>
</tr>
<tr>
<td></td>
<td><strong>Bhimdhunga</strong></td>
<td>Rural</td>
<td>Forest/agriculture</td>
<td>Kathmandu/West</td>
<td>27°43'37&quot;N, 85°14'31&quot;E 1487</td>
</tr>
<tr>
<td></td>
<td><strong>Naikhandi</strong></td>
<td>Rural</td>
<td>Agriculture</td>
<td>Kathmandu/South</td>
<td>27°36'37&quot;N, 85°17'54&quot;E 1413</td>
</tr>
<tr>
<td></td>
<td><strong>Tinpiple</strong></td>
<td>Rural</td>
<td>Forest/agriculture</td>
<td>Kathmandu/Northwest</td>
<td>27°46'31&quot;N, 85°16'44&quot;E 1482</td>
</tr>
<tr>
<td></td>
<td><strong>Nagarkot</strong></td>
<td>Rural</td>
<td>Forest/agriculture</td>
<td>Bhaktapur/Northeast</td>
<td>27°43'22&quot;N, 85°31'28&quot;E 1932</td>
</tr>
<tr>
<td></td>
<td><strong>Nala Pass</strong></td>
<td>Rural</td>
<td>Forest/agriculture</td>
<td>Bhaktapur/Southeast</td>
<td>27°39'38&quot;N, 85°30'39&quot;E 1481</td>
</tr>
</tbody>
</table>

\(^{(1)}\) Site type is based on local GIS data from rds.icimod.org. Furthermore, this classification is supported by approximate distance (in km) from Kathmandu city’s core ring road. Urban < 3km; 3km < Suburban < 6km; and Rural > 6km. Land use type adopted from GIS data viewer (rds.icimod.org).
(2) Region classification is based on geographic location with respect to the main ring road surrounding Kathmandu city. Sites within the core ring road are classified as central regions. Kathmandu Valley includes three districts: Kathmandu, Bhaktapur, and Lalitpur.

(3) Coordinates and altitude, in meters, adopted from Google Earth and IASS POTSDAM database.

2.2 SusKat-ABC Campaign

A large scale study termed the Sustainable Atmosphere for the Kathmandu Valley–Atmospheric Brown Clouds (SusKat-ABC) campaign was carried out during December 2012–June 2013 by an international team of scientists in order to characterize the air pollutant emissions, ambient distributions, atmospheric processes, and potential health and environmental impacts in the Kathmandu Valley, surrounding regions in the Himalayan foothills, and the base of Mt. Everest (Rupakheti et al, 2016). As the second largest international air pollution measurement campaign ever conducted in South Asia, the campaign was undertaken by the Institute for Advanced Sustainability Studies (IASS), Potsdam, Germany, and the International Centre for Integrated Mountain Development (ICIMOD), Kathmandu, Nepal. More than 40 scientists from 18 research groups in 9 countries participated in the campaign.

In the course of this campaign, high-quality atmospheric data were collected including 644 week-long measurements of nitrogen oxides (NOx), nitrogen dioxide (NO2), surface ozone (O3), sulfur dioxide (SO2), and ammonia (NH3) using Ogawa passive samplers at multiple sites in the Kathmandu Valley between March-May 2013 across 15 sites.

During the following year in 2014, as part of a field study looking at traffic officers’ personal exposure to air pollutants, 72 week-long measurements of the same gaseous pollutants, with the exception of NH3, were collected between February-April and July-September 2014 from 13 sites (Appendices: Measurement from 2014). The study design was particularly focused on studying personal exposure among traffic officers, rather than addressing regional background measurements in the valley as the 2013 dataset. Furthermore, unlike 2013 measurements, most of
the samples from 2014 were taken within close proximity to major roadways, at least in the case of the urban on-road sampling sites. Therefore, due to lack of extensive regional measurement dataset and insufficient data to make direct comparison to the 2013 dataset, I have moved the 2014 data into an appendix (Appendix: I-V), and hence not discussed here.

![Timeline of Sampling Periods](image)

Figure 3: A chart showing the timeline of the 2013 sampling period and laboratory analysis duration of measured components

2.3 **Geography, Climate and Demographics**

Kathmandu Valley, where the capital of Nepal is located, lies between latitude 27°32′13″ and 27°49′10″ N and longitudes 85°11′31″ and 85°31′38″ E. The Valley basin is situated at the average elevation of 1350 m above mean sea level surrounded by a ring of mountains ranging from 2000 to 2800 m above sea level that create a distinctive bowl shaped area of approximately 340 km² (Panday & Prinn, 2009) (Figure 2). 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). The climate is influenced by the South Asian summer monsoon as it receives up to 90% of its annual rainfall during the three (June, July and August) summer months (Panday, 2006). The relative humidity reaches more than 80% in monsoon season than in the dry season (50%) in Kathmandu Valley (Giri et al., 2008).

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.

2.4 Passive sample collection

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 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.
2.4.1 Sampling during 2013

During the 2013 sampling, 644 week-long passive samples of NOx, NO\(_2\), SO\(_2\), O\(_3\) and NH\(_3\) were collected using Ogawa diffusive samplers (Model PS-100, Ogawa USA, Inc.) for 8 consecutive weeks between March 23\(^{rd}\) and May 18\(^{th}\) 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 2, Figure 14). 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.

During the same sampling period, ozone data were collected at a stationary site using online ozone monitor (Model-400E, Teledyne Technologies, Inc., USA) collocated with a passive sampler at one of the sampling sites, Bode, that served as the supersite for SusKat-ABC campaign (Naja et. al, 2015). Among the 15 sampling sites, 5 were classified as urban, 4 as suburban, and 6 as rural sites (Table 2). NO was calculated as the difference between NOx and NO\(_2\).

2.5 Meteorological parameters

Meteorological parameters such as temperature, relative humidity, amount of rainfall, wind speed and direction were monitored at 6 locations that overlapped with sampling sites
(Bode, Pakanajol, Nagarkot, Naikhandi and Bhimdhunga) and also from publicly available meteorological data from Tribhuvan International Airport.

2.6 Laboratory analysis

After the completion of sampling, filters were carefully removed from Ogawa samplers and stored in air-tight bottles. Samplers were stored in Nepal for approximately 5 months prior to being shipped to our laboratory for chemical 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 O₃, SO₂ 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. Method Detection Limits (MDL) were calculated as three times the standard deviation of a lab blank concentration (µg/ml) for each measured compound. Laboratory blanks and a selected standard were analyzed in between every 10ᵗʰ sample for all measured species during their respective laboratory analysis techniques. For standards and laboratory blanks liquid concentrations (in µg/ml) were propagated to µg/m³ by assuming typical measurement conditions, 10000 minute sampling time, 20 degrees Celsius, 40% Relative Humidity and, associated conversion coefficients.

Using the equations in Ogawa sampling protocols shown in section 2.1.1, 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 (Ogawa & Company, Pompano Beach, USA). The lowest and upper detectable ranges for NO₂, NOx, SO₂ and O₃ using the Ogawa passive
samplers for 168 hours (7days) sampling duration are presented in the table below (Table 3) (ogawausa.com). The expected concentrations from this study, based on limited previous work done in Kathmandu Valley, are within these upper and lower ranges which makes this Ogawa passive sampling technique a suitable method.

Table 3. Upper and lower detection limits by Ogawa passive samplers for a 7-days sampling duration reported by the manufacturer (adopted from ogawausa.com).

<table>
<thead>
<tr>
<th>Detectable Range</th>
<th>Sampling duration</th>
<th>NO₂</th>
<th>NOx</th>
<th>SO₂</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower</td>
<td>7 days</td>
<td>0.32</td>
<td>0.61</td>
<td>0.32</td>
<td>1.01</td>
</tr>
<tr>
<td>Upper</td>
<td>7 days</td>
<td>3600.0</td>
<td>6889.4</td>
<td>3600.0</td>
<td>11381.6</td>
</tr>
</tbody>
</table>

For ammonia, the lowest method detection limit has been reported to be 3.7 µg/m3 for a 1-day deployment and 0.26 µg/m3 for a 14-day sampling duration (Roadman et al., 2003), while the upper detection limit (293 µg/m3) have been found in another study for a 14-day sampling duration (Puchalski et al., 2011).

I was able to assess the detection limits provided by the manufacturer (Table 3) and also by the studies mentioned in the above paragraph for ammonia based on the calibration information I generated (Section 2.1.2) For example, the upper limit can be estimated from the highest laboratory standard while lower detection limit were assessed by computing three times the standard deviation of each pollutant detected in laboratory blanks and then propagating the liquid concentrations (in µg/ml) to atmospheric concentration in µg/m³.

### 2.6.1 Concentration conversion equations

Gas specific conversion equations:

- NO₂ concentration (ppb) = \((α \text{ NO}_2 \times \text{W}~\text{NO}_2) / t\)
- NO concentration (ppb) = \((α \text{ NO} \times (\text{W}~\text{NOx} − \text{W}~\text{NO}_2)) / t\)
- NO\(_x\) concentration (ppb) = NO (ppb) + NO\(_2\) (ppb)
- SO\(_2\) concentration (ppb) = (\(\alpha\) SO\(_2\) \times W\(\sim\)SO\(_2\)) / t
- NH\(_3\) concentration (ppb) = (\(\alpha\) NH\(_3\) \times W\(\sim\)NH\(_3\)) / t
- O\(_3\) concentration (ppb) = (\(\alpha\) O\(_3\) \times W\(\sim\)O\(_3\)) / t

Wherein:
- W\(\sim\)NO\(_x\), W\(\sim\)NO\(_2\): NO\(_2\) quantity (ng) collected in NO\(_x\) and NO\(_2\) collection elements
- W\(\sim\)SO\(_2\): (SO\(_4\))\(^{2-}\) quantity (ng) collected in SO\(_2\) collection element
- W\(\sim\)NH\(_3\): NH\(_3\) quantity (ng) collected in NH\(_3\) collection element
- W\(\sim\)O\(_3\): O\(_3\) quantity (ng) converted from NO\(_3\) quantity collected in O\(_3\) element
- \(\alpha\) NO, \(\alpha\) NO\(_2\), \(\alpha\) SO\(_2\), \(\alpha\) NH\(_3\), \(\alpha\) O\(_3\): ppb concentration conversion coefficient in ((ppb.min) / ng)
  - For example, \(\alpha\) NO = 60, \(\alpha\) NO\(_2\) = 56, \(\alpha\) SO\(_2\) = 39.4, \(\alpha\) NH\(_3\) = 43.8, \(\alpha\) O\(_3\) = 46.2 at 20 °C and 70% RH
- t: exposure time (min); ng: nanogram; ppb: parts per billion; °C: Degree Celsius; % RH: Relative Humidity (%)

The following equation was used to convert from ppb to \(\mu\)g/m\(^3\):
\[
\mu\text{g/m}^3 = \frac{(\text{ppb} \times 12.187 \times \text{MW})}{(\text{T})}
\]

Wherein:
- \(\mu\)g/m\(^3\) = micrograms per cubic meter; T = ambient air temperature, in Kelvin (K) = 273.15 + °C
- MW = Molecular Weight of compound
  - MW NO\(_2\) = 46.01 g/mol; MW NO = 30.01 g/mol; MW SO\(_2\) = 64.07 g/mol; MW NH\(_3\) = 17.04 g/mol; MW O\(_3\) = 48 g/mol
- 12.187 = conversion factor (1/0.08205; 0.08205 = Universal Gas Law constant, in \([\text{atm} \cdot \text{l}] / (\text{mol} \cdot \text{K})\), atm = absolute atmospheric pressure in atmospheres; mol = gram mole; l = liter

2.6.2 Calibration curves, laboratory and field blank analysis for each measured pollutant

Laboratory standard calibration curves were generated for each analyzed pollutant. Results from duplicate standard runs were used for quality control, including results from corresponding laboratory blanks and are presented below.

For oxides of nitrogen (NO\(_x\) and NO\(_2\)), laboratory analysis was performed between October 19, 2013 and January 8, 2014. Per Ogawa Sampler Protocol, dried Sodium Nitrite was used to generate the following Nitrite calibration standards: 0.1, 0.2, 0.4, 0.6, 0.8 µg/ml dissolved in ultrapure deionized water. Nitrite liquid aliquot solutions were used to analyze both NO\(_x\) and NO\(_2\) samples. Using the assumed typical laboratory measurement conditions mentioned in Section 2.1, liquid concentrations (in µg/ml) were propagated to µg/m\(^3\) and yielded 9.71, 19.36, 38.61, 57.77 and 76.83 µg/m\(^3\) of NO\(_2\), for 0.1, 0.2, 0.4, 0.6, 0.8 µg/ml nitrite solution, respectively.

For NO\(_x\) samples, standards ranging from 0.1-0.8 µg/ml Nitrite were generated and analyzed on the following dates: October 19, 2013, October 31, 2013, November 5, 2013, and November 18, 2013. Calibrations curves associated with each analysis day are presented below (Standard Curve 1-4 shown in Fig. A-D, respectively). The middlemost standard (i.e. 0.4 µg/ml Nitrite solution) was run on each day samples were analyzed to check for instrument precision. And the relative standard deviation (RSD) of this internal standard was found to be 6.2% among 4 duplicate runs of this particular standard.
The average Nitrite concentrations detected in laboratory blanks was \(0.62 \pm 0.42 \mu g/m^3\) for NOx with values ranging from \(0.07 - 1.08 \mu g/m^3\). Each blank value (in \(\mu g/m^3\)) was subtracted from the respective 10 unknown samples analyzed before the blank sample in a given analysis date. This blank correction procedure was applied for each analyzed gaseous specious. The MDL for NOx, calculated as three times the standard deviation of a lab blank concentration for the measured compound, was \(2.1 \mu g/m^3\). This was slightly higher compared to the NOx LOD from the manufacturer (\(1.01 \mu g/m^3\)).

Figure 4: Standard calibration curve for NOx analysis generated from spectrophotometer absorption of Nitrite standards prepared on October 19, 2013

\[y = 0.8884x + 0.0724\]

\[R^2 = 1\]
Figure 5: Standard calibration curve for NOx analysis generated from spectrophotometer absorption of Nitrite standards prepared on October 31, 2013.

Figure 6: Standard calibration curve for NOx analysis generated from spectrophotometer absorption of Nitrite standards prepared on November 5, 2013.
Figure 7: Standard calibration curve for NOx analysis generated from spectrophotometer absorption of Nitrite standards prepared on November 18, 2013

For NO$_2$ samples, analysis was completed on the following dates: December 19, 2013 and January 8, 2014. Freshly prepared calibration standards were mixed and analyzed on two dates (Standard Curve 1-2 shown in Fig. E and F, respectively). Similar to NOx calibration process, Sodium Nitrite was used to generate the following internal Nitrite calibration standards: 0.1, 0.2, 0.4, 0.6, 0.8 µg/ml Nitrite solution. The middlemost standard (i.e. 0.4 µg/ml Nitrite solution) was run on each day samples were analyzed to check for instrument precision. The relative standard deviation (RSD) of this internal standard was found to be 2.45% among 6 duplicate runs of this particular standard during the dates NO$_2$ samples were analyzed.

The average Nitrite concentrations detected in laboratory blanks was 0.04 ± 0.02 µg/m$^3$ for NO$_2$ with values ranging from 0.004 – 0.06 µg/m$^3$. The MDL for NO$_2$, calculated as three times the standard deviation of a lab blank concentration for the measured compound, was 0.7 µg/m$^3$ and was consistent to the LOD reported by the manufacturer (0.61 µg/m$^3$). Since NO was calculated as the difference between NOx and NO$_2$, the MDL for NO was calculated from the
amount of Nitrite detected in respective lab blanks used for NO\textsubscript{2} and NO\textsubscript{x} measurement. The MDL for NO was found to be 0.33 \(\mu\text{g}/\text{m}^3\).

Figure 8: Standard calibration curve for NO\textsubscript{2} analysis generated from spectrophotometer absorption of Nitrite standards prepared on December 19, 2013

Figure 9: Standard calibration curve for NO\textsubscript{2} analysis generated from spectrophotometer absorption of Nitrite standards prepared on January 2, 2014
For SO₂, laboratory analysis was performed between June 29, 2014 and July 14, 2014. A sulfate primary standard was used to generate the following ranges of internal calibration standards used for SO₂ calculation: 0.05, 0.1, 0.25, 0.5, 1, 2 µg/ml sulfate solution. The actual concentrations obtained from Ion Chromatography (IC) analysis are shown in the figures shown below (Fig. H and I) for standards analyzed on June 29, 2014 and July 14, 2014, respectively.

The middlemost standard (i.e. 0.5 µg/ml sulfate solution) was analyzed in between every 10th unknown sample on each day that samples were analyzed to check for instrument precision. The relative standard deviation (RSD) of this internal standard was found to be 5.25% (among 10 duplicate runs) and 7.26% (among 7 duplicate runs) for the days the instrument was operating from June 29 - July 2, 2014, and July 13-14, 2014, respectively.

The concentrations obtained from IC analysis were propagated to µg/m³ by assuming typical measurement conditions. The resulting ranges of standard concentrations were between 10.48 – 176.67 µg/m³ of SO₂ and 3.16 – 166.61 µg/m³ of SO₂ for standards run on June 29 and July 14, 2014, respectively.

The average Sulfate concentrations detected in laboratory blanks was 0.051 ± 0.034 µg/ml, with values ranging from 0.0009 – 0.088 µg/ml. These liquid concentrations can be propagated to SO₂ concentrations in the same manner as that of the internal standards indicated above. This yields average SO₂ concentrations detected in laboratory blanks (4.25 ± 2.83 µg/m³), with values ranging from 0.07 – 7.32 µg/m³. The MDL for SO₂, calculated as three times the standard deviation of a lab blank concentration for the measured compound, was 3.11 µg/m³. Compared to the LOD from the manufacturer (1.44 µg/m³), the MDL calculated in the laboratory is showed slightly elevation, partly due to slightly elevated sulfate concentrations detected in all laboratory blanks.
For O₃ samples, laboratory analysis was performed between July 19, 2014 and July 25, 2014. Based on the Ogawa protocol, Nitrate standard was used to generate the following ranges of internal calibration standards used for O₃ calculation: 0.32, 0.64, 1.6, 3.2, 8 µg/ml Nitrate
solution. The actual concentrations obtained from Ion Chromatography (IC) analysis is represented in the figure below (Fig. J) for internal standards analyzed on July 19, 2014.

The middlemost standard (i.e. 1.6 µg/ml nitrate solution) was analyzed in between every 10th unknown sample on each day that samples were analyzed to check for instrument precision. And the relative standard deviation (RSD) of this internal standard was found to be 1.58% among 16 duplicate runs of this particular standard.

The internal standard concentrations obtained from IC analysis were propagated to µg/m³ by assuming typical measurement conditions. The resulting ranges of concentrations were between 7.74 – 145.73 µg/m³ of O₃ for standards run on July 19, 2014.

The average nitrate concentrations detected in laboratory blanks was 0.042 ± 0.003 µg/ml, with values ranging from 0.0039 – 0.047 µg/ml. These liquid concentrations can be propagated to O₃ concentrations in the same manner as that of the internal standards indicated above. This yields an average O₃ concentration detected in laboratory blanks as 0.75 ± 0.05 µg/m³, with values ranging from 0.7 – 0.85 µg/m³. The MDL for O₃, calculated as three times the standard deviation of a lab blank concentration for the measured compound, was 0.16 µg/m³, this was surprisingly lower compared to the LOD from the manufacturer (0.78 µg/m³).
For NH$_3$, laboratory analysis was performed between September 4, 2014 and September 8, 2014. Based on the Ogawa protocol, Ammonium standard was used to generate the following ranges of internal calibration standards used for NH$_3$ calculation: 0.1, 0.5, 1, 2, 4 µg/ml ammonium solution. The actual concentrations obtained from Ion Chromatography (IC) analysis is represented in the figure below (Fig. K) for internal standards analyzed on September 4, 2014.

The selected middle standard (i.e. 2 µg/ml nitrate solution) was analyzed in between every 10$^{th}$ unknown sample on each day that samples were analyzed to check for instrument performance. And the relative standard deviation (RSD) of this internal standard was found to be 5.74% among 11 duplicate runs of this particular standard.

The internal standard concentrations obtained from IC analysis were propagated to µg/m$^3$ by assuming typical measurement conditions. The resulting ranges of concentrations were between 2.65 – 93.38 µg/m$^3$ of NH$_3$ for standards run on September 4, 2014.

The average nitrate concentrations detected in laboratory blanks was 0.001 ± 0.0023 µg/ml, with values ranging from 0.00001 – 0.01 µg/ml. These liquid concentrations can be propagated to O$_3$ concentrations in the same manner as that of the internal standards indicated above. This yields an average NH$_3$ concentrations detected in laboratory blanks which was 0.026 ± 0.058 µg/m$^3$, with values ranging from 0.0004 – 0.2 µg/m$^3$. The MDL for NH$_3$, calculated as
three times the standard deviation of a lab blank concentration for the measured compound, was 0.15 µg/m³.

![Standard Curve (NH₃)](image)

Figure 13: Standard calibration curve for NH₃ analysis generated from Ion Chromatograph quantification of Nitrate standards prepared on September 4, 2014

In this study field blanks were not collected at each site, other than at five key representative sites (namely: Bhimdhunga, Bode, Budhanilkantha, Nagarkot and Naikhandi). The average field blank concentrations of pollutants at each available site are presented in the table below (Table 4). For most measured elements, field blank concentrations were consistent, but slightly higher than laboratory blanks. An exception to this was ozone, where field blanks were significantly higher. The limited field blanks shown here were not subtracted in calculation since concentration of measured pollutants was highly variable across and within sites and thus doing so would increases uncertainty. Therefore, only lab blanks are included in concentration calculations since ten out of fifteen sites did not have field blanks.
Table 4: Mean field blank concentrations at five site (out of fifteen) for all measured pollutants in $\mu$g/m$^3$

<table>
<thead>
<tr>
<th>Field Sampling sites</th>
<th>N</th>
<th>NOx</th>
<th>NO</th>
<th>NO$_2$</th>
<th>O$_3$</th>
<th>SO$_2$</th>
<th>NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bhimdhunga</td>
<td>6</td>
<td>2.57±0.63</td>
<td>0.49±0.34</td>
<td>1.08±0.85</td>
<td>21.56±18.42</td>
<td>4.85±3.44</td>
<td>4.52±2.32</td>
</tr>
<tr>
<td>Bode</td>
<td>8</td>
<td>2.82±0.50</td>
<td>1.01±0.19</td>
<td>0.45±0.72</td>
<td>18.00±13.31</td>
<td>3.38±3.28</td>
<td>7.52±8.99</td>
</tr>
<tr>
<td>Budhanilkantha</td>
<td>7</td>
<td>2.26±0.53</td>
<td>0.57±0.25</td>
<td>0.49±0.09</td>
<td>8.55±4.78</td>
<td>4.44±3.44</td>
<td>6.42±3.09</td>
</tr>
<tr>
<td>Nagarkot</td>
<td>7</td>
<td>4.97±3.47</td>
<td>1.57±1.35</td>
<td>0.82±0.69</td>
<td>40.95±29.73</td>
<td>2.88±1.33</td>
<td>7.73±4.93</td>
</tr>
<tr>
<td>Naikhandi</td>
<td>8</td>
<td>2.29±0.79</td>
<td>0.60±0.29</td>
<td>1.03±1.07</td>
<td>16.37±7.37</td>
<td>6.42±2.09</td>
<td>5.71±2.24</td>
</tr>
</tbody>
</table>

N – Number of samples from site
SD – Standard deviation

2.7 Statistical analysis

Microsoft Excel 15.0 and R 3.3.2 analysis software were used to analyze data and present the tables, and graphs. Variation among site type was assessed by computing an Analysis of Variance (ANOVA) test followed by a Bonferroni Post-Hoc test. Results were considered significant at $p<0.05$. Pearson correlation analysis was used for identifying the relationship between the active vs. passive sampling done for O$_3$ at least in one of the sampling sites, Bode.
CHAPTER 3

RESULTS

3.1 Variability across sites

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 2013 sampling period is presented in Table 5, while results from 2014 are presented in Appendix II. Data collected during 2013 is also further classified by sampling week and presented in Table 6. In addition, 8-week average concentrations from 2013 are shown in Figure 15. The overall concentrations of all trace gases collected during three discrete seasons in 2013 and 2014 sampling periods are shown in Figure 4, including includes pollution-rose plot for real-time O$_3$ measurement (µg/m$^3$) at Bode, the SusKat supersite from the 2013 sampling period.
Figure 14: Geographic location of all sampling sites in the Kathmandu Valley, and respective pollutant concentrations (µg/m³). The figure also includes pollution-rose plot for the active, real-time O₃ measurement (µg/m³) at Bode, the SusKat supersite, during 2013.
3.1.1. Measurements from 2013

The overall average concentrations of trace gases for 2013 winter season are shown in Figure 15. Although the 2013 measurements are limited to the winter season only, we observed spatial profile of trace gases in the valley. In addition, 2013 measurements are further classified based on recognized emission sources such as traffic intensity (Figure 16) and distance from brick factories (Figure 17) for oxides of nitrogen and SO₂, respectively. The measurements in 2013 indicated that for all trace gaseous pollutants except O₃, the average concentrations are highest in urban sites followed by suburban and rural sites. The reverse holds true for O₃ concentrations with the highest O₃ concentrations at rural sites in 2013 (Figure 15). From measurements taken during 2013, NOx, NO₂, NO and O₃ concentrations were statistically different among urban, suburban and rural site types (ANOVA test, p<0.05).

Table 5: 8-week mean concentrations of NO₂, NOx, NO, O₃, NH₃ and SO₂ in µg/m³ of 2013 measurements. Eight consecutive weeks beginning on March 23rd and ending on May 18th, 2013.

<table>
<thead>
<tr>
<th>Site type</th>
<th>Site</th>
<th>NO₂</th>
<th>NOx</th>
<th>NO</th>
<th>SO₂</th>
<th>O₃</th>
<th>NH₃</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>Nagarkot</td>
<td>3.9 ± 2.0</td>
<td>5.8 ± 2.3</td>
<td>2.2 ± 2.0</td>
<td>6.8 ± 3.0</td>
<td>137.4 ± 19.1</td>
<td>14.4 ± 5.8</td>
</tr>
<tr>
<td></td>
<td>Naikhandi</td>
<td>6.2 ± 0.7</td>
<td>7.8 ± 1.5</td>
<td>1.9 ± 1.1</td>
<td>11.7 ± 7.7</td>
<td>104.9 ± 25.6</td>
<td>26.5 ± 8.4</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>
<tr>
<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>
</tbody>
</table>

"Concurrent measurements of all gases at a given site"
3.1.1.1. Oxides of Nitrogen

Mean weekly concentrations of nitrogen oxide species (NOx, NO2 and NO) were highest at urban sites (NO2 25.8 ± 6.5 µg/m³, NOx 30.5 ± 6.8 µg/m³, NO 5.7 ± 1.2 µg/m³) and lowest in rural sites (NO2 9.6 ± 4.6 µg/m³, NOx 11.5 ± 4.6 µg/m³, NO 2.4 ± 0.6 µg/m³) (Figure 15). Concentrations of these gases were highly variable with observed weekly concentrations in the valley ranging from 12.4 - 0.4, 46.0 - 0.2, and 46.7 - 4.1 µg/m³ for NO, NO2, and NOx, 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

Figure 15: 2013 pre-monsoon season mean concentrations (µg/m³) 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
suburban, and urban and rural site types, but not between suburban and rural site types. Further classification of site types based on distance (in km) from main core ring road with high traffic activity is shown in Figure 16. Sampling locations within 2 km of Ring Road showed the highest levels of NOx (ANOVA test, p<0.05).

![Figure 16: 2013 mean concentrations (µg/m³) of NO₂, NOx and NO categorized by distance (in km) from main core ring road with high traffic activity. Error bars = standard deviation](image)

**Note:** Sites within 2 km from core ring road include: Maharajgunj, Suryabinayak, Mangal Bazaar, Indrachowk, Kirtipur, Bhaisepati and Bode. Sites located between 2 km and 6 km include: Budhanilkantha, Bhimdhunga, Naikhandi, Tinpiple and Lubhu. Sites located 6 km or more include: Sankhu, Nagarkot and Nala Pass.

### 3.1.1.2. Sulfur Dioxide

SO₂ concentrations during 2013 varied from site to site as shown in Table 5. The weekly mean SO₂ concentrations at urban sites (16.6 ± 12.9 µg/m³) were higher than suburban (9.3 ± 2.1 µg/m³) and rural sites (6.9 ± 2.5 µg/m³) (Figure 15). However, the spatial variation of SO₂ did
not show statistically significant differences among site categories when an ANOVA test was performed.

The average SO$_2$ concentrations between Bode, Suryabinayak and Lubhu were in the range of 39.2-12.0 µg/m$^3$ with the highest weekly average SO$_2$ 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 Lubhu (12.0 ± 5.1 µg/m$^3$), a suburban site. These three sites are located within 3 km of at least 10 brick factories (Figure 17). In contrast, sampling sites located with similar proximity but to fewer brick kiln factories are observed with lower SO$_2$ 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. The lowest average concentration of SO$_2$ was measured at Bhimdhunga with an overall average of 4.7 ± 1.6 µg/m$^3$. 

![Graph showing SO$_2$ concentrations at different site types](image-url)
Figure 17: 2013 mean concentrations (µg/m³) of SO₂ categorized by district and sampling site location with respect to distance from brick kiln factories. Error bars = standard deviation

*Note:* Within 3Km (<10 brick kilns): Sites included in this category are: Naikhandi, Bhaisepati and Kirtipur. These sites are located within 3 km of less than 10 sparsely located Brick Kiln factories.

*Within 3Km (10+ brick kilns):* Sites located within 3 Km of included in Bhaktapur district include Lubhu from Lalitpur district. Sites included in this classification are: Bode, Suryabinayak and Lubhu. These sites are located within 3 km of more than 10 densely located Brick Kiln factories.

*Within 3Km (No brick kilns):* Sites included in this category are: Sankhu, Nagarkot, Tinpiple and Bhimdhunga. No brick kiln factories are present within 3 km of these remote sites.

### 3.1.1.3. Ammonia

The weekly mean concentrations of ammonia at urban sites (27.2 ± 6.3 µg/m³) were higher than suburban (20.7 ± 2.6 µg/m³) and rural sites (19.8 ± 4.9 µg/m³) (Figure 15). NH₃ concentrations varied from site to site as shown in Table 5; however, the variation was not significantly different across site categories. Weekly concentrations in the valley varied from 3.0-50.4 µg/m³, with highest weekly averages in Suryabinayak (35.2 ± 15.2 µg/m³) followed by Indrachowk (30.8 ± 14.0 µg/m³), while the lowest weekly mean concentrations are in Nagarkot (14.4 ± 5.8 µg/m³) and Sankhu (15.2 ± 10.0 µg/m³), mainly forested areas. Further classification of sampling sites was based on land use type and proximity to rivers (Figure 18). Sites classified as being agricultural sites had levels (26.0 ± 5.4 µg/m³) comparable to sites located downstream of major rivers (i.e. Bagmati, Manohara and Bishmati rivers) (25.8 ± 5.5 µg/m³), while sites upstream of these rivers had lower levels (19.9 ± 3.6 µg/m³) (Figure 18).
Figure 18: 2013 mean concentrations (µg/m$^3$) of NH$_3$ based on land use type and proximity to rivers. Error bars = standard deviation

*Note:* Sites located upstream from Bagmati, Manohara and Bishmati rivers include: Maharajgunj, Budhanilkantha, Sankhu and Tinpiple. Sites located downstream from these rivers include: Indrachowk, Mangal Bazar, Bhaisepati and Naikhandi. Sites where agriculture is the prominent land use type include: Suryabinayak, Lubhu, Tinpiple, Nala pass and Naikhandi.

### 3.1.1.4. 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 Figure 15. 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 O$_3$ 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 (1895m 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/m³), an urban location.

Polar plots for O₃ concentrations monitored with an online instrument at the Bode site, based on frequency of count by local wind direction and wind speed are presented in (Figure 14 and Figure 19). The plots indicate that lowest O₃ concentrations occur when easterly wind direction is accompanied by low wind speed. On the other hand, highest ozone was observed with southwesterly winds with strong wind speed. In addition, a time series plot showing comparison between the weeklong measurement using passive sampling and 8-hour moving average using active sampling of ground level ozone concentrations in µg/m³ from March 23rd to May 18th, 2013 is shown in Figure 20, along with the WHO 8-hour standard of 100 µg/m³ and measurement from passive sampling. 5 out of 8 (63%) passive samples exceeded the WHO guideline, while active monitoring captured exceedance in 60% of sampling time.
Figure 19: Weekly pollution-rose plot for active O₃ measurement at Bode during 2013. Note: For the lowest concentrations of O₃, the wind direction is dominated by easterly winds, and relatively low wind speeds. The highest concentrations of ozone are dominated by relatively strong southwesterly winds.

Figure 20: Time series showing 7-days measurement using passive sampling and 8-hour moving average using active sampling of ground level ozone concentrations in µg/m³ from March 23rd to May 18th, 2013. The WHO 8-hour standard of 100 µg/m³ (red dotted line) and measurement from passive sampling (black solid line) are also shown.

3.2 Temporal variations

3.2.1. Measurements during 2013

Week to week variation in the valley during 2013 is presented in Table 6. In rural sites, NO₂ concentration variation between the first two sampling weeks (i.e. March 23rd to April 6th, 2013) and the last two sampling weeks (i.e. May 4th to May 8th, 2013) was found to be significant (ANOVA test, p<0.05). NO₂ levels in urban and suburban regions showed higher concentration in May than March, although not statistically significant. NOx 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 (ANOVA: p=0.001, p=0.003, p=0.01 at urban, suburban and rural, respectively).

Table 6: Week to week variation of gaseous pollutants in 2013 stratified by site type

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>Urban</td>
<td>25.9 ± 8.4</td>
<td>21.6 ± 5.9</td>
<td>30.0 ± 10.4</td>
<td>24.8 ± 8.2</td>
<td>28.6 ± 9.4</td>
<td>26.8 ± 3.8</td>
<td>23.3 ± 7.1</td>
<td>29.5 ± 6.6</td>
</tr>
<tr>
<td></td>
<td>Suburban</td>
<td>9.7 ± 4.0</td>
<td>9.5 ± 7.3</td>
<td>12.4 ± 6.2</td>
<td>11.5 ± 2.3</td>
<td>8.5 ± 6.3</td>
<td>10.7 ± 2.5</td>
<td>10.3 ± 3.5</td>
<td>13.8 ± 6.7</td>
</tr>
<tr>
<td></td>
<td>Rural</td>
<td>6.0 ± 3.5</td>
<td>8.0 ± 3.7</td>
<td>8.7 ± 3.4</td>
<td>10.6 ± 4.8</td>
<td>8.6 ± 2.8</td>
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<td>7.7 ± 3.2</td>
<td>20.0 ± 15.3</td>
</tr>
<tr>
<td>NOx</td>
<td>Urban</td>
<td>32.9 ± 8.1</td>
<td>29.5 ± 6.6</td>
<td>35.7 ± 8.8</td>
<td>27.4 ± 8.4</td>
<td>32.5 ± 10.0</td>
<td>29.4 ± 4.5</td>
<td>26.9 ± 5.9</td>
<td>31.3 ± 7.2</td>
</tr>
<tr>
<td></td>
<td>Suburban</td>
<td>14.5 ± 4.6</td>
<td>13.6 ± 6.6</td>
<td>15.3 ± 5.3</td>
<td>13.5 ± 3.3</td>
<td>12.8 ± 5.2</td>
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<td>11.7 ± 3.9</td>
<td>14.1 ± 6.4</td>
</tr>
<tr>
<td></td>
<td>Rural</td>
<td>10.6 ± 5.1</td>
<td>10.2 ± 3.5</td>
<td>10.6 ± 3.4</td>
<td>11.2 ± 4.6</td>
<td>10.7 ± 4.3</td>
<td>10.0 ± 2.6</td>
<td>8.6 ± 3.1</td>
<td>20.1 ± 15.2</td>
</tr>
<tr>
<td>NO</td>
<td>Urban</td>
<td>8.9 ± 2.0</td>
<td>8.0 ± 2.6</td>
<td>5.7 ± 2.2</td>
<td>4.9 ± 1.0</td>
<td>4.9 ± 4.5</td>
<td>3.5 ± 1.9</td>
<td>3.5 ± 2.1</td>
<td>2.9 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>Suburban</td>
<td>4.8 ± 1.8</td>
<td>4.2 ± 1.1</td>
<td>3.0 ± 1.1</td>
<td>2.0 ± 1.0</td>
<td>4.3 ± 3.7</td>
<td>1.9 ± 1.0</td>
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<td>2.2 ± 0.5</td>
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CHAPTER 4
DISCUSSION

4.1. Variability across sites

4.1.1. Measurements from 2013

4.1.1.1. Oxides of Nitrogen

NO₂ forms quickly from on- and off-road vehicular 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/m³) (Table 5). This contrasts with much lower concentrations (3.9 ± 2.0 µg/m³) 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 winter season were highly elevated. Our measurements of NO₂ at urban sites (range: 19.3-32.3 µg/m³) are comparable to what Byanju et al. (2012) have found during the 2008 dry season (8.2-32.2 µg/m³). These levels are also comparable to passive sampling results from urban and suburban locations of two major cities, Delhi and Kanpur, India (Behera et al., 2015). Week-long monitoring of NO₂ (0.2 - 46.0 µg/m³) indicated that levels likely remained below the NAAQS.
24-hr level (80 µg/m³) 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 NOx pollution in Kathmandu Valley where the transport sector in the valley is responsible for 86% of total anthropogenic NOx 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 Figure 16. Sampling locations within 2 km of Ring Road have the statistically significant highest levels of NOx (ANOVA test, p<0.05). Although sampling locations within 2 km of Ring Road had the highest levels compared to sites between 2-6km and 6km, post-hoc analysis did not show meaningful difference amongst the other groups. NO₂ is emitted directly from 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/NOx 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 NO\textsubscript{2}/NO\textsubscript{X} ratios in the Kathmandu Valley which were higher than what many previous studies have reported. Carslaw (2005) noted an increasing trend over time of NO\textsubscript{2}/NO\textsubscript{X} in London, UK, explained by an overall decrease in NO\textsubscript{X} emissions in the diesel fleets, and an increasing fraction of primary NO\textsubscript{2} within this NO\textsubscript{X}. 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 NO\textsubscript{X}, 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 NO\textsubscript{2}/NO\textsubscript{X} 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 (Liquefied 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 O\textsubscript{3} concentrations observed at urban sites during the winter season suggest that ground level ozone most likely undergoes rapid NO\textsubscript{X} 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 O$_3$ 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 NO$_2$ 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 NO$_2$ levels. Prevailing southwesterly winds were dominant during the winter sampling period (Figure 19) 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.

4.1.1.2. Sulfur Dioxide

Coal combustion in brick factories are likely to contribute to elevated ambient levels of SO$_2$. More than 100 brick kilns throughout the valley produce over 350 million bricks per year, and they are significant emission sources of SO$_2$ and PM in the Kathmandu Valley, contributing to over 60% of total SO$_2$ and particulate matter emissions (Joshi and Dudani, 2008, Pariyar et al., 2013). Moreover, 74% of total anthropogenic SO$_2$ 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 SO$_2$ emission in the valley (Pradhan et al., 2012), indicating that SO$_2$ sources are mainly point sources such as brick kilns.

The average SO$_2$ concentrations between Bode, Suryabinayak and Lubhu were in the range of 39.2-12.0 µg/m$^3$ with the highest weekly average SO$_2$ concentration observed at Bode
(39.2 ± 21.6 µg/m³) and Suryabinayak (15.8 ± 7.4 µg/m³), both urban locations, and somewhat lower levels in Lubhu (12.0 ± 5.1 µg/m³), a suburban site. In addition to the increased presence of mobile and stationary generators that use low-quality (i.e. high sulfur content) diesel fuel in urban/suburban sites, these three sites are located within 3 km of at least 10 brick factories (Figure 17), 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/m³ and 11.7 ± 7.7 µg/m³, respectively. 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/m³. Bhimdhunga is a rural location with no nearby brick kilns and other major SO₂ sources.

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 (Joshi and Dudani, 2008; Raut, 2006), this suggests a plausible source of SO₂ observed in high concentrations at Bode, Suryabinayak and Lubhu, all of which are located in the south and southeastern region of the valley and close to the brick kilns. High levels of SO₂ in Naikhandi (11.7 ± 7.7 µg/m³), 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/m³) in southeastern region of the valley where over several brick kilns are located (Byanju et al., 2012; Pradhan et al., 2012). Much higher SO₂ levels were also measured in 2001 dry season (36.7-78.6 µg/m³) at sites mainly surrounded by brick kilns (Regmi and Kitada, 2003).
4.1.1.3. Ammonia

NH₃ concentrations varied from site to site as shown in Table 5; 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. 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 in the valley (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 Bishumati 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/m³ on average. Generally, regions located downstream of major rivers in the valley had elevated NH₃ levels (Figure 18), 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. Extensive sampling is needed near these polluted rivers in Kathmandu valley in order to observe a clear association between NH₃ levels and contaminated rivers. Since this was not planned in the SuSKat study design, our assessment of NH₃ near polluted rivers is based on fairly limited data.

4.1.1.4. Ozone

The weekly mean concentrations of ground level ozone at rural sites (110.7 ± 17.0 µg/m³) were higher than suburban (95.9 ± 3.7 µg/m³) and urban sites (84.9 ± 10.2 µg/m³) as shown in Figure 15. 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 Bhimdhunga, 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/m³ and 117.0 ± 23.4 µg/m³, 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 (Figure 14 and 9) 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.

4.2. Temporal variations

4.2.1. Measurements during 2013

Increased NO level in urban areas indicates 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 NOx 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 NO₂. 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$_y$ (total odd nitrogen) that includes HNO$_3$, NO$_3$ and N$_2$O$_5$ (Hayden, 2003).

Another interesting observation is that NH$_3$, O$_3$ and SO$_2$ 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$^{th}$-13$^{th}$, 2013) than rest of the sampling period. Winter and sunny days during late March and early April possibly contributed to factors leading 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$_2$, were operating from around 20$^{th}$ Jan to 20$^{th}$ 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$_3$ remained within 24-hr NAAQS limits throughout the sampling period. The higher O$_3$ in March-April is also linked to regional scale enhancement in O$_3$ due to extensive forest fire and agro-residue burning in the region.

A total of 50 (42%) weekly O$_3$ measurements in the valley exceeded 100 µg/m$^3$. It can be inferred from the weekly average O$_3$ concentrations that O$_3$ 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$_3$ 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$^3$ (Figure 20). Online continuous measures of ozone monitored at the same site shows that 8-hour running mean concentrations remained between 60-
160 µg/m³ 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 O₃ in Europe (Bytnerowicz et al., 2002a) and North America (Bytnerowicz et al., 2002b). Nonetheless, this has important public health relevance as O₃ levels higher than 100 µg/m³ 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 Figure 20. Pudasainee and colleagues (2006) found that enhanced ozone concentrations were due in part to long sunshine hours during the spring season (i.e. March to 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 Pulchowk (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/m³. Our findings, on average, were observed to be somewhat higher than previous measurements with hourly maximums peaking up to 200 µg/m³ (Figure 20). 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.
CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Measurements of NO₂, O₃, SO₂ and NH₃ at 15 sites in the Kathmandu Valley, Nepal during 2013 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, particularly low-quality coal combustion in brick kiln factories. 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. Evidence also 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.

In the context of public health and exposure to these pollutants, it is known that exposure to these gasses has been associated with a variety of adverse health effects, especially when levels exceed a certain threshold. Our measurements from 15 sites across the valley clearly indicate that O₃, which is toxic to both human and plants, is an important pollutant of concern that demands urgent attention. In Kathmandu valley, amongst all of the measured pollutants, we have observed frequent threshold exceedance, particularly for ozone. This has important public
health relevance for the people residing in Kathmandu valley as exposure to ozone levels higher than 100 µg/m³ (i.e. WHO guideline) have been shown to cause several health outcomes such as, rise in daily mortality and increased hospital admissions rates due to illnesses such as pneumonia and COPD. Therefore, due to the health detriments attributed to these gaseous pollutants, ozone predominantly, this pollutant is an important pollutant of concern that requires immediate attention and control through mitigation of its precursors such as nitrogen oxide species in the valley.

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 pollutants that pose serious health risks to 3.5 million residents of the valley, and thus requires priority mitigation actions. 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.

5.2 Recommendations

5.2.1 Limitations leading to alternative/complementary sampling techniques

Globally, more than 3 million premature deaths occur annually due to outdoor air pollution; more than 80% occurring in the developing world (WHO, 2012). Because most of our understanding of this morbidity arises from studies in the developed world, dose-response relationships might not be applicable for exposures in highly polluted areas, such as Nepal. Hence, from a public health standpoint, increased measurements of air pollutants in outdoor environments is critical for assessing exposure to air pollution and the potential health effects in low income countries.
Due to their simplicity, low cost and capabilities of providing similar performance to expensive active samplers in terms of sensitivity and reproducibility, passive samplers have been widely used as an effective alternate for conventional active samplers in exposure and health effects studies, especially in developing countries. However, one of the major limitations to passive samplers is a long sampling time (often integrated over 7 days at a minimum) is usually required in order to get enough mass for detection.

As we have learned from the findings of this study, at least for ozone pollution, guideline exceedances were captured within weekly averages. However, direct comparison to national standards was not possible because Nepal’s NAAQS and WHO recommendations are based upon 8-hour and 24-hour averages. That raises important questions such as: during which particular day(s) was ozone at toxic level(s) within the weeks that exceeded healthy levels? What were the diurnal patterns of ozone and other precursor gases in the Kathmandu valley during the sampling periods? Is there a better way to make more frequent measurements and gain better spatiotemporal profile of pollutants within the financial confines of resource limited countries?

Even though the use of a passive sampling technique is much more cost effective compared than robust continuous analyzers mostly used in the developed world, there exists a large potential benefit in exploring other cost-effective methods to permit more frequent (hourly or daily) measurements, and either generate standalone, reliable data or augment the aggregated weeklong data collected by passive sampling technique.

To that effect, a similar low-cost sampling technique that has the potential of being successfully utilized in developing nations is the application of small sensor technology. More recently, there have been a number of attempts by scholars around the world investigating the
environmental health applications of small sensor technology that enable frequent air quality measurements based on open-source processor platforms.

Although these easily accessible and inexpensive hardware and software microprocessors toolkits were originally created for applications in actuator control functions such as in simple robotics, their discovery has allowed for professionals along with citizen scientists to gain ease of access for operating low-priced environmental sensors. A good example here can be the use of semiconductor metal oxide (SMO) gas sensors that have been widely used in the auto industry for monitoring vehicle cabin air quality (Galatsis and Wlodarski, 2006). In recent times, these SMO gas sensors have found other applications in measuring traces gases such as carbon monoxide and NOx (Fine et al., 2006), and ozone (Gerboles and Buzica, 2009) in the ambient atmosphere with low-priced data processing platforms able to process, display, and store sensor signals within seconds.

The applicability of such inexpensive environmental sensors and processing platforms is exciting. An Arduino, for instance, is equipped with simple programming language, open source software, digital and analog pins which can be interfaced to a variety of expansion boards and circuitry embedded in, for instance, an electrochemical or a metal oxide gas sensor or an optical particle counter. This can be assembled and coded by anyone with internet access and required no significant background in circuitry or measurements.

Since the turn of the new millennia, low-cost air sensors have continuously entering the global market and are commercially available in a wide variety of design and capabilities. Recent studies have shown there is a potential in exploring low-cost small sensors use in field studies. Holstius and colleagues, for instance, have found that Shinyei-PPD42NS (an off-the-shelf optical sensor costing less than $15 USD) yielded comparable performance compared to commercially
available optical instruments costing considerably more (for instance: Dylos: ~$500; TSI DustTracker: ~$9,000; GRIMM ASP: ~$5000) based on 1-hour integration times at a regulatory monitoring site in Oakland, California (Holstius et al., 2014). In another example, a research group at Texas Tech University found that MiCS-2614 metal-oxide ozone sensor, assembled for less than $150, is capable of reasonably detecting ambient ozone levels ranging 20-100 ppb (Cao and Thompson, 2016). The cost and detection range of this particular ozone sensor is quite appealing when compared to, for instance, the online ozone monitor (Model-400E, Teledyne Technologies, Inc., USA) that was used during the SusKat-ABC campaign at Bode site, costing around $3000 USD. Such cost-effective innovative approaches have the potential to transform peoples’ lives by increasing our society’s understanding of the dynamic properties of toxic pollutant in the air that we breathe. Hence, inexpensive and portable sensors have the capability to provide individuals, health professionals, and public health researchers with new and unprecedented amounts of data that can be used to tackle contemporary challenges attributed to air pollution.

Small sensors ability to generate vast amount of data and be manufactured quickly on a large scale makes them a desirable technology to exploit; however, most are sold without proper testing and rigorous evaluation by their respective manufacturers. In most cases, manufacturer provided specification sheets are poorly written and often posses incomplete information such as the range of operating conditions, calibration information, known interferences, and other technical specification of the sensors. Even though the simplicity of small sensor devices and advances in fabrication methods keeps production costs down and allows affordability by almost any stakeholder, their use comes with a peril of producing unverified and unreliable data. In response to this quickly evolving technology that is rapidly growing in popularity, the U.S.
Environmental Protection Agency has recently released a comprehensive guidebook (Air Sensors Guidebook) in 2014 in order to address the concerns associated with the accuracy, precision, overall capabilities and limitations of newly emerging small sensors and their associated technologies. In the guidebook, the EPA puts forth important considerations (such as detection range/limit, calibration requirement, and response time and so forth) consumers should make prior to purchasing a sensor that may be appropriate for the anticipated use.

The application of small air sensors ranges from use in information/awareness creation to personal monitoring to supplementing existing monitoring data to other applications in the research sector. And, depending of the anticipated use of the sensors, EPA recommends certain level of acceptable bias and error reported by small sensors when compared to regulatory monitors. For example, if the application of a selected sensor is intended for educational purpose (to gain only qualitative understanding), for example to demonstrate to high school student that a particular pollutant exists somewhere in the range of concentration, then a large measurement error, arising from perhaps poor detection limit of the sensor, is acceptable. The EPA guidebook suggests that a precision error of up to 50% (compared to regulatory reference monitor is acceptable in such sensor application areas. However, in application areas where sensors are considered for supplementing an existing monitoring, a sensor yielding no more than 20% precision error is considered satisfactory. EPA attempts to identify the capabilities and limitations of emerging sensors by collaborating with other agencies such as South Coast Air Quality Management District in California that continuously seek to validate newly emerging sensors by making them go though laboratory and field testing. This sensor validation method and calibration approach opens a door for consumers, for instance, those who are interested in developing, testing and validating and then deploying sensors to a poor country where regulatory
grade monitors are unavailable. A sensor’s applicability in supplemental monitoring might have strong value in potentially providing additional air quality data to complement existing monitoring techniques—passive sampling techniques included.

The applicability of not-yet-fully understood low-cost sensors is still far from complementing federal monitoring methods in the developed world. However, since there is an urgent need to monitor air quality in poor countries where pollution is often high, there lies an opportunity for scientists, policymakers and stakeholders to invest on understanding the acceptable limitations of low-cost sensors rather than perfecting them. The questions we would then need to answer are: to what extent is the limitation of a sensor acceptable to actively monitor air quality in places that don’t have regulatory grade instruments? Can there be a systematic approach to validate a selected sensor, and identify its weaknesses, so that it can gather meaningful data in areas where no such data has ever been gathered before? And, to what extent can the sensor generate dependable and acceptable standalone data, or perhaps augmented by similarly low-costing passive samplers that may help verify data accuracy?

From domestic challenges arising from poor indoor air quality in remote parts of the developing world to global implications of a changing climate, we might not get the chance to completely eradicate the effects of air pollution in the near future. However, we need to sustain our efforts towards investing on meaningful initiatives that explore innovative, low-cost approaches to measure, monitor, regulate and abate the looming effects of air pollution. Now more than ever, there is an urgent need to empower people with the appropriate, dependable and affordable technologies so that we can all generate valid and robust spatiotemporal data of pollutants and contribute to sound science in a field of global importance.
Moving into the future, there is a growing importance, global application and demand in the development, evaluation and use of more portable and affordable online monitoring instruments based on low-cost sensors that may offer a means to supplement and extend existing infrastructure, increasing the density and coverage of empirical measurements and ultimately improve exposure science and mitigation strategies, particularly in highly polluted developing countries.
APPENDIX

MEASUREMENT FROM 2014

A.I: Sampling Methods

As part of a larger study that assessed personal exposure levels among traffic officers working in Kathmandu Valley, a small subset of ambient passive samples were collected in 2014 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 NOx, 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 to 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 7).
Table 7: Description of passive sampling sites

<table>
<thead>
<tr>
<th>Season</th>
<th>Site Type(1)</th>
<th>Land use type(1)</th>
<th>District/Region(2)</th>
<th>Geographic Location/Altitude (m)(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014 Winter</td>
<td>Urban</td>
<td>Built-up/Road side</td>
<td>Kathmandu/Northwest</td>
<td>27°43′54″N 85°18′16″E 1304</td>
</tr>
<tr>
<td>(February-April)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gaushala *</td>
<td>Urban</td>
<td>Built-up/Road side</td>
<td>Kathmandu/East</td>
<td>27°42′28″N 85°20′36″E 1334</td>
</tr>
<tr>
<td>Koteshwor *</td>
<td>Urban</td>
<td>Built-up/Road side</td>
<td>Kathmandu/East</td>
<td>27°40′43″N 85°20′58″E 1317</td>
</tr>
<tr>
<td>Jawalakhel *</td>
<td>Urban</td>
<td>Built-up/Road side</td>
<td>Kathmandu/Central</td>
<td>27°40′48″N 85°19′02″E 1319</td>
</tr>
<tr>
<td>Tripureshwor *</td>
<td>Urban</td>
<td>Built-up/Road side</td>
<td>Kathmandu/Central</td>
<td>27°41′38″N 85°18′51″E 1298</td>
</tr>
<tr>
<td>Baneshwor</td>
<td>Urban</td>
<td>Built-up/residential</td>
<td>Kathmandu/Central</td>
<td>27°41′36″N 85°20′06″E 1316</td>
</tr>
<tr>
<td>Dadihikot</td>
<td>Urban</td>
<td>Built-up/agriculture</td>
<td>Bhaktapur/Southeast</td>
<td>27°40′03″N 85°23′04″E 1312</td>
</tr>
<tr>
<td>Lainchaur</td>
<td>Urban</td>
<td>Built-up/residential</td>
<td>Kathmandu/Central</td>
<td>27°43′10″N 85°18′55″E 1320</td>
</tr>
<tr>
<td>Lokanahi</td>
<td>Urban</td>
<td>Built-up/residential</td>
<td>Bhaktapur/West</td>
<td>27°40′14″N 85°21′02″E 1304</td>
</tr>
<tr>
<td>2014 Monsoon</td>
<td>Suburban</td>
<td>Residential</td>
<td>Kathmandu/West</td>
<td>27°40′54″N 85°17′16″E 1328</td>
</tr>
<tr>
<td>(July-September)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kirtipur</td>
<td>Suburban</td>
<td>Residential</td>
<td>Bhaktapur/SouthEast</td>
<td>27°40′14″N 85°21′35″E 1302</td>
</tr>
<tr>
<td>Balkot</td>
<td>Suburban</td>
<td>Residential</td>
<td>Bhaktapur/SouthEast</td>
<td>27°41′21″N 85°13′05″E 1491</td>
</tr>
<tr>
<td>Thankot</td>
<td>Rural</td>
<td>Forest/agriculture</td>
<td>Kathmandu/West</td>
<td>27°40′37″N 85°21′25″E 1443</td>
</tr>
<tr>
<td>Godawari</td>
<td>Rural</td>
<td>Forest/agriculture</td>
<td>Lalitpur/South</td>
<td></td>
</tr>
</tbody>
</table>

Note: * sites used in both dry and monsoon season of 2014

(1) Site type is based on local GIS data from rds.icimod.org. Furthermore, this classification is supported by approximate distance (in km) from Kathmandu city’s core ring road. Urban < 3km; 3km < Suburban < 6km; and Rural > 6km. Land use type adopted from GIS data viewer (rds.icimod.org).

(2) Region classification is based on geographic location with respect to the main ring road surrounding Kathmandu city. Sites within the core ring road are classified as central regions. Kathmandu Valley includes three districts: Kathmandu, Bhaktapur, and Lalitpur.

(3) Coordinates and altitude, in meters, adopted from Google Earth and IASS POTSDAM database.
A.II: Results (Variability across sites)

Concentration data from passive sampling of NO₂, NOx, NO, SO₂ and O₃ in 2014 is presented in Table 8. In monsoon season alone, mean concentrations of nitrogen oxide species (NOx, NO₂ and NO) were highest at urban sites (NO₂ 66.2 ± 56.1 µg/m³, NOx 109.2 ± 107.8 µg/m³, NO 77.5 ± 94.3 µg/m³) and lowest in rural sites (NOx 6.2 ± 1.1 µg/m³, NO 0.2 µg/m³), with the exception of NO₂ measuring lowest levels at suburban sites (4.9 ± 1.0 µg/m³) (Figure 22). The weekly mean concentrations of O₃ at rural sites (15.2 ± 11.7 µg/m³) were slightly higher than urban sites (15.1 ± 6.2 µg/m³) and lowest in suburban sites (13.8 ± 0.3 µg/m³). SO₂ weekly mean concentrations at urban sites (15.6 ± 15.6 µg/m³) were higher than rural (5.0 µg/m³) and suburban sites (4.3 µg/m³) (Figure 22).
Table 8: Weekly concentration of NO₂, NOx, NO, O₃ and SO₂ in µg/m³ 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</th>
<th>NO₂</th>
<th>NOx</th>
<th>NO</th>
<th>SO₂</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dry</strong></td>
<td>Urban</td>
<td>Feb 23rd – 28th</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 2nd – 7th</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 9th – 14th</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 23rd – 28th</td>
<td>Tripureshwor</td>
<td>93.6</td>
<td>185.6</td>
<td>92</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mar 30th – Apr 4th</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><strong>Monsoon</strong></td>
<td>Urban</td>
<td>Jul 27th – Aug 1st</td>
<td>Balaju</td>
<td>88</td>
<td>88</td>
<td>-</td>
<td>32.5</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aug 6th – 10th</td>
<td>Jawalakhel</td>
<td>184.4</td>
<td>184.4</td>
<td>-</td>
<td>31.1</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aug 10th – 15th</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 18th – 22nd</td>
<td>Gaushala</td>
<td>115.1</td>
<td>335.6</td>
<td>220.5</td>
<td>-</td>
<td>11.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sep 13th – 19th</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></td>
<td></td>
<td>Aug 31st – Sep 7th</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></td>
<td></td>
<td>Sep 6th – 13th</td>
<td>Dadhikot</td>
<td>24.7</td>
<td>28.8</td>
<td>4.1</td>
<td>-</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sep 13th – 21st</td>
<td>Lainchaur</td>
<td>17.1</td>
<td>17.12</td>
<td>-</td>
<td>0.3</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aug 27th – Sep 3rd</td>
<td>Lokanthali</td>
<td>11.9</td>
<td>11.9</td>
<td>-</td>
<td>-</td>
<td>13.2</td>
</tr>
<tr>
<td><strong>Suburban</strong></td>
<td>Urban</td>
<td>Aug 27th – Sep 3rd</td>
<td>Kirtipur</td>
<td>4.2</td>
<td>47</td>
<td>42.8</td>
<td>4.3</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sep 4th – 12th</td>
<td>Balkot</td>
<td>5.6</td>
<td>6.2</td>
<td>0.6</td>
<td>-</td>
<td>13.6</td>
</tr>
<tr>
<td><strong>Rural</strong></td>
<td></td>
<td>Sep 6th – 12th</td>
<td>Thankot</td>
<td>6.7</td>
<td>6.9</td>
<td>0.2</td>
<td>5.0</td>
<td>23.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aug 23rd – Sep 3rd</td>
<td>Godavari</td>
<td>5.4</td>
<td>5.4</td>
<td>-</td>
<td>-</td>
<td>6.9</td>
</tr>
</tbody>
</table>

- Below Method Detection Limit (MDL)

a Measurements conducted in consecutive weeks at one site at a time
Figure 22: One week concentrations (µg/m^3) of gases from monsoon season of 2014 classified by site type. Note: On-road urban sites not included. Error bars = standard deviation

A.III: Results (Temporal variations)

Dry winter and monsoon measurements of NO₂, NOx, NO, SO₂ and O₃ were made at five on-road urban locations in 2014 (Figure 23). NO₂, NOx and NO concentrations showed higher levels in the winter season (NO₂ 103.9 ± 15.7 µg/m^3, NOx 211.2 ± 58.5 µg/m^3, and NO 134.0 ± 41.6 µg/m^3) compared to the monsoon season (NO₂ 102.0 ± 51.2 µg/m^3, NOx 177.7 ± 99.6 µg/m^3, and NO 126.2 ± 94.3 µg/m^3). The weekly mean concentrations of O₃ during the monsoon season (16.6 ± 6.5 µg/m^3) were higher than measurements from the dry season (14.0 ± 9.6 µg/m^3), while SO₂ levels were also higher during the monsoon season (25.5 ± 11.0 µg/m^3) than measurements from the dry season (6.8 ± 0.4 µg/m^3) (Figure 23).
A.IV: Discussion (Variability across sites)

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 NO$_2$ (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 NO$_2$ concentrations were observed from on-road vehicle sources with NO$_2$/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 O$_3$ 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).

SO\textsubscript{2} levels remained low throughout the dry season (Table 8, and Figure 22). Although a large fraction of the data was below the detection limit, higher average SO\textsubscript{2} levels were observed during the rainy season (25.4 ± 11 µg/m\textsuperscript{3}) compared to winter season (6.7 ± 0.4 µg/m\textsuperscript{3}) at urban sites. As discussed earlier, the major source of SO\textsubscript{2} in suburban and rural locations is brick production, an industry which does not normally operate in rainy season and hence the SO\textsubscript{2} concentrations were expected to be lower in rainy season. Also, frequent rain events wash away SO\textsubscript{2} from the atmosphere through acidic rain formation. Incomplete site type and missing data limits our spatial variability interpretation of the SO\textsubscript{2} concentrations observed during the winter season alone. In contrast, spatial variability is observed during the monsoon season (Figure 23). Mean SO\textsubscript{2} levels were lower in urban areas (0.7 ± 0.7 µg/m\textsuperscript{3}) compared to suburban (4.3 µg/m\textsuperscript{3}) and rural (5.0 µg/m\textsuperscript{3}) sites. O\textsubscript{3} levels in the monsoon season (14.0 ± 1.1 µg/m\textsuperscript{3}) remained similar among all site types and also were comparable to winter season (14.0 ± 9.6 µg/m\textsuperscript{3}). Moreover, mean concentrations of NO\textsubscript{2} at urban sites (21.4 ± 8.7 µg/m\textsuperscript{3}) in the monsoon season were higher than suburban sites (NO\textsubscript{2} 4.9 ± 1.0 µg/m\textsuperscript{3}) while mean concentrations of NO\textsubscript{x} and NO at urban sites (NO\textsubscript{x} 23.6 ± 11.1 µg/m\textsuperscript{3}, NO 4.4 ± 0.4 µg/m\textsuperscript{3}) were lower than suburban sites (NO\textsubscript{x} 26.6 ± 28.8 µg/m\textsuperscript{3}, NO 21.7 ± 29.8 µg/m\textsuperscript{3}) during the same monsoon season. Large NO deviation observed in (Figure 22) indicates that one site in particular, Kirtipur (Table 8), was responsible for deriving the average levels of NO and NO\textsubscript{x} 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, lowest levels of NOx and NO (6.2 ± 1.1 µg/m³ and 1.0 µg/m³, 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/m³) were slightly higher than suburban sites (4.9 ± 1.0 µg/m³), however, this can be explained either by NO₂ long range transports (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.

A.V: Discussion (Temporal variations)

The overall average concentrations of trace gases for 2014 winter and monsoon seasons are shown in Figure 23. From the 2014 measurements, it is interesting to note that monsoonal on-road concentrations were no lower (with the exception of SO₂) than compared to winter season trace gas levels (Figure 23), 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 (Figure 23). Similar NO₂ levels in the two seasons, likely because the focus of this study was on-road emissions in busy roadways. Our findings of NO₂ levels (103.9 ± 15.7 µg/m³ and 102 ± 51.2 µg/m³ during, dry and wet season, respectively) are at least a factor of two higher than the urban on road NO₂ levels reported in 2008 (18.9-52.6 µg/m³ and 12.4-33.6 µg/m³ during dry and rainy season, respectively) (Byanju et al., 2012).

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 mean levels of trace gas with the exception of ozone, where it was often highest (Figure 22). \( \text{SO}_2 \) and \( \text{O}_3 \) levels were elevated in the monsoon season (\( \text{SO}_2 \) 25.4 ± 11 µg/m\(^3\) and \( \text{O}_3 \) 16.6 ± 6.5 µg/m\(^3\)) compared to the winter season (\( \text{SO}_2 \) 6.7 ± 0.4 µg/m\(^3\) and \( \text{O}_3 \) 14 ± 9.6 µg/m\(^3\)). This is contrary to the previous study (Byanju et al., 2012) that reported higher levels of \( \text{SO}_2 \) during the winter season. It should be noted that fewer samples of \( \text{SO}_2 \) are available in this study because 50% of collected on-road samples were below the detection limit (Table 8). Comparing \( \text{SO}_2 \) levels at Jawalakhel, where both monsoon and winter levels are available (Table 8), 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, \( \text{NO} \) levels during monsoon season were below the detection limit possibly because of reaction with high \( \text{O}_3 \), suggesting high ozone levels (Table 8). In addition, lowered \( \text{O}_3 \) levels during the winter season could be partly explained by the presence of higher \( \text{NO} \) levels in the winter season compared to the monsoon season; leading to enhanced \( \text{O}_3 \) titration by \( \text{NO} \). These five on-road urban sites are in the immediate vicinity of very large \( \text{NO} \) 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 \( \text{NOx} \) species and \( \text{O}_3 \) levels.
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