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Near-road sampling of $PM_{2.5}$, BC, and fine particle chemical components in Kathmandu Valley, Nepal

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Abstract

Semi continuous $PM_{2.5}$ and BC concentrations, and 24-hour integrated $PM_{2.5}$ filter samples were collected near roadways in the Kathmandu Valley, Nepal. Instruments were carried by a group of volunteer traffic police officers in the vicinity of six major roadway intersections in the Kathmandu Valley across two sampling periods in 2014. Daily $PM_{2.5}$ filter samples were analyzed for water soluble inorganic ions, elemental carbon (EC) and organic carbon (OC), and 24 elements. Mean $PM_{2.5}$ and BC concentrations were 124.76 μg m^{-3} and 16.74 μgC m^{-3} during the drier spring sampling period, and 45.92 μg m^{-3} and 13.46 μgC m^{-3} during monsoonal sampling. Despite the lower monsoonal $PM_{2.5}$ concentrations, BC and

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several elements were not significantly lower during the monsoon, which indicates an important contribution of vehicle-related emissions throughout both seasons in this region. During the monsoon, there was an enhanced contribution of chemical species (elements and water soluble inorganic ions) except secondary inorganic ions, and BC to $PM_{2.5}$ (crustal elements: 19%; heavy metals: 5%; BC: 39%) compared to those in spring (crustal elements: 9%; heavy metals: 1%; BC: 18%). Silica, calcium, aluminum, and iron were the most abundant elements during both spring and the monsoon, with the total concentrations of 12.13 and 8.85 μg m^{-3}, respectively. $PM_{2.5}$ and BC showed less spatial variation compared to that for individual chemical species.

1 Introduction

Particulate matter is a worldwide air pollution burden but often most onerous in the developing nations (Han and Naeher, 2006). One such example is the Kathmandu Valley in Nepal where degraded air quality is a major environmental and societal issue. The valley has gone through transformative social and economic changes over last two decades. With its current population of about 3.5 million, the Kathmandu Valley is growing at a rate of 4 percent per year (CBS, 2014). The Kathmandu Valley has the highest population density (2800 persons/sq. km.) in the nation (CBS, 2014), and concomitant with population growth, the number of vehicles in the Bagmati zone, one of the fourteen administrative zones where the Kathmandu Valley is located, has increased by almost nine-fold over two decades, with a total of 922,900 vehicles in 2014/15 (Department of Transportation Management, 2015). Motorcycles and passenger vehicles (cars, jeeps, and vans) are the main vehicle types, amounting to 92% of the total registered

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vehicles in Bagmati zone by the year 2014-15. Out of total gasoline and diesel consumption across Nepal, about half the gasoline and one fifth of the diesel is consumed by Kathmandu alone (Malla, 2014).

Continued operation of older vehicles and poor road conditions are another cause of aggravated air quality problems in the valley. Shrestha et al. (2013) estimated that vehicle emissions from similar engines driving under the poor conditions in Kathmandu Valley were higher compared to other cities in developing countries in Asia. Traffic-related PM is especially important because it has been implicated in reducing lung function, in increasing respiratory diseases, cardiac arrhythmias, asthma, and changes in heart rate variability (Pope and Dockery, 2006; Gauderman et al., 2007; Zanobetti et al., 2010; Shakya et al., 2016). Several studies have reported the health effects associated with specific PM components (Ghio and Devlin, 2001; Janssen et al., 2013; Wu et al., 2013), emphasizing the importance of chemical composition information as essential to assess the health effects of PM and to understand its sources.

Besides emissions from vehicles and re-suspended road dust due to vehicles, emissions from more than 100 brick kilns, the widespread use of small captive power generators during scheduled power cuts, and burning household/municipal wastes are other major sources of air pollution in the valley (ICIMOD, 2007; Shakya et al., 2010; The World Bank, 2014; Kim et al, 2015). The Kathmandu Valley has been facing rapidly deteriorating air quality at a metropolitan scale resulting from rapid urbanization and modernization, high population growth, the increasing number of vehicles and fuel consumption throughout the region.

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Limited information exists for $PM_{2.5}$ (particles smaller than 2.5 micrometers in diameter) pollution (Aryal et al., 2009, Gurung and Bell, 2013; Stone et al., 2010) in this location, and even less information is available for PM chemical composition in the valley (Shakya et al., 2010; Chen et al., 2015). As developing nations continue towards economical and societal growth, they are likely to be faced with critical decisions on energy consumption, transportation infrastructure, and public health protection measures. In order to make the best informed decision on efficient and effective regulation, it is important to understand aerosol climatology by understanding spatiotemporal patterns, and to provide foundational emissions inventory data to support advanced emissions models. This is particularly true with complex meteorology, where there are significant seasonal monsoon circulation and precipitation that can substantially alter regional air quality, but its effect at the local level may be uncertain.

In this study, we investigated the variability in aerosol concentrations ($PM_{2.5}$ and BC) and $PM_{2.5}$ chemical composition to which people are exposed in the vicinity of six major traffic intersections of the Kathmandu Valley in two different seasons (spring/dry season and monsoon/wet season of the year). To our knowledge, this is the first comprehensive study of wide spatial and temporal variation of $PM_{2.5}$ pollution, notably $PM_{2.5}$ chemical composition, in the Kathmandu Valley, and builds upon related work (Shakya et al., 2016; Kiros et al., 2016) on anthropogenic air pollution exposure and health effects in this community.

2. Methods

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Aerosol sampling was conducted on roadsides at six locations in the Kathmandu Valley during two distinct sampling periods: Phase 1 in the spring (dry) season (February 16 – April 4, 2014) and Phase 2 in monsoon (wet) season (July 20 – August 22, 2014). The six sites were selected to observe spatial distributions of air quality across the central urban core of the Kathmandu Valley. With this aim, we selected six locations: Kalanki, Balaju, Chabahil, Koteswor, Thapthali, and Jawalakhel (Figure 1), and each location was sampled for 5-6 days. At each location, up to six adult volunteers, who were employed as traffic police officers, carried a small bag containing battery-operated sampling equipment. A small GPS was included to collect geolocation data every 15 seconds. Sampler inlet tubes were attached to the chest of the traffic volunteers, and connected to a scattering nephelometer (pDR-1500, Thermo Scientific, USA) and a microaethelometer (AE51, AethLabs, San Francisco, USA). Volunteers carried the equipment both during work hours (typically during the day) and continued sampling throughout the overnight hours. Overnight sleeping quarters were located on the ground floors of buildings adjacent to these major intersections at all sites except Jawalakhel, where the sleeping quarters were located about 50 meters from the main intersection. Samples were collected continuously by these officers from the beginning of their work week (Sunday mornings) through the end of their week (Friday afternoons). With this arrangement, up to six instrument packages were in use at any given time, with traffic officers stationed on or near roadways across their neighborhood during the day, and all officers returning to a common sleeping barracks at night. At the conclusion of a weeklong sampling deployment, the equipments were collected, quality assured, and relocated to a new neighborhood location. Four sites, Kalanki, Balaju, Chabahil, Koteshwor are located on Kathmandu's busy Ring Road, while the remaining two sites, Thapathali and Jawalakhel, are located in urban area inside the Ring Road.

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105 Because of the high concentrations of PM, weekly cleaning of inlet cyclones was performed with
106 deionized water. pDR nephelometer instruments were zeroed using a HEPA filter each week, and
107 volumetric flow rates were checked, and adjusted if necessary, with a traceable flowmeter. Filter tabs for
108 microaethalometer were always changed at least once every day, or more frequently depending on the
109 warning given by the microaethalometer. Final concentrations from filter measurements for various
110 chemical constituents were blank corrected by subtracting corresponding field blank values.

111

112 The pDR is calibrated against Arizona Test Dust (ISO 12103-1, Powder Technology, Inc, USA) by the
113 manufacturer, and operates at an accuracy of 5%. The instrument operated at 1.52 liters per minute on a
114 5 minute time base. Similarly, the microaethelometers operated at a 5 minute time base, but at 50 cc/min
115 because of the high BC loading anticipated in this measurement location. The Microaethalometer was
116 calibrated by the manufacturer before deployment in the field. Because of the impressive levels observed
117 in this study, techniques such as optimized noise-reduction averaging were deemed to be unnecessary in
118 order to obtain high quality data.

119

120 **2.1 $PM_{2.5}$ and BC sampling**

121 $PM_{2.5}$ and black carbon (BC) concentrations were measured in real time recording data every 5-minutes
122 by a portable scattering nephelometer (pDR-1500, Thermo Inc., US) and a microaethalometer (AE51,
123 Aeth Labs, US), respectively. Both instruments were fitted with individual $PM_{2.5}$ cyclone heads to sample
124 only particles less than 2.5 micrometers, and no denuding devices were employed.

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Daily (24-hour) $PM_{2.5}$ filter samples were collected on 37 mm filters (polyflourotetraethylene filters or pre-baked Quartz fiber filters) by the pDR instrument at a flow rate of 1.52 liters per minute. Filters were changed every morning. Polyflourotetraethylene (PTFE) filter and Quartz filter (QFF) were alternated every other day across all six sampler sets (i.e., all six samplers collected QFF on one day, and PFTE the next, and so on). Quartz fiber filters were baked at 850^{o}C for 4 hours prior to the use for sampling in Kathmandu Valley. After sampling, the filters were shipped to our laboratory for further chemical composition analyses.

2.2 $PM_{2.5}$ Chemical speciation

Elements: X-ray fluorescence (XRF) spectrometer (QUANT'X, Thermo Inc., US) was used to analyze elements on the particulate matter samples collected on a PTFE filter. Five scans were made for each filter with X-ray tube at 10-50 keV following EPA compendium methods for inorganic metal speciation (USEPA, 1999). Thin film element standards were used for calibrating elements.

Water soluble inorganic ions: After non-destructive XRF analyses, the PTFE filters were digested by adding 5 µL of ethanol and 25 mL and deionized water. The solutions were sonicated for two hours and stored at 4^{o}C before analyses. The solution was then analyzed for water-soluble ions: chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), sodium (Na^+), potassium (K^+), ammonium (NH_4^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) using Ion Chromatography (Thermo Inc., US). IC calibration was based on NIST-traceable standards following our laboratory standard operating protocol for serial dilution.

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EC-OC: A 1.24 cm^2 punch was taken from the QFF for elemental and organic carbon analysis using a Sunset Laboratory OC/EC analyzer (Sunset Labs, US) following NIOSH-based thermo-optical methods (Birch and Cary, 1996). The instrument was validated with both external sucrose standards and an internal methane standard following the manufacturer's recommendations.

3. Results and discussion

3.1 Seasonal and diurnal variability of $PM_{2.5}$ and BC concentration

Hourly average $PM_{2.5}$ concentrations in the vicinity of six major road intersections in the Kathmandu Valley were observed to vary in the range of nearly zero to 800s of μg m^{-3} (Figures 2 and 3) with the 5-minute maxima reaching above 1000 μg m^{-3} during the spring sampling period. As expected, $PM_{2.5}$ levels were decreased during the monsoon season with only one hourly average value exceeding 100 μg m^{-3}. The median hourly average $PM_{2.5}$ concentration in spring (101.2 μg m^{-3}) was nearly three times higher than that in the monsoon (36.3 μg m^{-3}). It is interesting to note that BC levels were not much different during the two seasons (Figure 2).

$PM_{2.5}$ concentration showed strong diurnal variability with two distinct peaks occurring during the mornings and evenings (Figure 3) which correspond to rush hour traffic. Such peaks occurred during the measurements in both seasons, though unsurprisingly, they were attenuated during the monsoonal sampling. BC also exhibited similar diurnal variability, and suggests that vehicle emissions are an important PM source in the valley. The BC concentration spikes during these rush hours were more

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pronounced with larger peak concentrations at rush hours compared to other hours. Past studies (Panday and Prinn, 2009; Aryal et al., 2009; Sharma et al., 2012) have shown that morning and evening peaks for PM_{10}, $PM_{2.5}$, BC, and carbon monoxide (CO) have been observed in the Kathmandu Valley. Morning peaks during the spring were qualitatively larger than evening peaks in spring compared to monsoon for both $PM_{2.5}$ and BC. Such differences are likely due to strong nocturnal inversion layers and stagnant conditions during spring in Kathmandu Valley (Panday and Prinn, 2009). This latter study was based on measurement sites that were at a significant distance away from busy roads, and morning and evening peaks were found even on days without a regular rush hour.

A source of PM thought to be important in Kathmandu are brick kilns, which are important economic engines that manufacture bricks for construction. These kilns are operated only in the winter and spring, and often use coal for a fuel source. With one exception, the selected sampling locations were more than 10 km away from active brick kilns. The Kalanki location, however, is located approximately 5 km to the east from a small cluster of kilns, and may have been affected by this emission source.

In this current study, the highest $PM_{2.5}$ concentrations occurred between 6-10AM during spring and returned to pre-6AM concentrations after 11AM (Figure 3a). However, during the summer monsoonal sampling (Figure 3b), $PM_{2.5}$ concentrations quickly rose after 6AM and these elevated concentrations persisted well into the evening. BC diurnal pattern were qualitatively similar to $PM_{2.5}$ during the monsoon and spring sampling campaigns with a rapid increase in concentration between 6-10AM, a falling

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concentration during midday, and a second peak in concentration during the afternoon rush hour period. Diurnal variations for BC were similar to that for $PM_{2.5}$ (Figures 3c and 3d).

24-hour $PM_{2.5}$ average was calculated from the hourly average of 5-minute measurements. These data exceeded the WHO guidelines for 24-hour mean concentration (25 μg m^{-3}) for all of 32 days of the sampling period during spring, and for 20 days out of 23 days in monsoon. The 24-hour ambient $PM_{2.5}$ standard set by the Nepal government is 40 μg m^{-3}. All days during spring and 13 days out of 23 days in summer exceeded the national 24-hour ambient $PM_{2.5}$ standard of Nepal. The 24-hour $PM_{2.5}$ mean was 124.8 ± 55.9 and 45.1 ± 16.4 μg m^{-3} during spring and monsoon, respectively. It should be noted, however, these data were based on samples collected by mobile traffic personnel who lived and worked near busy roadways and reflects a composite of both on-road, near-roadway and sometimes indoor samples; the measurements were not made from the fixed monitors typically used in regulatory monitoring and do not necessarily reflect typical urban conditions subjected to regulatory action.

Spatial variability of $PM_{2.5}$ levels was similar during both seasons. Though the monitoring at the six sites was performed on six different weeks, we can compare the overall variation among the sites for the same season. Balaju had the largest $PM_{2.5}$ concentrations (198.4 μg m^{-3}) compared to other sites (94.3 - 120. 6 μg m^{-3}) during spring (Figure 2). During the summer monsoon, $PM_{2.5}$ ranged from 25.6 to 57.9 μg m^{-3} with the highest and lowest concentrations at Balaju and Thapathali, respectively. This was consistent with observed results from Balaju, a neighborhood adjacent to a large bus terminal where the highest

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207 $PM_{2.5}$ concentrations were observed. Thapathali and Jawalakhel, with the lowest $PM_{2.5}$ levels, are located
208 inside the city, and have paved roads with minimal road dust compared to other sites.
209
210 Overall, there was 57-74% reduction in $PM_{2.5}$ concentrations (based on mean concentration) at four sites
211 during summer-monsoon season compared to spring. During the monsoon, there was greater reduction at
212 Jawalakhel (73%) and Thapathali (72%) compared to Balaju (61%) and Chabahil (55%). The monsoon
213 season was characterized by higher ambient temperature and more frequent rain events (~80% of total
214 annual precipitation occurs during June-September period) leading to both less energy use (such as
215 absence of brick production, significantly less number of captive power generator sets, less burning of
216 trace). The use of air conditioners in the Kathmandu Valley is not common, however electric home
217 heaters, heaters that use bio-briquettes, kerosene and LPG are common in the cooler winter. Scheduled
218 power outages are also reduced in summer-monsoon leading to a lower usage of diesel generators in the
219 summer-monsoon.
220
221 Daytime concentrations were computed as the average from 6AM to 8PM and nighttime concentrations
222 were averaged as 8PM to 6AM from hourly averages of 5-minute measurements. $PM_{2.5}$ concentrations
223 were higher in the spring than in the monsoon (Figure 4a and 4b). However, such differences between
224 two seasons were much larger for daytime compared to nighttime. Daytime $PM_{2.5}$ concentrations
225 exceeded nighttime by ~1.5 times during spring, while these were ~3 times higher during the monsoon.
226 Balaju had the largest daytime and nighttime $PM_{2.5}$ levels in both seasons. Many long-route night buses
227 operate from the Balaju (Gongabu) bus terminal, and this may partially explain these results. Balaju,

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Chabahil, Koteswor, and Kalanki, sites that are located along the Ring Road, had larger spring daytime $PM_{2.5}$ levels compared to the two sites located inside the Ring Road, Thapathali and Jawalakhel. Heavy-duty trucks, vehicles failing emission tests, and trucks carrying construction material are not allowed to enter inside the Ring Road during the daytime. Diesel trucks, pickups and jeeps are thought to cause more pollution than diesel cars and vans in Kathmandu valley (Ale and Nagarkoti, 2003), and heavy-duty vehicles are expected to cause more road dust suspension than lighter duty vehicles (Charron and Harrison, 2005; Garg et al., 2000). This, along with poorer road conditions around the four sites on the Ring Road, might be the reason for higher PM concentrations observed at these four sites on the Ring Road compared to the other two sites during daytime.

Daytime and nighttime BC levels in the two seasons followed a spatial variation similar to $PM_{2.5}$ (Figures 4c and 4d). The seasonal difference of BC concentration was much smaller during the daytime compared to nighttime. Traffic conditions (except diesel trucks) across the two seasons are not expected to be very different, which is indicated by a much smaller difference in BC concentration during two seasons despite the large seasonal difference in $PM_{2.5}$. The number of diesel trucks on roads are decreased during summer-monsoon because of the reduction in brick production and less demand in other construction materials. Such trucks could comprise the significant number (more than half) of vehicle movement in certain regions in the valley (JICA, 2012). While there is somewhat enhanced BC in the spring, this may be due to the stronger nighttime inversion and increased combustion and energy demand during spring. Increased BC concentration may also be partially explained by reliance on diesel-generators which are frequently used during the winter and spring dry months in the Kathmandu Valley to meet electrical power

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requirements by hospitals, hotels, industries, banks, and commercial operations (The World Bank, 2014) since electricity is often in short supply throughout the region in winter and spring. Such persistent emission of BC not only poses a serious threat to residents in Kathmandu Valley, but BC is also an important short-lived climate forcing agent. Black carbon also contributes to atmospheric brown cloud formation and it affects regional climate, and glacier melting in the Himalayan region (Ramanathan and Carmichael, 2008).

3.2 Association of BC and $PM_{2.5}$

$PM_{2.5}$ and BC were correlated with each other (Figure 5) during both spring ($r = 0.65$, $p<0.001$) and monsoon seasons ($r = 0.70$, $p<0.001$), suggesting that a large fraction of $PM_{2.5}$ in the valley is co-emitted with BC directly from primary emission sources. While BC concentrations did not differ much during the two seasons, $PM_{2.5}$ concentrations were substantially lower during monsoon. The ratio of $PM_{2.5}$ to BC, based on simple linear regression relationship, was much lower during monsoon (slope = 1.37) compared to spring (slope = 4.24).

3.3 Chemical characteristics of $PM_{2.5}$

Carbonaceous aerosol constituents (EC and OC) dominate the $PM_{2.5}$ chemical components (Table 1). Among the water-soluble inorganic ions: sulfate (SO_4^{2-}), ammonium (NH_4^+), calcium (Ca^{2+}), potassium (K^+), chloride (Cl^-), and nitrate (NO_3^-) had the largest concentrations (Figure 6). Elemental analysis results showed silica (Si), calcium (Ca), aluminum (Al), iron (Fe), potassium (K) as the major elements with individual concentrations greater than 1 μg m^{-3} in both phases. Other dominant elements such as

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magnesium (Mg), zinc (Zn), sulfur (S), sodium (Na), chlorine (Cl), barium (Ba), and scandium (Sc), though not having greater than 1 μg m^{-3} in both phases, contributed about 5.4 μg m^{-3} in spring and 3.8 μg m^{-3} in monsoon. Elements such as silica, scandium (Sc), manganese (Mn), magnesium (Mg), potassium (K), iron (Fe), copper (Cu), chromium (Cr), calcium (Ca), and aluminum (Al) also were highly correlated with each other (Figure 7) during spring. This suggests that dust resuspension is an important contributor to PM concentration in spring.

3.3.1 Carbonaceous aerosol

Carbonaceous aerosol constitutes the major fraction (64%) of $PM_{2.5}$ concentration during spring (Table 1). EC and OC are moderately correlated with each other in spring ($r = 0.37$, $p<0.001$) (Figure S1). The 24-hour average $PM_{2.5}$-EC from filter analysis and 24-hour mean BC (from 5-minute average measurement) measured with a microaethalometer indicate good agreement with each other (Figure S2). The EC concentrations were larger than BC concentrations during spring, and likely suggest the possibility of overestimation of EC in our measurements. Previous studies have showed some deviations in BC and EC measurements (Allen et al., 1999; Kim et al., 2013). Lower BC values compared to EC values have also been recorded in other studies (Babich et al., 2000; Salako et al. 2012), and these results are likely attributed to analytical measurement differences and measurement uncertainty.

Both OC and EC concentrations were the highest in Balaju during spring, showing this site to be more polluted compared to other five sites in the Kathmandu Valley. QFF samples collected during the monsoonal period were contaminated irretrievably and are, unfortunately, not included in the discussion.

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292 **3.3.2 Water-soluble ions**

293 Water-soluble inorganic ions exhibited high spatial and temporal variability across six sites in the
294 Kathmandu Valley (Figure 6). The average concentrations of 11 water-soluble ions from all sites were
295 23.6 and 9.1 μg/m^3 during spring and monsoon, respectively. Among ions, SO_4^{2-}, NH_4^+, Ca^{2+}, and K^+
296 were the major ions dominating the $PM_{2.5}$ chemical composition (by mass) during both seasons (Table
297 1). Though Ca^{2+} concentrations were similar in both seasons, SO_4^{2-} and NH_4^+ concentrations were reduced
298 by about a factor of five during the monsoon. NO_3^- was reduced by a factor of two in the monsoonal
299 period. High concentrations of SO_4^{2-} observed in Kathmandu Valley during spring may have been derived
300 by the increased emission of precursor gas (i.e. SO_2) during spring from activities such as operation of
301 brick kilns (which use high sulfur containing coal), diesel-generators, and diesel-trucks. There was a slight
302 increase in Ca^{2+} concentration in monsoon than in spring (lacking statistical significance, however). This
303 suggests that dust contributions are either the same or slightly enhanced in monsoon compared to spring,
304 a surprising finding. Ca^{2+} concentrations have also been used to indicate Asian dust in several studies
305 (Choi et al., 2001; Shen et al., 2008). Again, monsoon $PM_{2.5}$ concentrations were lower by about a factor
306 of three compared to spring. Thus, the similar loading of Ca^{2+} suggests an impressive persistent dust
307 burden, even during the monsoon. Road conditions were worse around Balaju and Chabahil compared to
308 other sites, and it's likely that resuspension of road dust was an important emissions component in these
309 areas. Thus, it is not surprising that Ca^{2+} levels were the largest at Balaju and Chabahil during both spring
310 and monsoon seasons.

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Other water soluble ions, such as Mg^{2+} and K^{+} concentrations, were decreased in monsoon compared to spring. The concentration of K^{+} exceeded 1 μg m^{-3} at all sites except Thapathali during the spring. The K^{+} concentration ranged from 1.2 to 1.8 μg m^{-3} during the spring, and 0.1 to 1.0 μg m^{-3} during monsoon. During the monsoon, K^{+} concentration decreased by greater than a factor of five (<0.5 μg m^{-3}) at all sites except Balaju. This suggests an increased contribution from biomass burning sources during spring as K^{+} is a good marker for biomass burning emissions (Andreae, 1983; Duan et al., 2004), and is likely to be related to more open burning practices and refuse burning taking place during winter and spring months. High concentration of phosphate (PO_4^{2-}) (comparable to Mg^{2+} and Na^{+}) also suggest the increased contribution of residential burning to aerosol mass (Anderson et al., 2010).

During the spring, the largest SO_4^{2-} concentrations (15.2 μg m^{-3}) were observed at Thapathali despite this site having the smallest $PM_{2.5}$ concentrations. Such SO_4^{2-} spikes might be related to the increased operation of diesel-powered power generators at nearby hospitals, commercial showrooms, and many commercial businesses located in Thapathali area. Daily power outages are about 12 hours per day in spring, and this leads to increased use of small-scale diesel-powered generators at commercial and tourist facilities. Thapathali is a popular business district in Kathmandu.

With two exceptions (nitrite and calcium), mean concentrations of water-soluble inorganic ions was larger during spring compared to monsoon (Table 1). The largest difference was for SO_4^{2-} and NH_4^{+}-, when the spring concentrations were larger by a factor of ~5 compared to monsoon. The NO_3^{-} concentrations were more than two times higher in spring than in monsoon. $PM_{2.5}$ in general was higher in spring than

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monsoon due to additional emission sources and atmospheric stagnation during spring. The lower levels of the water-soluble ions during monsoon could mainly be due to wet removal of particles containing these ions. Increased levels of NO_3^-, SO_4^{2-}, and NH_4^+ in spring compared to monsoon might also be contributed by the low temperature and increased relative humidity favoring ammonium nitrate or ammonium sulfate formation and their partition into particulate phase. Not surprisingly, NH_4^+ was strongly correlated with SO_4^{2-} ($r = 0.65$ in spring and $r = 0.90$ during monsoon). NO_2^- and Ca^{2+} were about 20% and 10% higher, respectively, during the monsoon than during spring.

Among the inorganic ions, fluoride (F^-) had the lowest concentrations (0.01 - 0.04 μg m^{-3}) in both seasons, though still quantifiable. Potential fluoride sources could be coal combustion, phosphorus fertilizer, soil dust, and biomass burning (Feng et al., 2003; Jayarathne et al., 2014).

3.3.3 Elemental composition

Crustal elements such as Al, Si, Ca, and Fe were observed at higher concentrations (2-6 μg m^{-3}) during both seasons (Table 1). Among the analyzed elements, Si mass was the highest which reinforces the large contribution of soil/sand and crustal material to $PM_{2.5}$ mass concentrations near roadways in Kathmandu valley. Silica in PM also comes from cement used in construction work, road surface dust, and tire wear (Kreider et al., 2010). Crustal elements such as Al, Si, Ca, Fe, and also Mg were 2-3 times higher at Balaju and Chabahil compared to other four sites during both spring and monsoon. These elements were found to have higher concentrations at Koteshwor during the monsoon. These elements are likely to have originated from road dust due to the poor road conditions at both Balaju and Chabahil, and road

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construction occurring in the Koteshwor-Satdobato segment of the Ring Road during the sampling period. Additionally, some evidence suggests Fe, Mg, and Ca can also be emitted from diesel vehicles (Sharma et al., 2005). Tracer elements (Ba, Cu, and Zn) contributed 0.8 and 1.2 μg m^{-3} in the Kathmandu Valley during the spring and monsoon, respectively. They are likely associated with traffic-related emissions. Zn may be attributed to several traffic-related sources, such as tire wear, brake dust, automobile exhaust, and metallic barriers (Lough et al., 2005; Kreider et al., 2010). Cu and Ba were found to be among the major elements in abrasion dusts from brake pads manufactured in Japan (Iijima et al., 2007). Fe and titanium (Ti) were also commonly found in brake dust samples (Thorpe and Harrison, 2008).

Crustal elements were well correlated with each other, and this relationship was stronger in spring than in the monsoon sampling (Figure 7). Elements related with traffic (such as Cu and Zn) were also positively correlated with each other. One exception to this was Ba, which was correlated with Cu only during the monsoon. Total concentrations of eight heavy metals, Cr, Mn, cobalt (Co), Cu, Zn, arsenic (As), mercury (Hg), and lead (Pb), ranged from 0.2 to 1.1 μg m^{-3} at six sites during both sampling periods. Jawalakhel had the largest heavy metal concentration during spring and the second largest during monsoon. This site may be influenced by emissions from small metalcraft industries located 2-3 km from Jawalakhel.

3.3.3.1 Elemental enhancement during monsoon

Despite lower $PM_{2.5}$ concentrations in the monsoon compared to spring, most of the elements were enhanced in $PM_{2.5}$ in the monsoonal sampling (Figure 8). An enhancement ratio (ratio of $PM_{2.5}$-

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374 normalized elemental concentration during monsoon to spring) is plotted for 11 major elements observed
375 in this study.
376
377 The enhancement ratio is the largest for Ba suggesting the consistent and large contribution of traffic-
378 related $PM_{2.5}$ sources (Lough et al., 2005; Iijima et al., 2007) in the valley. The enhancement ratios were
379 within the range of 2-4 for Si, Ca, Fe, K, Al, Mg, and Na. High enhancement ratios for the elements
380 suggest that emissions of these elements were not concomitantly decreased in the monsoon compared to
381 spring even though total $PM_{2.5}$ was clearly decreased during the monsoonal sampling. This finding is
382 important for source apportionment activities, where monsoonal effects on emissions profiles might be
383 assumed to be proportionately reduced due to washout.
384
385 Among these elements, S is the only element that was not enhanced (ratio<1) in the monsoon relative to
386 spring. Non-enhancement of sulfur is also on par with the decrease of secondary inorganic ion
387 concentrations in the monsoon. Coal combustion is not likely the major sulfur emission source in the
388 valley in monsoon period, and if sulfur aerosol is formed from secondary sources, monsoonal loss of such
389 sulfur is likely. The major sulfur source probably arises from diesel fuel used in the Kathmandu Valley
390 throughout the year. An additional contribution is coming from coal combustion used in brick factories
391 during winter and spring months.
392
393 When the elements measured by XRF spectroscopy and the water-soluble ions of the same elements were
394 compared for such enhancements, it indicated consistent enhancement ratios between two techniques,

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except for Cl and Mg (Figure S3). For chlorine, water-soluble chloride ion was more enhanced in monsoon compared to total chlorine while water-soluble magnesium ion was less enhanced in monsoon compared to total magnesium.

3.4 Enrichment factor

Because of the relative importance of crustal material to aerosol loading in the Kathmandu Valley, we use an enrichment factor technique to assess potential aerosol sources. The enrichment factor (EF) is computed based on chemical composition of a generic upper continental crust (Taylor and McLennan, 1995) by using:

$$EF = \frac{(E_x/E_{Al})_{aerosol}}{(E_x/E_{Al})_{crust}}$$

Where $(E_x/E_{Al})_{aerosol}$ is the ratio of element ($\varkappa$) concentration to Al concentration in aerosol, and $(E_x/E_{Al})_{crust}$ is the ratio of the element ($\varkappa$) concentration to Al concentration in upper continental crust. In this exercise, Al is used as the reference element in crustal particles. Al was strongly correlated (r > 0.8) with the crustal elements, Si, Fe, Ca, and Mg during both seasons. Lower EF values (close to 1) suggest natural crustal origin while the higher EF values (greater than 10) suggest anthropogenic origin (Duan et al., 2006; Cong et al., 2010).

Mg has an EF less than 1 and is not shown in the illustration (Figure S4). Si also has an EF less than 1, but only during the monsoon. Si also had the lowest EF ratio among all the elements during spring. This suggests Mg and Si have mostly crustal origin. During the monsoon, Na, K, Ca, Mn, and Fe all have EF less than 10. These elements are also likely to be associated with crustal/dust sources during the monsoon.

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416

417 The elements Ca, Mn, and Na have EFs less than 10 or around 10 during spring suggesting them to be of
418 mostly crustal origin. Other trace elements have much larger EF suggesting the emissions from
419 anthropogenic sources. Potassium has EF <10 during monsoon and but EF >10 during spring, suggesting
420 additional anthropogenic sources of K during spring. This is consistent with the open burning practices
421 such as refuse burning, wood combustion, forest fires, and agro-residue burning taking place during spring
422 months (March-May) in the region. Elements such as Cu, Zn, and nickel (Ni) have EFs larger than 100,
423 suggesting the strong contribution of anthropogenic sources. Zn and Cu were strongly correlated (r>0.85)
424 in both seasons suggesting the origin of particles from the similar sources or common sources, such traffic
425 related sources such as tire wear and braking (Kreider et al., 2010). This confirms that traffic emissions
426 remain as one of the most important $PM_{2.5}$ source in Kathmandu Valley, and this is consistent with the
427 work by Sharma et al. (2000) that suggested urban air in Kathmandu is heavily influenced by local
428 anthropogenic sources such as automobile exhaust or fossil-fuel related emissions.

429

430 **3.5 Source apportionment by chemical components**

431 Though more than 300 filter samples were speciated in this study, there were only 12-18 samples collected
432 from each site in one week in each season. Among these 12-18 samples from each location, we analyzed
433 elemental and water-soluble ionic species; a second set of filters was collected on QFF, which was used
434 for analyzing carbonaceous species. Thus, the number of samples was inadequate to perform a robust
435 source apportionment using models such as the positive matrix factorization or similar technique for each

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location. Instead of such advanced models, we used a cruder method as follows to estimate the contributions of tracer species to $PM_{2.5}$ at each of our six sampling locations in both seasons.

By pooling six sets of measurements taken during the same week at each of the site and a season, we grouped chemical components of $PM_{2.5}$ into five potential source and chemical components: crustal, trace elements, secondary inorganic aerosols, biomass burning tracers, black carbon, and others (Figure 9). Crustal component was simply computed as the sum of five crustal elements, Mg, Al, Si, Ca, and Fe. Trace elements were a sum of 15 trace elements, P, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, cadmium (Cd), tin (Sn), Ba, As, and Pb. Sum of three water-soluble ions, sulfate, nitrate, ammonium, were used to indicate secondary aerosols. Cl and K are used as biomass burning tracers. "Others" accounts for sum of remaining water-soluble ions, organic matter, and remaining trace elements. Among the known (analyzed) chemical components, BC, crustal/dust, and secondary aerosols were the major components of $PM_{2.5}$. The percent contributions of BC, crustal, and trace elements components increased in monsoon compared to spring while secondary aerosols' contributions decreased in monsoon.

During spring, organic carbon (OC) contributed about 34 to 52% to $PM_{2.5}$ mass on the days when $PM_{2.5}$ samples were collected on QFFs. Carbonaceous aerosol (OC and EC) is the main component (~64%) of $PM_{2.5}$ during spring in the Kathmandu Valley. In a previous study during spring at an urban location in the Kathmandu Valley, carbonaceous aerosol contributed 63% to the total speciated aerosol (carbonaceous and ionic aerosols) (Shakya et al., 2010).

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457 It is interesting to note that BC contribution was larger and crustal contributions was smaller in the two
458 sites located inside inner cities, Jawalakhel and Thapathali, compared to other four sites (except
459 Koteshwor where no samples were collected in spring) during the monsoon. The sum of the five crustal
460 element concentrations were highest at Chabahil (spring: 16.9 μg m^{-3}, monsoon: 12.7 μg m^{-3}) and Balaju
461 (spring: 17.7 μg m^{-3}, monsoon: 10.5 μg m^{-3}), and the lowest at Thapathali (spring: 4.4 μg $m^{-3,}$ monsoon:
462 1.8 μg m^{-3}) and Jawalakhel (spring: 9.6 μg m^{-3}, monsoon: 5.8 μg m^{-3}). BC concentrations exceed crustal
463 elemental concentrations by a factor of 1.3-1.8 at Balaju, Chabahil, Jawalakhel, Kalanki, and Koteshwor.
464 This suggests dust and traffic emissions are the most important PM emission sources in the valley. One
465 exception is Kalanki, where the BC/dust ratio was 3.2, and Thapathali with BC/dust ratio of 2.8 and 6.2
466 during spring and monsoon, respectively. Concentrations of biomass burning tracers were the largest at
467 Balaju and Chabahil during both spring (4.1 - 4.6 μg m^{-3}) and monsoon (1.1 - 1.5 μg m^{-3}). Chabahil is
468 located near Pashupati, which is the main cremation site for the community. This process is biomass-
469 burning intensive and occurs year round, and may partially explain these results.
470
471 **3.6 Spatial variability within the sites**
472 The coefficient of divergence (COD) was computed within four locations for $PM_{2.5}$, BC, and several
473 chemical species (Figure 10) to explore the differences in concentrations within each of these specific
474 locations due to mobile nature of the sampling by six traffic volunteers at the same time. The higher COD
475 values indicate heterogeneity and lower COD values indicating homogeneity (Wilson et al., 2005). The
476 COD values lower than two are considered as homogeneous (Thornburg et al., 2009). Two locations (i.e.,
477 Kalanki and Koteshwor) did not have enough data points for both seasons, and they were excluded from

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the analysis. The COD is utilized to quantify the heterogeneity of the parameters measured from the same set of instruments carried around by six traffic police officers in the vicinity of a site. The six traffic police officers were within about 2 km from each other, and all the measurements were taken concurrently for a period of six days. Overall, Jawalakhel and Thapathali were the most heterogeneous for chemical species, suggesting the presence of more diverse sources at their vicinity. Balaju was the least heterogeneous for most of the chemical species. BC and $PM_{2.5}$ were the most homogeneous (COD<0.2) among the four sites, while chemical components were the most heterogeneous. BC had the least spatial variation among all sites except Thapathali. This might be due to BC loadings from additional significant sources such as diesel-generators at Thapathali.

Tracers of dust particles and secondary inorganic ions had the highest intra-site variation. A large fraction of these samples were in the immediate vicinity of roads with heavy to moderate traffic and thus the traffic emissions being the prevalent source. Despite the similarity of measurements (within short distance and similar local settings) in Kathmandu Valley, chemical species were still variable within such short distances among these six sets of measurements. The COD values show that concentrations could vary even among the similar sites within a short distance. The differences in contributions of local sources, transient emission events, and measurement error (Pinto et al., 2004) might explain the high spatial variability observed in Kathmandu Valley.

Conclusions

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This study documented distinct seasonal (dry season versus wet season) and diel variations in $PM_{2.5}$ and BC levels in the Kathmandu Valley. The variability of $PM_{2.5}$ and BC was greater for nighttime levels than daytime levels, suggesting that local $PM_{2.5}$ emissions were not much reduced during monsoon. Meteorological factors such as higher temperature and wind speeds, change in wind directions, increased amount and frequency of rainfalls, absence of certain types of emissions (such as trash burning, brick production), and a weaker nocturnal boundary layer may have played the main role in lower concentrations of $PM_{2.5}$ in the Kathmandu Valley during the monsoon. BC was only marginally reduced by monsoonal sampling conditions. This indicates that there is prevalence of BC sources near roads, most likely traffic emissions, in the Kathmandu Valley, which pollutes the Valley's air with BC constantly throughout the year.

Organic carbon was abundant and ubiquitous aerosol component at all six locations in the Kathmandu Valley. OC aerosol contributed the largest fraction of $PM_{2.5}$ followed by EC, SO_4^{2-}, NH_4^+, and crustal elements. Not surprisingly, all samples from the six sites were heavily influenced by traffic-related emissions and dust, and vehicle emissions were found to be a major source of $PM_{2.5}$ chemical components in these locations. High concentrations of SO_4^{2-} in Kathmandu Valley point to the influence of diesel and coal combustion in valley's air pollution, particularly during the winter and spring months with fairly similar emission and meteorological characteristics. Despite the close proximity and similarity of the sites (close to busy traffic with a similar upwind regional emissions source), $PM_{2.5}$ chemical species were found to be spatially variable across specific chemical species, but less variable for bulk measurements of $PM_{2.5}$ and BC.

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520 For air quality management purposes in Kathmandu valley, this study suggests that traffic related
521 emissions and soil/dust/construction materials are the main sources of $PM_{2.5}$ near roadside locations.
522 Chemical components data also suggest that biomass burning, secondary ions, and dust contribute to
523 $PM_{2.5}$ during the drier spring, with a diminished effect in the rainier summer. In contrast, dust contribution
524 is much enhanced in $PM_{2.5}$ during monsoon period, while water-soluble ion concentrations were reduced
525 in the same period as they are efficiently washed out by rain. During monsoon, frequent rains on unpaved
526 roads may facilitate vehicles to resuspend dust particles.

527

528 More broadly, this unique dataset highlights a divergence in concentrations that were thought to be
529 downwardly affected by large scale meteorological effects. While $PM_{2.5}$ was substantially reduced during
530 the monsoon, there was no such decrease in BC levels; similar findings were observed for a number of
531 trace elemental components in ambient aerosol. These data have important relevance for promulgating
532 optimized air quality control measures, protection of human health, and assessment of climate forcing
533 effects from localized emissions. As a result, there remains much to understand in how highly polluted
534 communities in the developing world can affect local and regional air quality.

535

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703 in spring season and monsoon season at six locations in the Kathmandu Valley.

704 Figure 7. The matrix of correlation coefficients between elements, ions, BC, and $PM_{2.5}$ concentrations
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718 Table 1. Summary of $PM_{2.5}$ chemical composition (μg m^{-3}) in the Kathmandu Valley during spring season (Phase
719 1) and monsoon season (Phase 2).
720

Chemical species	Phase 1 (Spring)	Phase 2 (Monsoon)
$PM_{2.5}$	119.02 ± 33.36	41.88 ±20.85
BC	18.20 ±7.36	14.03 ±7.39
Carbonaceous (*n*=94 for Phase 1; *n*=70 for Phase 2)		
OC	48.39 ± 20.57	NA
EC	28.09 ± 16.40	NA
Water-soluble ions (*n*=86 for Phase 1; *n*=81 for Phase 2)		
F^-	0.09 ± 0.08	0.04 ± 0.13
Cl^-	0.79 ± 1.02	0.37 ± 0.51
NO_2^-	0.48 ± 0.82	0.58 ± 0.89
NO_3^-	0.69 ± 0.36	0.28 ± 0.34
PO_4^{2-}	0.17 ± 0.11	0.08 ± 0.06
SO_4^{2-}	10.67 ± 4.03	2.09 ± 1.89
Na^+	0.27 ± 0.23	0.18 ± 0.22
NH_4^+	5.42 ± 2.27	1.17 ± 1.09
K^+	1.39 ± 0.85	0.43 ± 0.76
Mg^+	0.17 ± 0.11	0.10 ± 0.09
Ca^{2+}	3.48 ± 2.39	3.81 ± 3.38
Elements (*n*=90 for Phase 1; *n*=80 for Phase 2)		
Na	0.52 ± 0.47	0.40 ± 0.43
Mg	0.26 ± 0.23	0.27 ± 0.25
Al	2.06 ± 1.77	1.83 ± 1.83
Si	5.67 ± 4.48	4.04 ± 4.11
P	0.14 ± 0.08	0.01 ± 0.01
S	2.25 ± 1.26	0.67 ± 0.55
Cl	1.49 ± 1.13	0.19 ± 0.23
K	1.97 ± 1.06	0.88 ± 0.75
Ca	2.24 ± 1.74	1.44 ± 1.34
Sc	0.17 ± 0.12	0.13 ± 0.12
Ti	0.19 ± 0.16	0.14 ± 0.13
V	0.01 ± 0.01	0.01 ± 0.01
Cr	0.03 ± 0.02	0.03 ± 0.03
Mn	0.05 ± 0.03	0.03 ± 0.03
Fe	2.16 ± 1.74	1.54 ± 1.45
Ni	0.02 ± 0.01	0.02 ± 0.02
Cu	0.03 ± 0.02	0.04 ± 0.05
Zn	0.35 ± 0.46	0.13 ± 0.07
Cd	0.03 ± 0.02	0.04 ± 0.05
Sn	0.08 ± 0.09	0.11 ± 0.19
Ba	0.75 ± 0.63	1.39 ± 1.98

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Hg	0.02 ± 0.02	0.07 ± 0.06
As	0.01 ± 0.01	0.01 ± 0.01
Pb	0.03 ± 0.02	0.02 ± 0.02

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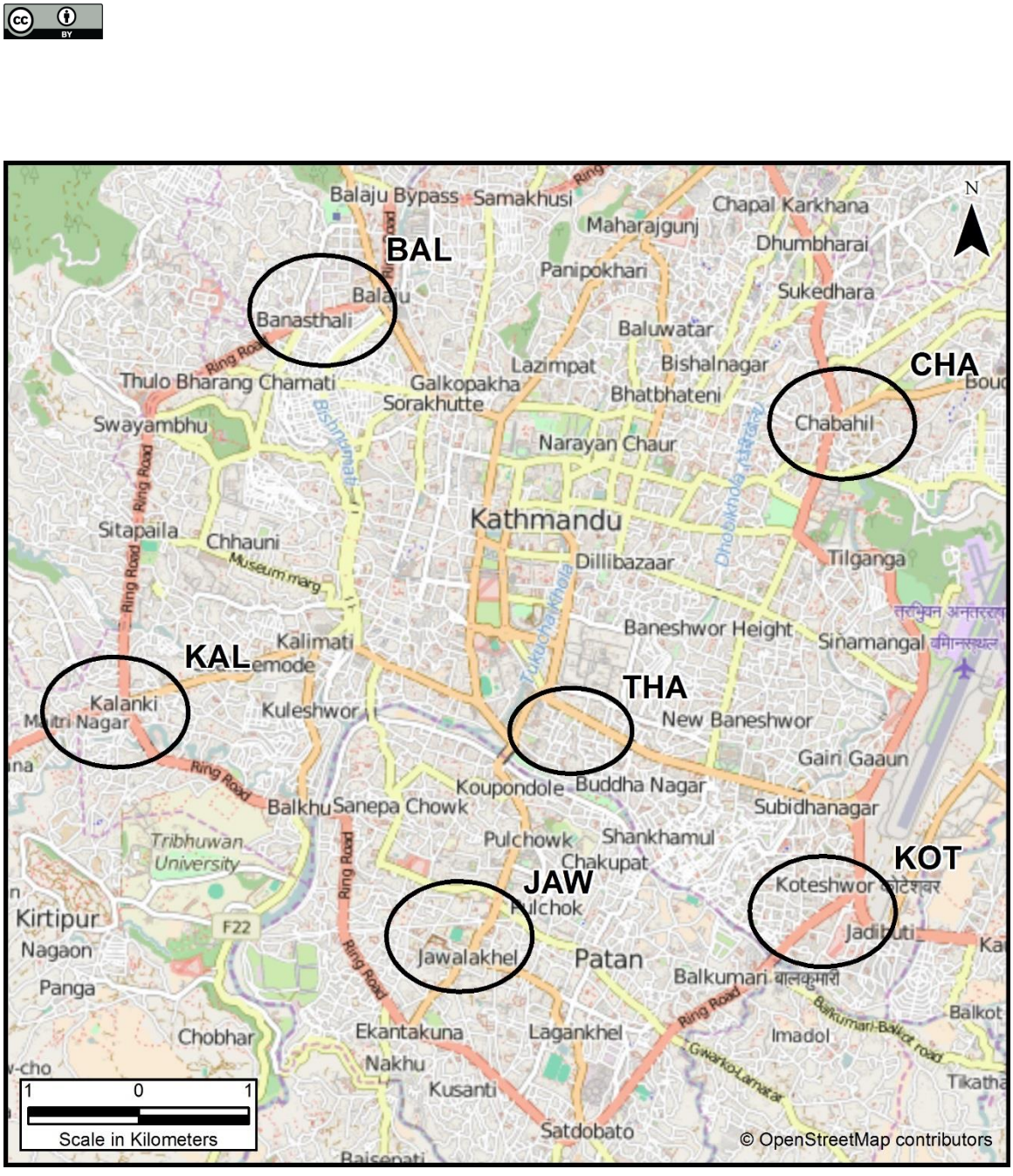

Figure 1. Six sampling sites used in this study. KAL: Kalanki, JAW: Jawalakhel, THA: Thapthali, KOT: Koteswor, CHA: Chabahil, BAL: Balaju.

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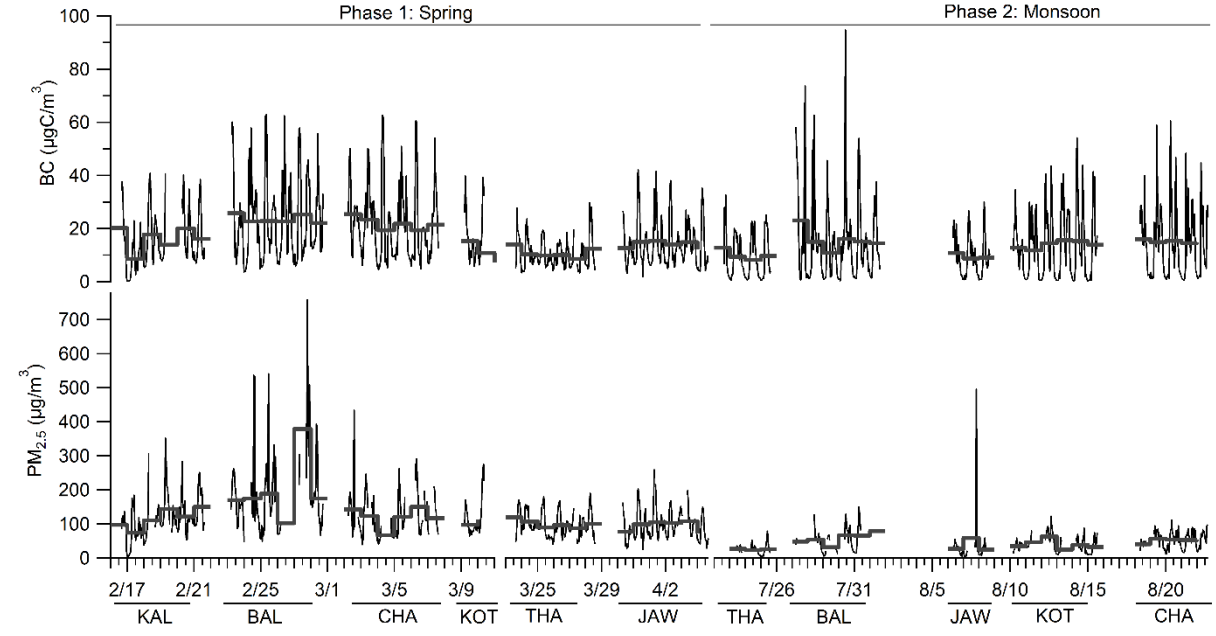

Figure 2. Time series of BC concentrations (upper panel) and $PM_{2.5}$ concentrations (lower panel) observed at six near-road locations in the Kathmandu Valley during measurement periods in spring and monsoon seasons of 2014. The thin solid line in each panel represents hourly average concentrations while the thick line represents 24-hour average concentrations.

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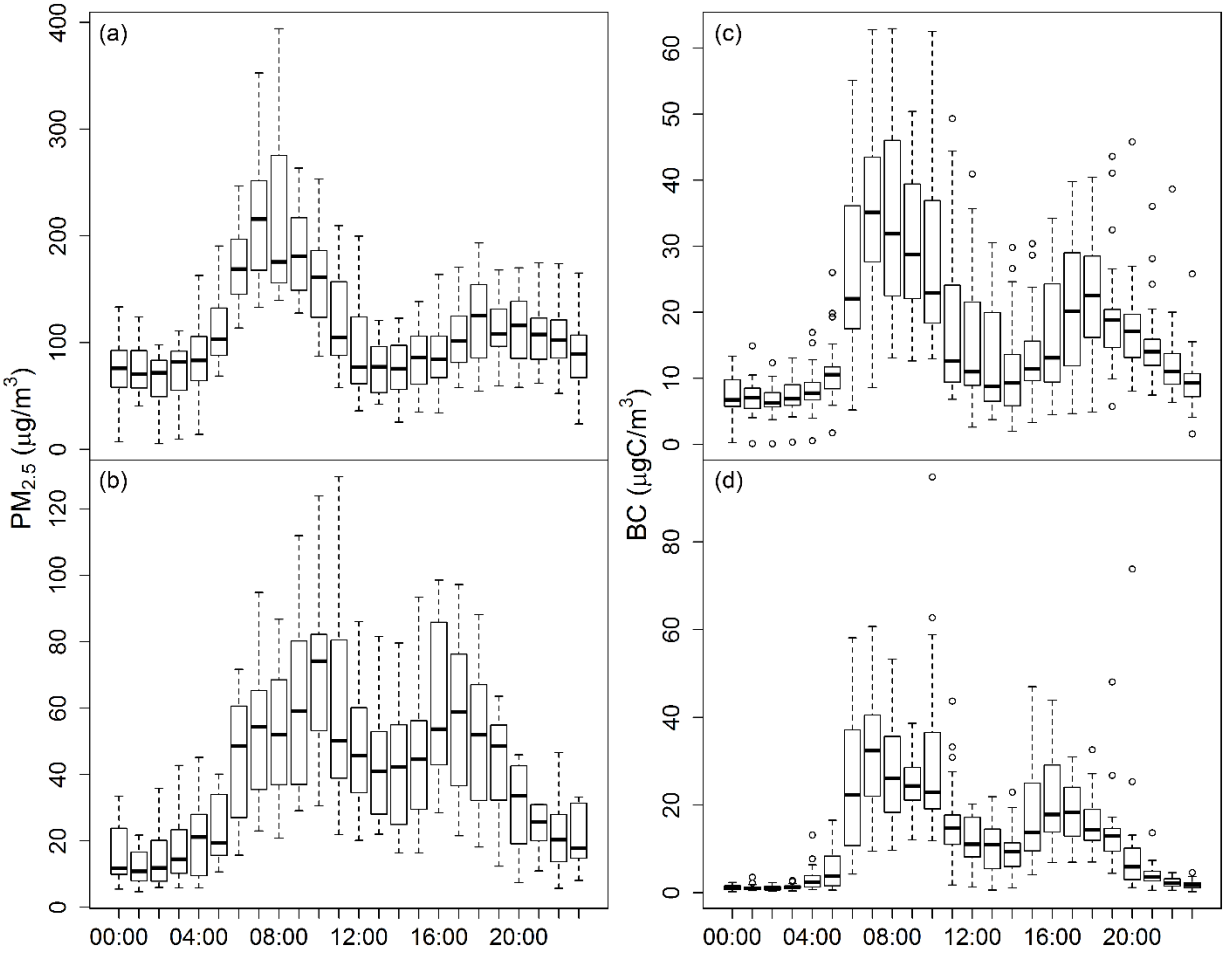

Figure 3. Diurnal variations of $PM_{2.5}$ and BC concentrations observed at six near-road sites in the Kathmandu valley for entire sampling periods in spring season (a and c) and monsoon season (b and d). The lower end and upper end of each box represents 25th and 75th percentile, respectively; whiskers represent 1.5 × interquartile range; black horizontal line in the middle of each box is the median for each hour of the day.

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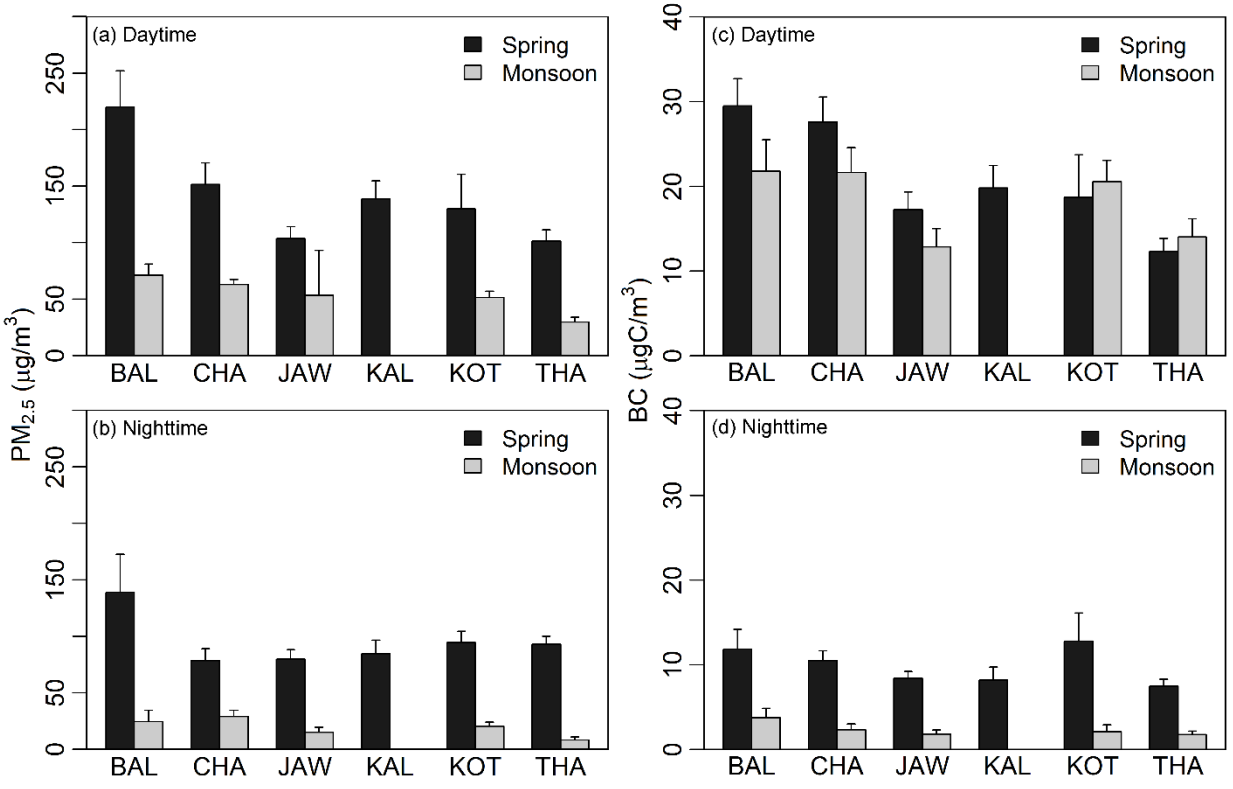

Figure 4. The mean concentrations of $PM_{2.5}$ (a and b) and BC (c and d) in nighttime (8pm-6am NST (Nepal Standard Time) and daytime (6AM-8PM NST) over the sampling periods in spring season and monsoon season of year 2014 observed at six near-roadside locations in the Kathmandu valley. Error bars are standard deviation of the measurements.

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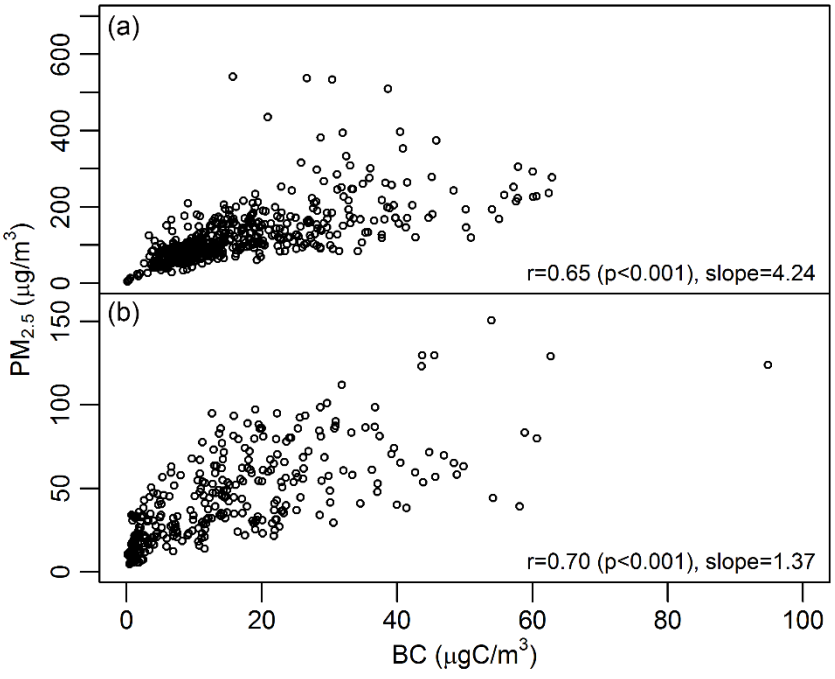

Figure 5. Correlation between $PM_{2.5}$ concentrations and BC concentrations observed at six near-road sites in the Kathmandu Valley over the sampling periods in (a) spring season and (b) monsoon season in 2014.

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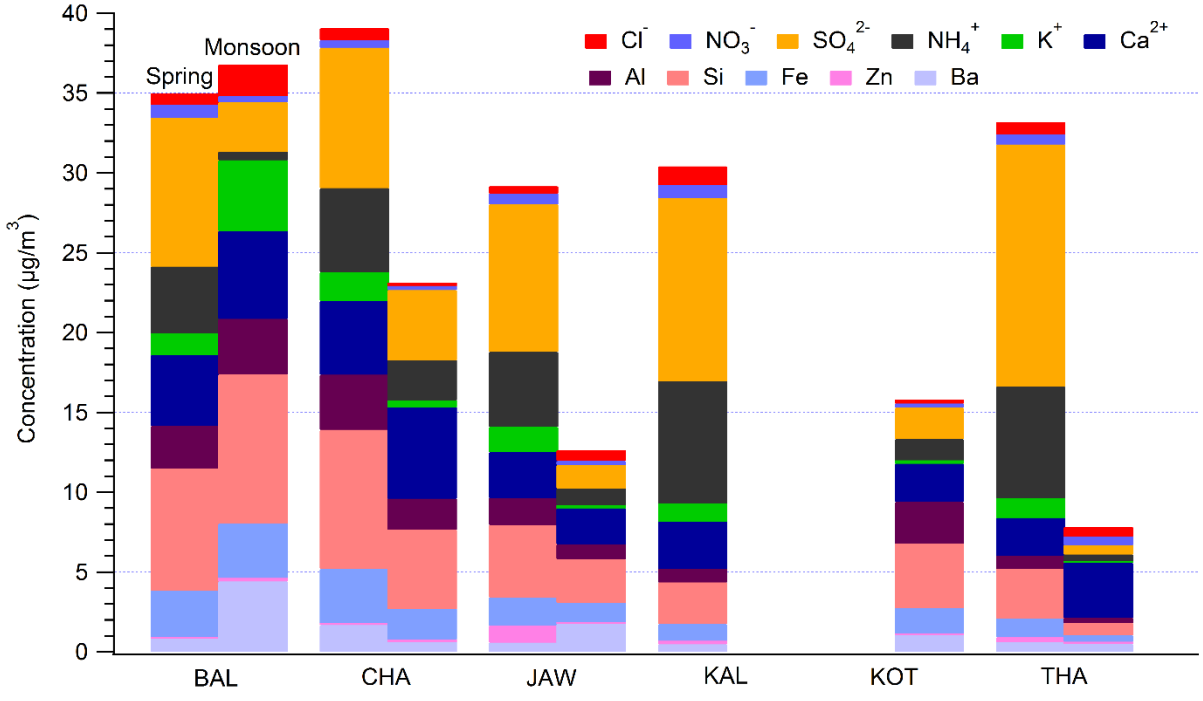

Figure 6. The average ambient concentrations of ions and elements in $PM_{2.5}$ over two sampling periods in spring season and monsoon season at six locations in the Kathmandu Valley.

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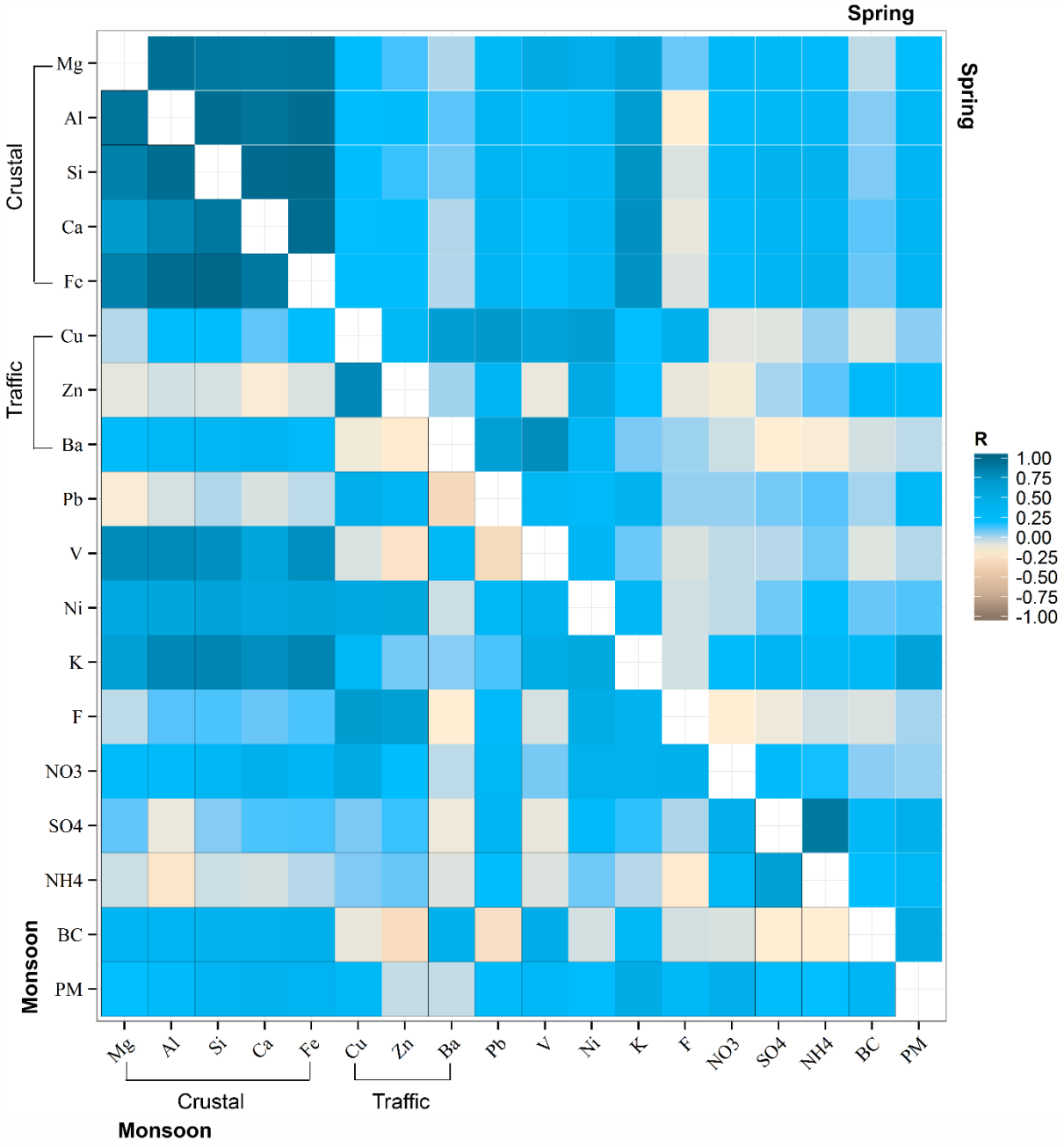

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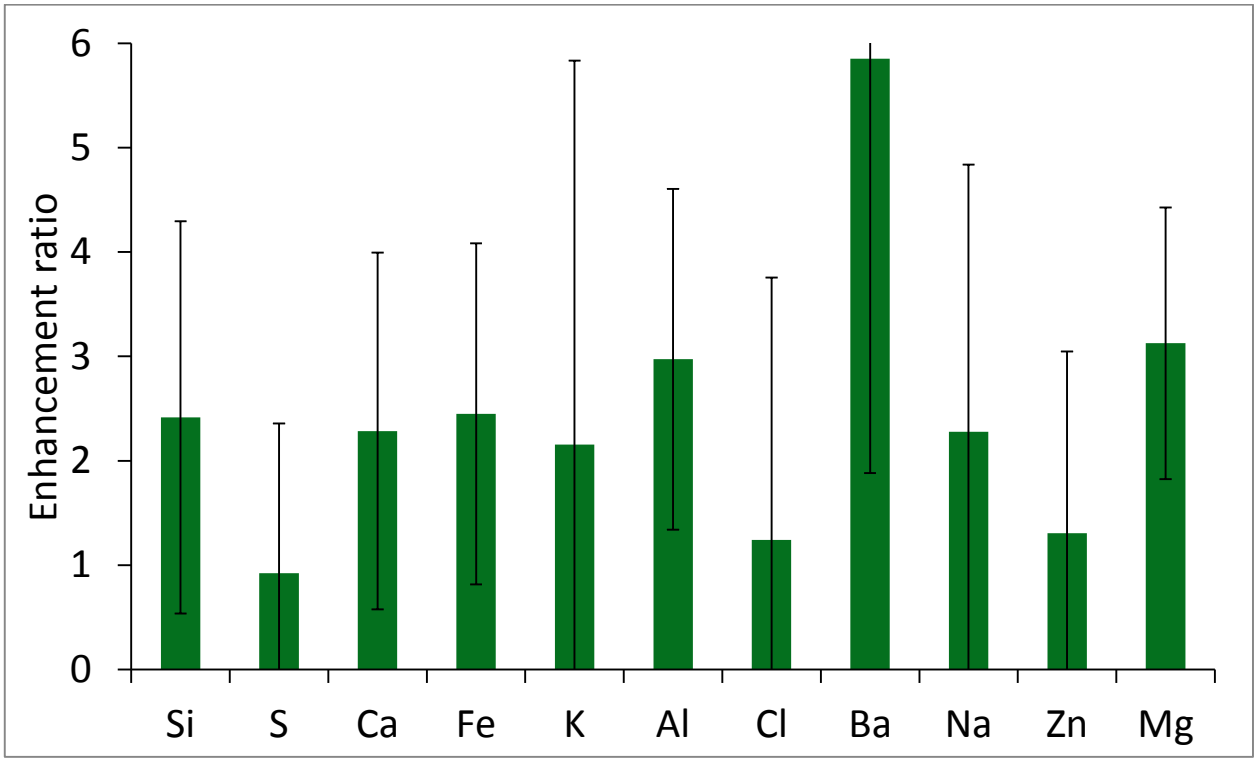

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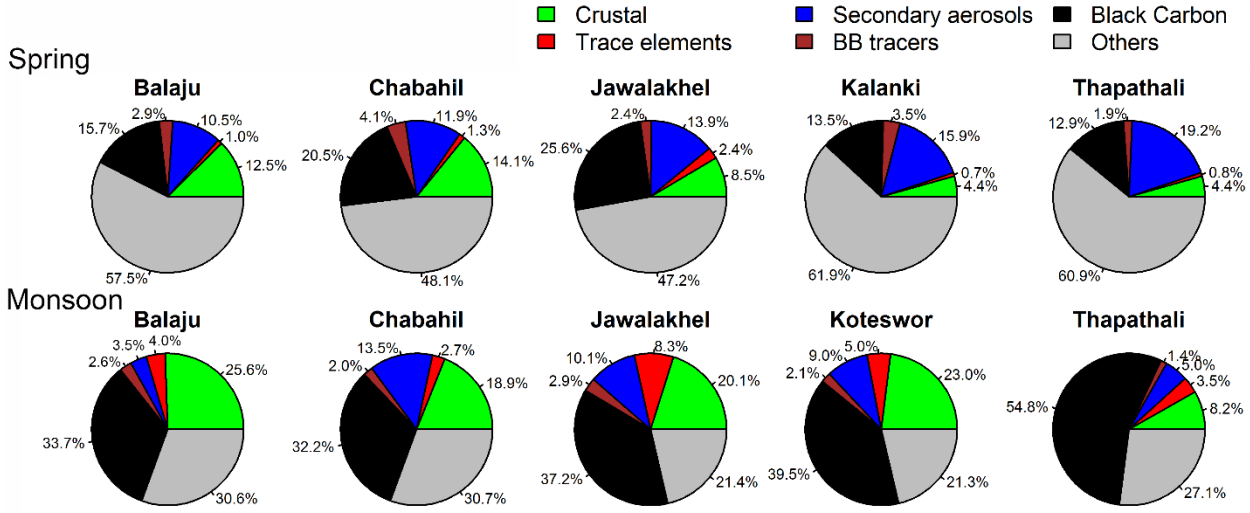

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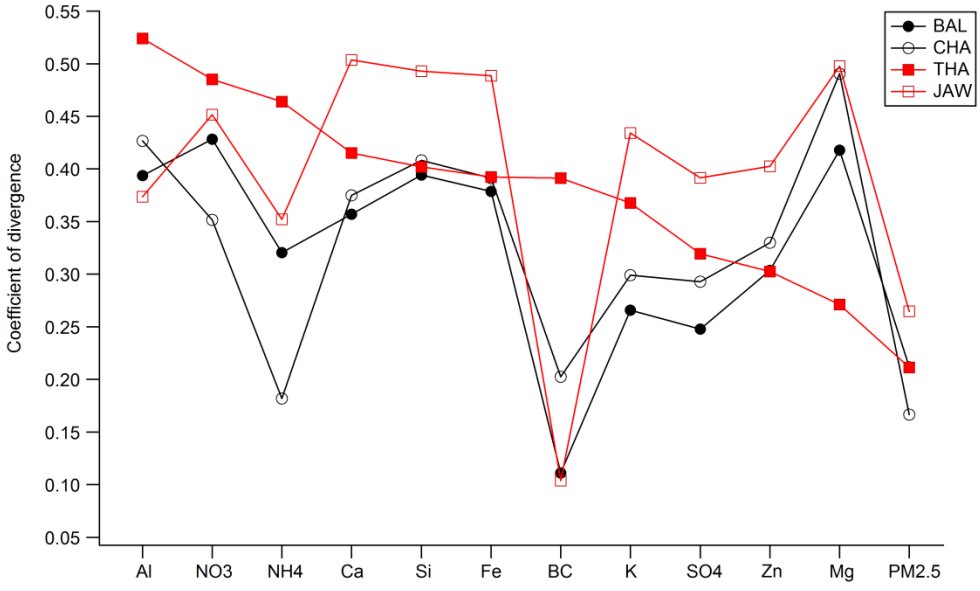

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