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 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 $\mu g\ m^{-3}$, 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 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 the Kathmandu Valley 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.

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

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 equipment 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.

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

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

2.1 $PM_{2.5}$ and BC sampling

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

Daily (24-hour) $PM_{2.5}$ filter samples were collected on 37 mm filters (polytetrafluoroethylene 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. Polytetrafluoroethylene (PTFE) filter and quartz fiber filter (QFF) were alternated every other day across all six sampler sets (i.e., all six samplers collected QFF on one day, and PTFE 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.

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 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 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. Early morning to late evening measurements were collected outdoors while six traffic personnel were working at one of six different locations within a distance of about 2 km of their work station. Nighttime measurements were based on indoor measurements in the traffic officer's dormitory, which was located within a few hundred meters of their on-street work location. Spikes in concentration during the daytime could be affected by their specific work location such as whether the traffic personnel were working on busy intersections or on less-travelled roadside locations with lighter traffic.

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 $PM_{2.5}$ concentrations were observed. Thapathali and Jawalakhel, with the lowest $PM_{2.5}$ levels, are located inside the city, and have paved roads with minimal road dust compared to other sites.

Overall, there was 57-74% reduction in $PM_{2.5}$ concentrations (based on mean concentration) at four sites during summer-monsoon season compared to spring. During the monsoon, there was greater reduction at Jawalakhel (73%) and Thapathali (72%) compared to Balaju (61%) and Chabahil (55%). The monsoon season was characterized by higher ambient temperature and more frequent rain events (~80% of total annual precipitation occurs during June-September period) leading to both less energy use (such as absence of brick production, significantly less number of captive power generator sets, less burning of trace).

The average temperature and relative humidity (Davis Automated Weather Station) at a monitoring station at Bode, Bhaktapur in the Kathmandu Valley was 14.8 ^{o}C and 73.2%, respectively, during the dry season, and 23.6 ^{o}C and 88.0%, respectively during the monsoon (rainy) season. The total precipitation during the dry and monsoon season was 50.47 mm and 266.6 mm, respectively.

The use of air conditioners in the Kathmandu Valley is not common, however electric home heaters, heaters that use bio-briquettes, kerosene and LPG are common in the cooler winter.

Scheduled power outages are also reduced in summer-monsoon leading to a lower usage of diesel generators in the summer-monsoon.

Daytime concentrations were computed as the average from 6AM to 8PM and nighttime concentrations were averaged as 8PM to 6AM from hourly averages of 5-minute measurements. $PM_{2.5}$ concentrations were higher in the spring than in the monsoon (Figure 4a and 4b). However, such differences between two seasons were much larger for daytime compared to nighttime. Daytime $PM_{2.5}$ concentrations exceeded nighttime by ~1.5 times during spring, while these were ~3 times higher during the monsoon. Balaju had the largest daytime and nighttime $PM_{2.5}$ levels in both seasons. Many long-route night buses operate from the Balaju (Gongabu) bus terminal, and this may partially explain these results. Balaju, 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 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), and potassium (K) as the major elements with individual concentrations greater than 1 μg m^{-3} in both phases. Other dominant elements such as 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 some of the samples. 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 (Salako et al. 2012), and these results are likely attributed to analytical measurement differences and measurement uncertainty. However, there are some limitations in the comparison in this study. The comparison between EC and BC concentrations is based on measurements from the six set of instruments by thirty six traffic personnel around six sites. Examining the comparisons of our measurements show that about half of measurements had BC/EC ratio between 0.70 and 1.19.

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.

3.3.2 Water-soluble ions

Water-soluble inorganic ions exhibited high spatial and temporal variability across six sites in the Kathmandu Valley (Figure 6). The average concentrations of 11 water-soluble ions from all sites were 23.6 and 9.1 $\mu g/m^3$ during spring and monsoon, respectively. Among ions, SO_4^{2-}, NH_4^+, Ca^{2+}, and K^+ were the major ions dominating the $PM_{2.5}$ chemical composition (by mass) during both seasons (Table 1). Though Ca^{2+} concentrations were similar in both seasons, SO_4^{2-} and NH_4^+ concentrations were reduced by about a factor of five during the monsoon. NO_3^- was reduced by a factor of two in the monsoonal period. High concentrations of SO_4^{2-} observed in Kathmandu Valley during spring may have been derived by the increased emission of precursor gas (i.e. SO_2)

during spring from activities such as operation of brick kilns (which use high sulfur containing coal), diesel-generators, and diesel-trucks. There was a slight increase in Ca^{2+} concentration in monsoon than in spring (lacking statistical significance, however). This suggests that dust contributions are either the same or slightly enhanced in monsoon compared to spring, a surprising finding. Ca^{2+} concentrations have also been used to indicate Asian dust in several studies (Choi et al., 2001; Shen et al., 2008). Again, monsoon $PM_{2.5}$ concentrations were lower by about a factor of three compared to spring. Thus, the similar loading of Ca^{2+} suggests an impressive persistent dust burden, even during the monsoon. Road conditions were worse around Balaju and Chabahil compared to other sites, and it's likely that resuspension of road dust was an important emission component in these areas. Thus, it is not surprising that Ca^{2+} levels were the largest at Balaju and Chabahil during both spring and monsoon seasons.

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).

364 During the spring, the largest SO_4^{2-} concentrations (15.2 μg m^{-3}) were observed at Thapathali
365 despite this site having the smallest $PM_{2.5}$ concentrations. Such SO_4^{2-} spikes might be related to
366 the increased operation of diesel-powered power generators at nearby hospitals, commercial
367 showrooms, and many commercial businesses located in Thapathali area. Daily power outages are
368 about 12 hours per day in spring, and this leads to increased use of small-scale diesel-powered
369 generators at commercial and tourist facilities. Thapathali is a popular business district in
370 Kathmandu.
371
372 With two exceptions (nitrite and calcium), mean concentrations of water-soluble inorganic ions
373 was larger during spring compared to monsoon (Table 1). The largest difference was for SO_4^{2-} and
374 NH_4^{+-}, when the spring concentrations were larger by a factor of ~5 compared to monsoon. The
375 NO_3^- concentrations were more than two times higher in spring than in monsoon. $PM_{2.5}$ in general
376 was higher in spring than monsoon due to additional emission sources and atmospheric stagnation
377 during spring. The lower levels of the water-soluble ions during monsoon could mainly be due to
378 wet removal of particles containing these ions. Increased levels of NO_3^-, SO_4^{2-}, and NH_4^+ in spring
379 compared to monsoon might also be contributed by the low temperature and increased relative
380 humidity favoring ammonium nitrate or ammonium sulfate formation and their partition into
381 particulate phase. Not surprisingly, NH_4^+ was strongly correlated with SO_4^{2-} ($r = 0.65$ in spring
382 and $r = 0.90$ during monsoon). NO_2^- and Ca^{2+} were about 20% and 10% higher, respectively, during
383 the monsoon than during spring.
384

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 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 $PM_{2.5}$-normalized elemental concentration during monsoon to spring) is plotted for 11 major elements observed in this study.

The enhancement ratio is the largest for Ba suggesting the consistent and large contribution of traffic-related $PM_{2.5}$ sources (Lough et al., 2005; Iijima et al., 2007) in the valley. The enhancement ratios were within the range of 2-4 for Si, Ca, Fe, K, Al, Mg, and Na. High enhancement ratios for the elements suggest that emissions of these elements were not concomitantly decreased in the monsoon compared to spring even though total $PM_{2.5}$ was clearly decreased during the monsoonal sampling. This finding is important for source apportionment activities, where monsoonal effects on emissions profiles might be assumed to be proportionately reduced due to washout.

Among these elements, S is the only element that was not enhanced (ratio<1) in the monsoon relative to spring. Non-enhancement of sulfur is also on par with the decrease of secondary inorganic ion concentrations in the monsoon. Coal combustion is not likely the major sulfur emission source in the valley in monsoon period, and if sulfur aerosol is formed from secondary sources, monsoonal loss of such sulfur is likely. The major sulfur source probably arises from diesel fuel used in the Kathmandu Valley throughout the year. An additional contribution is coming from coal combustion used in brick factories during winter and spring months.

When the elements measured by XRF spectroscopy and the water-soluble ions of the same elements were compared for such enhancements, it indicated consistent enhancement ratios between two techniques, 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 by using (Taylor and McLennan, 1995):

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

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. The crustal ratios used for the computation of enrichment factor are based on chemical composition of a generic upper continental crust (Taylor and McLenna, 1995). 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.

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

that suggested urban air in Kathmandu is heavily influenced by local anthropogenic sources such as automobile exhaust or fossil-fuel related emissions.

3.5 Source apportionment by chemical components

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

It is interesting to note that BC contribution was larger and crustal contributions was smaller in the two sites located inside inner cities, Jawalakhel and Thapathali, compared to other four sites (except Koteshwor where no samples were collected in spring) during the monsoon. The sum of the five crustal element concentrations were highest at Chabahil (spring: 16.9 μg m^{-3}, monsoon: 12.7 μg m^{-3}) and Balaju (spring: 17.7 μg m^{-3}, monsoon: 10.5 μg m^{-3}), and the lowest at Thapathali (spring: 4.4 μg m^{-3}, monsoon: 1.8 μg m^{-3}) and Jawalakhel (spring: 9.6 μg m^{-3}, monsoon: 5.8 μg m^{-3}). BC concentrations exceed crustal elemental concentrations by a factor of 1.3-1.8 at Balaju, Chabahil, Jawalakhel, Kalanki, and Koteshwor. This suggests dust and traffic emissions are the most important PM emission sources in the valley. One exception is Kalanki, where the BC/dust ratio was 3.2, and Thapathali with BC/dust ratio of 2.8 and 6.2 during spring and monsoon, respectively. Concentrations of biomass burning tracers were the largest at Balaju and Chabahil during both spring (4.1 - 4.6 μg m^{-3}) and monsoon (1.1 - 1.5 μg m^{-3}). Chabahil is located near Pashupati, which is the main cremation site for the community. This process is biomass-burning intensive and occurs year round, and may partially explain these results.

3.6 Spatial variability of exposure within the sites

The coefficient of divergence (COD) was computed within four locations for $PM_{2.5}$, BC, and several chemical species (Figure 10) to explore the differences in concentrations within each of these specific locations due to mobile nature of the sampling by six traffic volunteers at the same time. COD is expressed as (Wilson et al., 2005):

$$COD_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left[\frac{(S_{ij} - S_{ik})}{(S_{ij} + S_{ik})}\right]^2}$$

where S_{ij} and S_{jk} are the concentrations (of $PM_{2.5}$ or other parameters) for sampling day i for individual traffic personnel working at j and k locations; p represents the number of observations. The higher COD values indicate heterogeneity and lower COD values indicating homogeneity (Wilson et al., 2005). The COD values lower than two are considered as homogeneous (Thornburg et al., 2009). Two locations (i.e., Kalanki and Koteshwor) did not have enough data points for both seasons, and they were excluded from 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

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.

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

More broadly, this unique dataset highlights a divergence in concentrations that were thought to be downwardly affected by large scale meteorological effects. While $PM_{2.5}$ was substantially reduced during the monsoon, there was no such decrease in BC levels; similar findings were

observed for a number of trace elemental components in ambient aerosol. These data have important relevance for promulgating optimized air quality control measures, protection of human health, and assessment of climate forcing effects from localized emissions. As a result, there remains much to understand in how highly polluted communities in the developing world can affect local and regional air quality.

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792 Table 1. Summary of $PM_{2.5}$ chemical composition (μg m^{-3}) in the Kathmandu Valley during spring season
793 (Phase 1) and monsoon season (Phase 2).
794

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)		
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
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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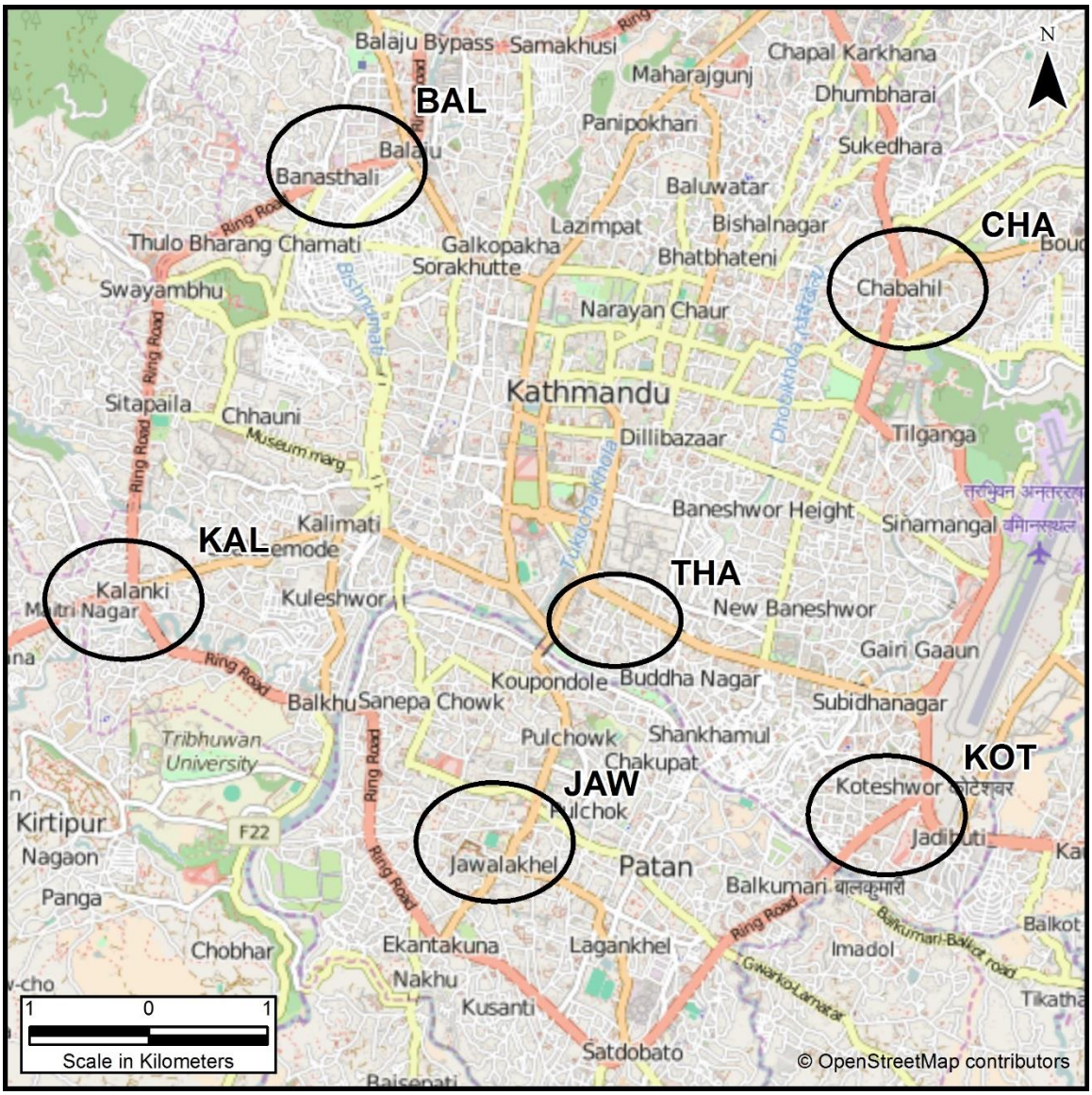

796

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

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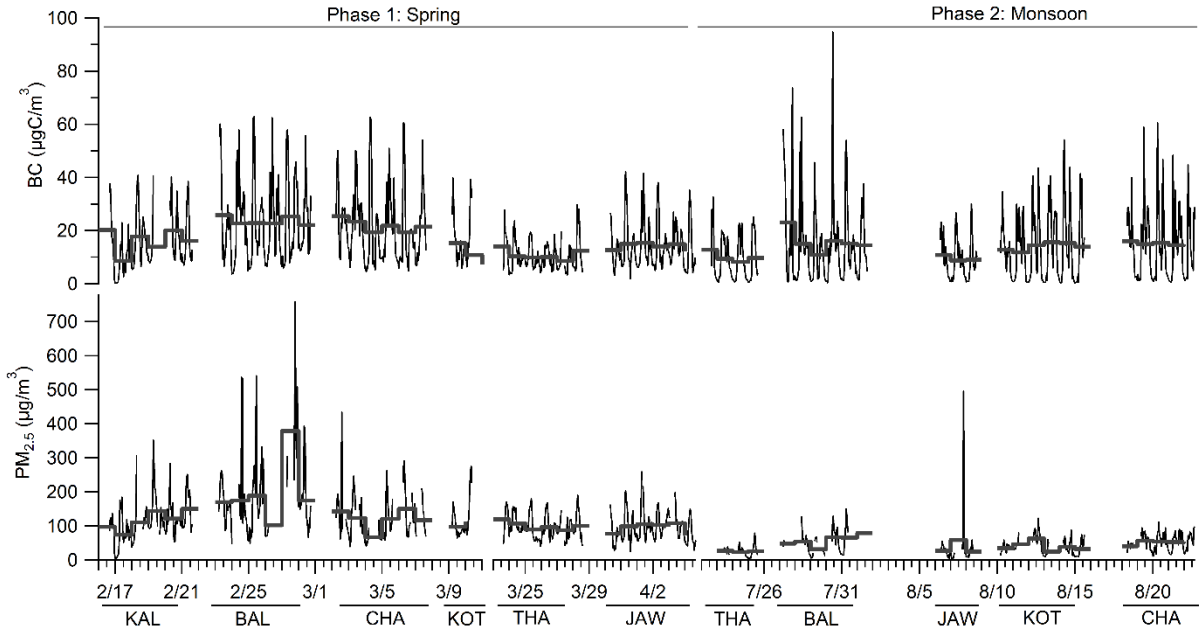


Figure 2. Time series of BC concentrations (upper panel) and $PM_{2.5}$ concentrations (lower panel) observed at six near-road locations in the Kathmandu Valley during measurement periods in spring and monsoon seasons of 2014. The thin solid line in each panel represents hourly average concentrations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

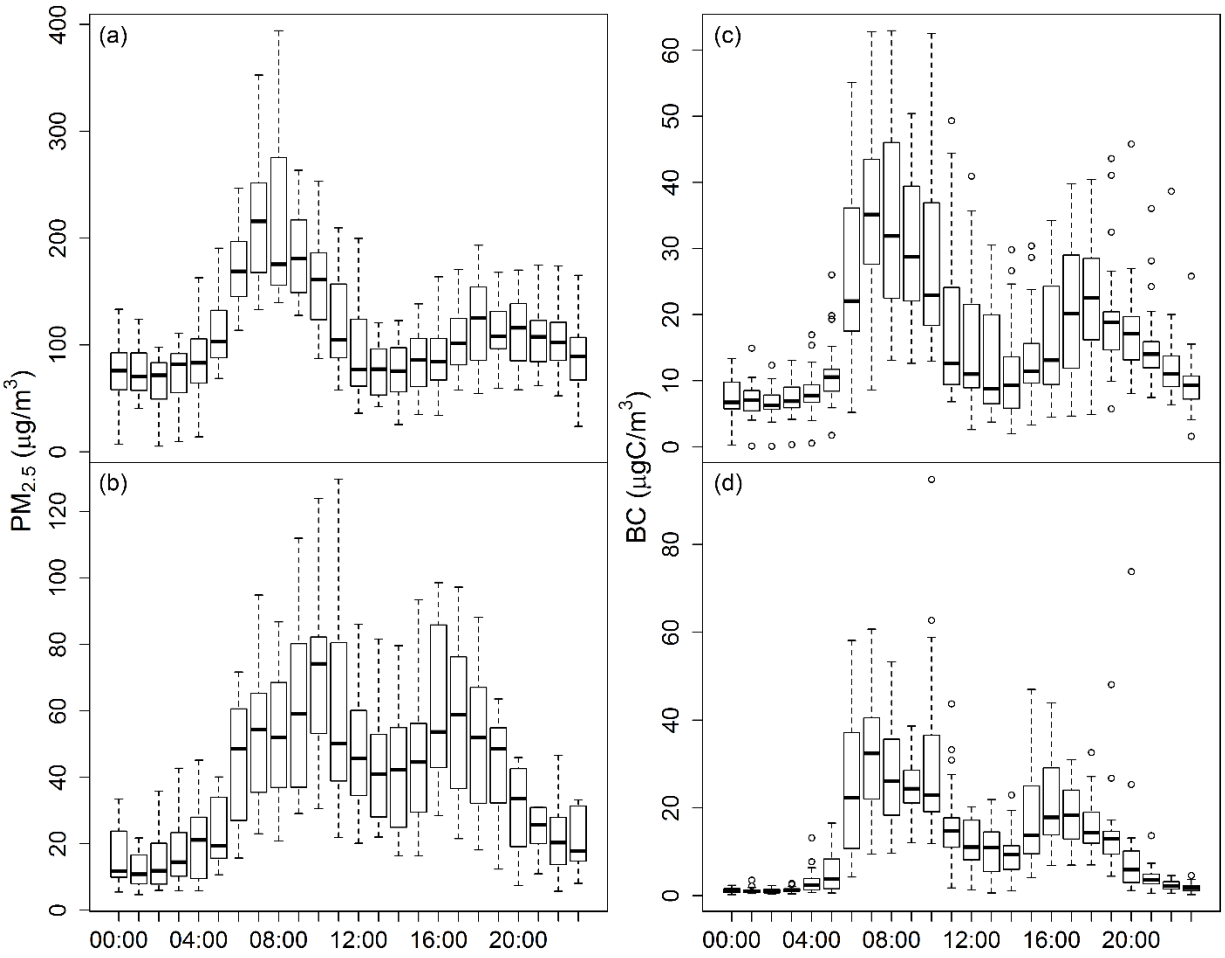
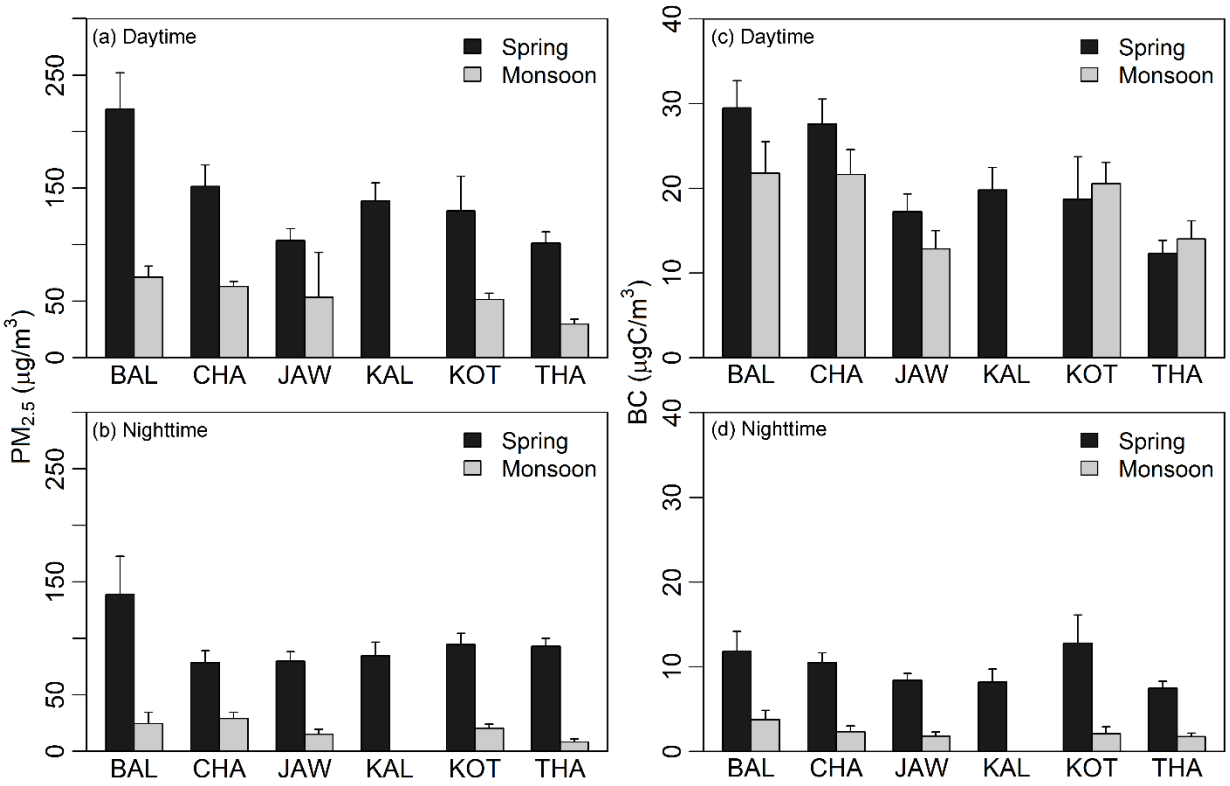


Figure 3. Diurnal variations of $PM_{2.5}$ and BC concentrations observed at six near-road sites in the Kathmandu valley for entire sampling periods in spring season (a and c) and monsoon season (b and d). The lower end and upper end of each box represents 25th and 75th percentile, respectively; whiskers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



825

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

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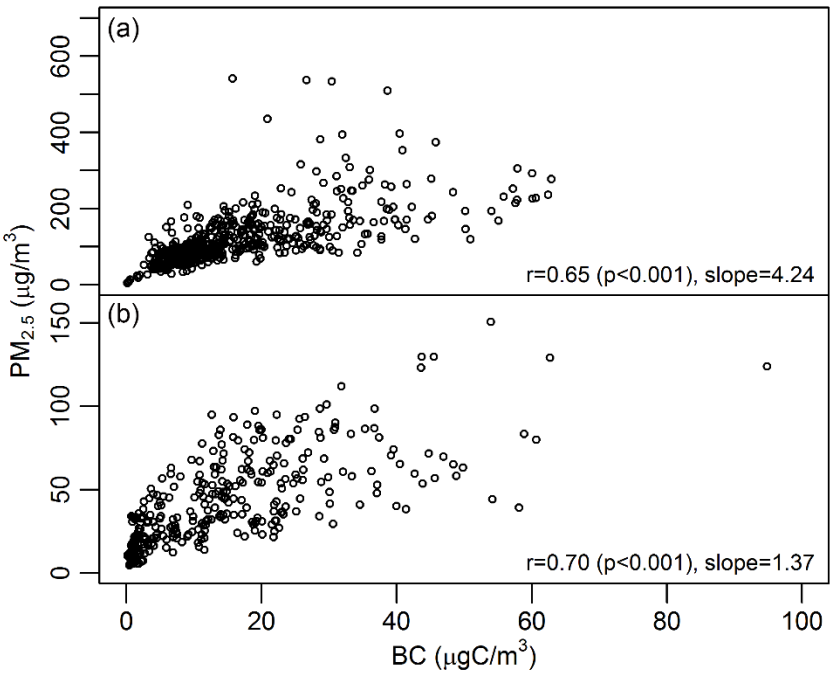

832

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

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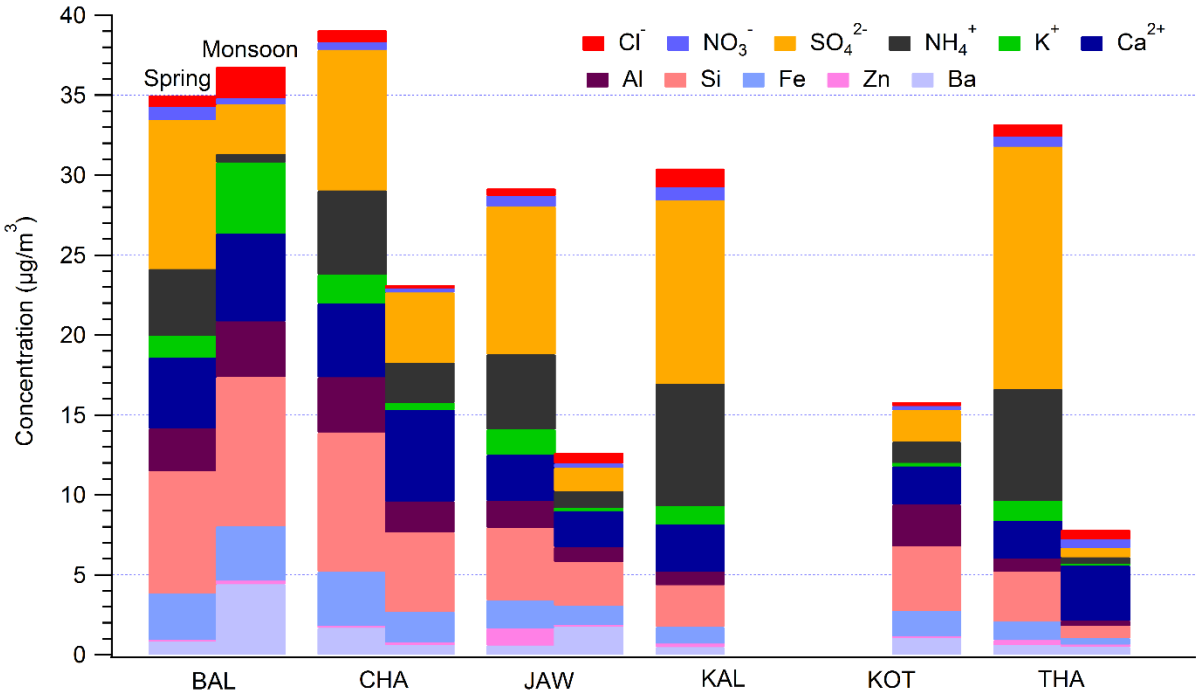

Figure 6. The average ambient concentrations of ions and elements in $PM_{2.5}$ over two sampling periods in spring season and monsoon season at six locations in the Kathmandu Valley.

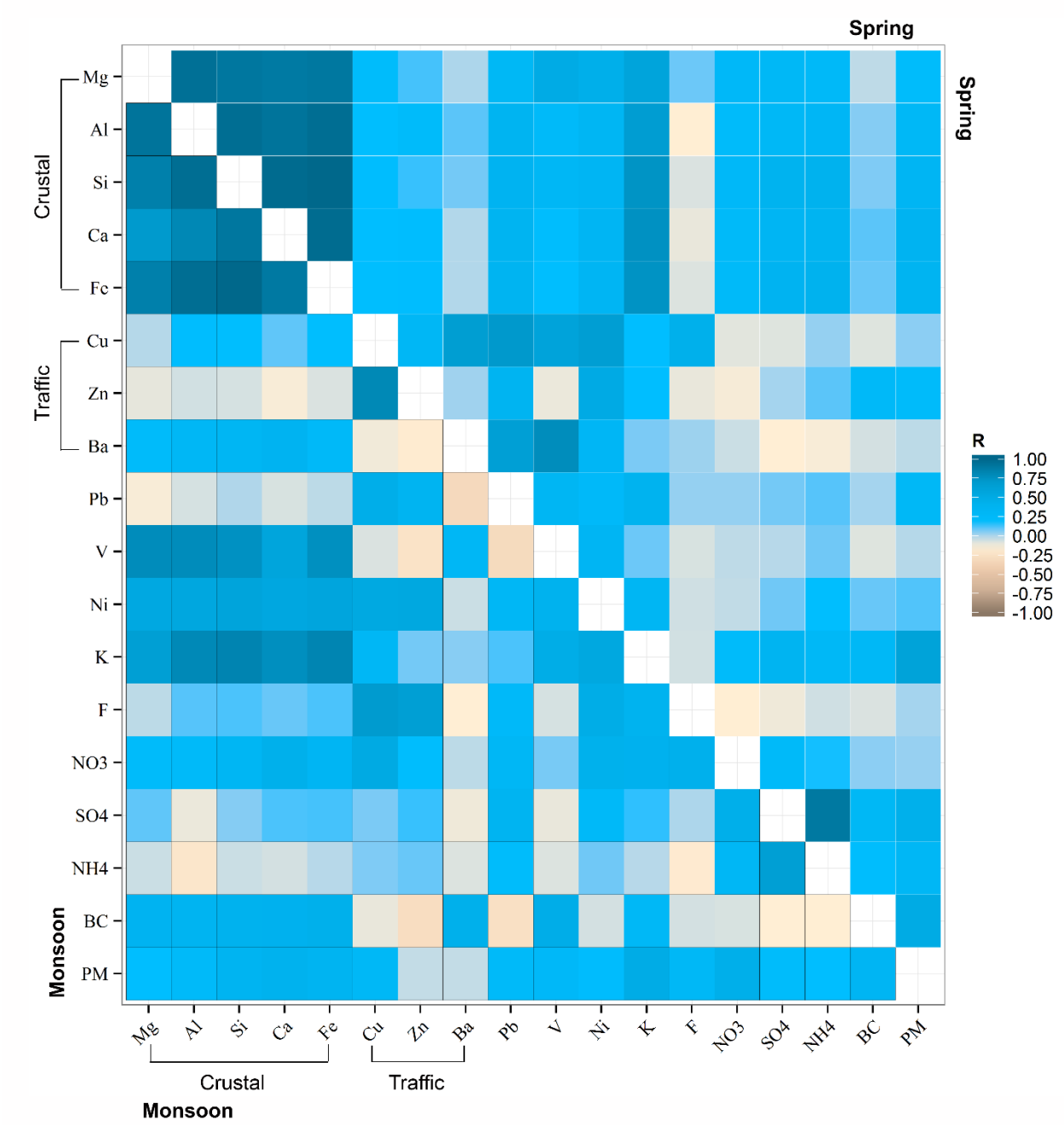

Figure 7. The matrix of correlation coefficients between elements, ions, BC, and $PM_{2.5}$ concentrations observed at six sites in the Kathmandu Valley in spring season (top-right; without border) and monsoon season (bottom-left; with black border).

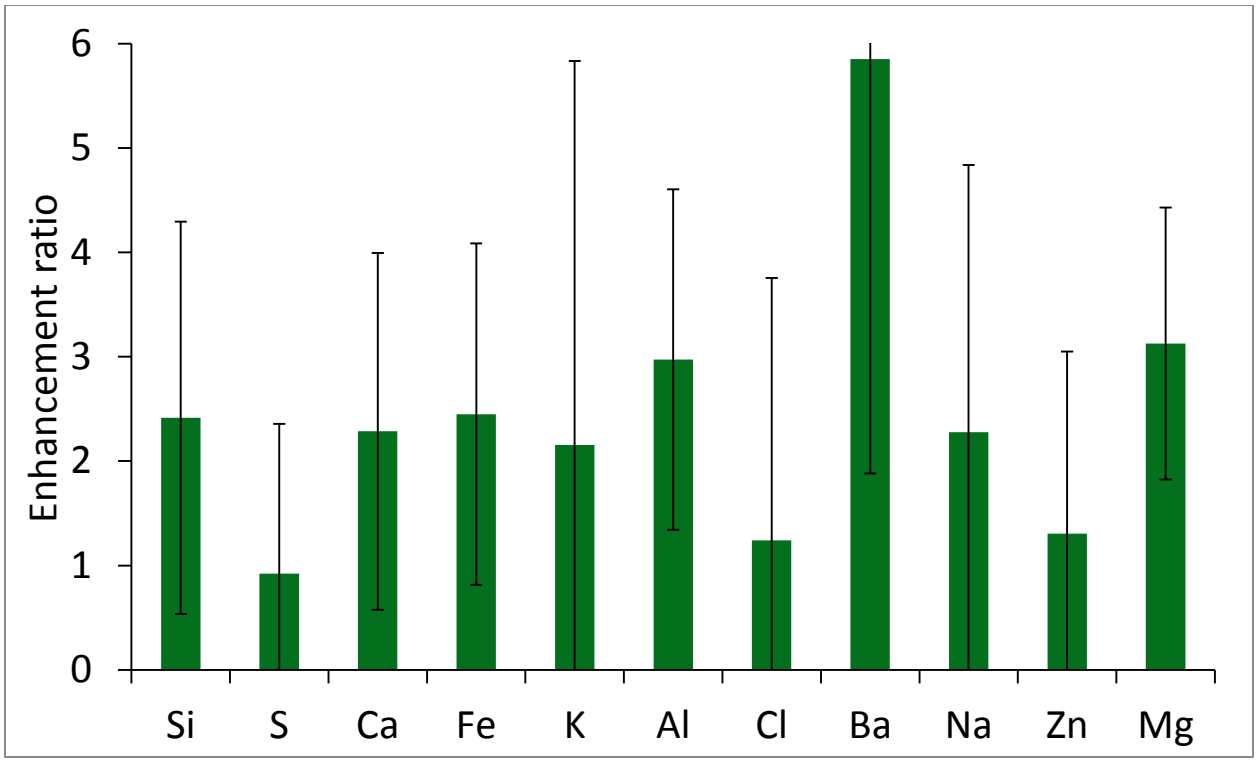

Figure 8. Enhancement ratio of elements in monsoon season compared to spring season at the Kathmandu Valley.

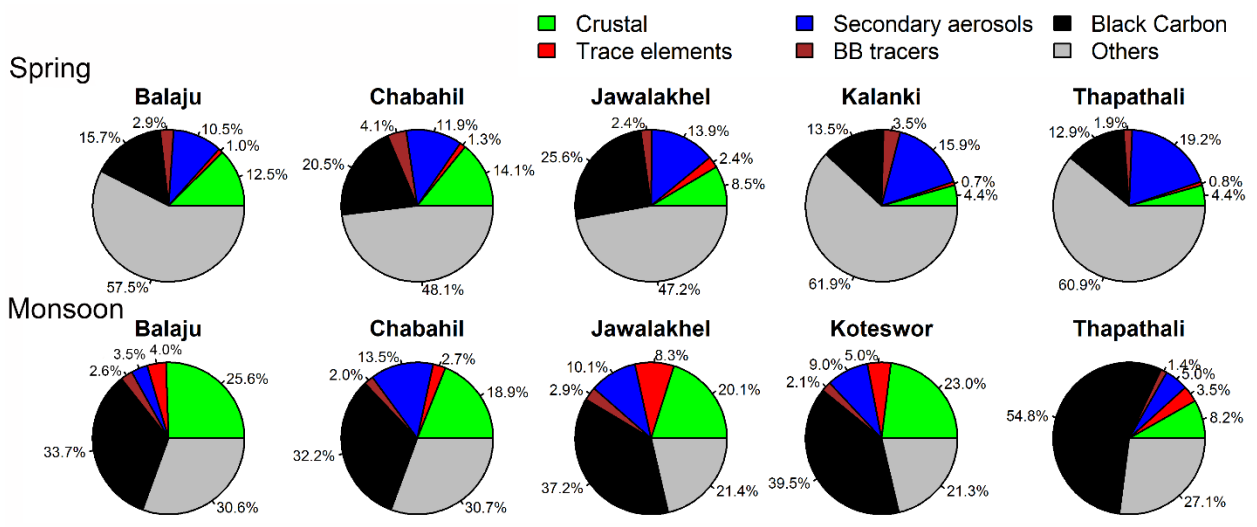

Figure 9. Chemical composition of ambient $PM_{2.5}$ [crustal elements (Mg, Al, Si, Ca, Fe), heavy metals (Cr, Mn, Co, Cu, Zn, As, Hg, Pb), secondary ions (NH_4^+, SO_4^{2-}, NO_3^-), BB tracers (K and Cl) and others (including organic material)] observed at six sites in the Kathmandu valley for two sampling periods in spring season (upper panel) and monsoon season (lower panel) in 2014.

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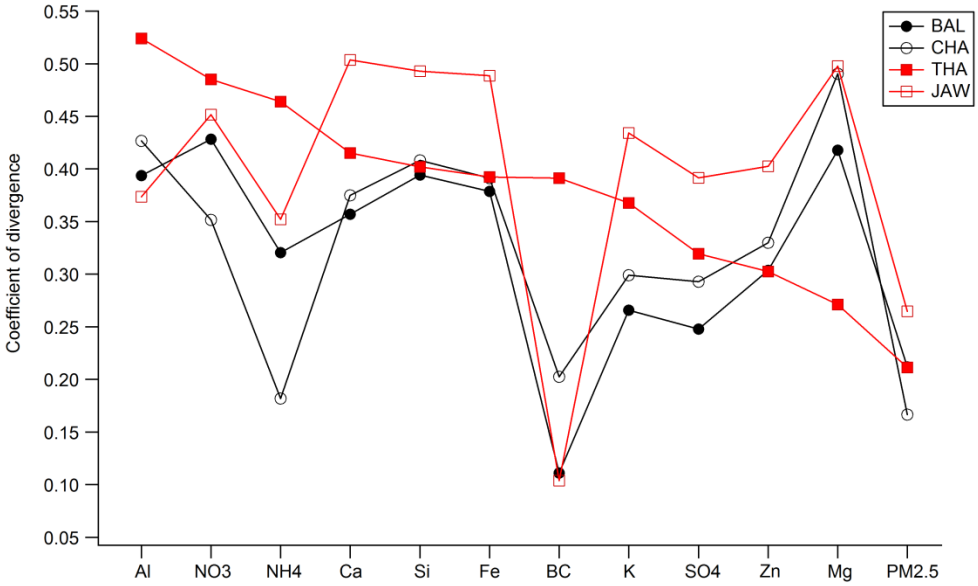

860

861 Figure 10. Mean coefficient of divergence (COD) for 24-hour average concentrations of $PM_{2.5}$, BC and
862 $PM_{2.5}$ chemical constituents at four sites during 2014.