



Characteristics and Sources of Carbonaceous, Ionic, and Isotopic Species of Wintertime Atmospheric Aerosols in Kathmandu Valley, Nepal

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ABSTRACT

To investigate the air pollution from aerosols in Kathmandu during winter, bulk aerosol samples were collected during winter 2007–2008 to characterize carbonaceous and ionic species and carbon and nitrogen isotopes. This study illustrates the applications of carbon and nitrogen isotope data for characterizing aerosols and their implications for identifying sources that were inconsistent with the results for the carbonaceous and ionic aerosols. Mean concentrations of organic carbon (OC), elemental carbon (EC), and water soluble organic carbon (WSOC) in Kathmandu during the period were 20.02 ± 6.59 (1σ), 4.48 ± 1.17 , and 10.09 ± 3.64 $\mu\text{gC}/\text{m}^3$, respectively. Elemental carbon and OC were correlated ($R^2 = 0.56$), likely indicating common sources for both species, as well as for the precursors that led to the formation of secondary organic carbon (SOC). The mean estimated SOC contribution to OC was 31%, suggesting that local emission is more important than transport and processing during winter in Kathmandu. On average, 50% of the OC was water soluble, and the correlation of SOC with WSOC ($R^2 = 0.66$) suggests that the majority of SOC and some primary organic carbon (POC) were water soluble in Kathmandu. The mean $\delta^{13}\text{C}$ of $-25.74 \pm 0.19\text{‰}$ observed in aerosols of Kathmandu confirms consistent anthropogenic sources such as fossil fuel combustion. Heavier carbon also was observed to be associated with the water-soluble fraction of OC in aerosols. The mean $\delta^{15}\text{N}$ of $9.45 \pm 0.87\text{‰}$ suggests the limited influence of biomass burning and its strong correlation with crustal cations Ca^{2+} ($R^2 = 0.74$, $p < 0.05$) and Mg^{2+} ($R^2 = 0.71$, $p < 0.05$) indicates distant sources. Principal component analysis revealed four major sources/pathways for particles: local and vehicular emissions, secondary gas-to-particle conversion, aqueous processing, and dust transport, each explaining ~39, 23, 11, and 9% of the variance.

Keywords: Carbonaceous aerosols; Kathmandu; Ionic aerosols; Isotope ratios.

INTRODUCTION

Respiratory ailments, including cough and bronchitis (Folinsbee, 1992), have been associated with particulate matter (PM), which also affects climate directly and indirectly and reduces visibility. Visibility reduction and the direct effect are related to absorption and scattering of radiation by aerosols (Charlson, 1969; Charlson *et al.*, 1992). The indirect effect is related to alteration of cloud albedo (Twomey, 1974) and lifetime through particles acting as cloud condensation nuclei and ice nuclei.

Carbonaceous aerosol species include elemental carbon (EC) and organic carbon (OC), where this distinction typically is based on thermal analysis (Birch and Cary, 1996). However, it should be stressed that EC is not

equivalent to black carbon (BC), which is defined and measured based on optical properties and absorbs light more strongly than EC. Elemental carbon is a primary pollutant emitted directly from combustion sources that absorbs light efficiently (because a significant fraction is BC) and has a direct effect on the radiative balance of the Earth surface. Organic carbon aerosol is emitted directly (known as primary OC or POC) and formed secondarily (known as secondary OC or SOC) from the partitioning to the condensed phase of semi- or non-volatile products of the oxidation of volatile organic compounds or by aqueous-phase processing. POC and SOC are generated from both anthropogenic and biogenic sources (Jacobson *et al.*, 2000).

In addition to carbonaceous material, aerosols also include inorganic species, often as cations and anions in an aqueous phase. For example, oxidation of sulfur dioxide and nitrogen oxides leads to the formation of sulfate (SO_4^{2-}) and nitrate (NO_3^-) in aerosols via sulfuric and nitric acids, respectively. Ammonium (NH_4^+) ions buffer these acidic species, which typically exist in ambient aerosol as

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partially or fully neutralized salts. Inorganic species may also be emitted directly to the atmosphere in the particulate phase.

Stable carbon isotope ratios of ^{13}C to ^{12}C ($\delta^{13}\text{C}$) reveal the chemical fractionation associated with processes involved in PM formation such as photosynthesis, atmospheric oxidation (Jacobson *et al.*, 2000), and phase changes. This ratio also reveals the relative contributions of C_3 (Calvin-Benson cycle) or C_4 (Hatch-Slack cycle) plants (Cachier, 1989). Similarly, nitrogen isotope ratios can be used to characterize atmospheric aerosol (Turekian *et al.*, 1998).

Kathmandu, the capital of Nepal, has a land area of 395 km², a rapidly increasing population of 1.08 million, and a vehicle usage rate that is growing by approximately 10 percent per year (CBS, 2005; Faiz *et al.*, 2006). The city is located inside a valley with restricted free wind movement, resulting in poor air quality, especially with regard to PM. For example, Aryal *et al.* (2009) observed concentrations of PM with diameters smaller than 2.5 micron ($\text{PM}_{2.5}$) of 90 ± 24 (1σ) $\mu\text{g}/\text{m}^3$ during the 2006–2007 winter in Kathmandu. The main objective of this study is to characterize the winter ambient aerosols of Kathmandu in terms of OC, EC, water-soluble organic carbon (WSOC), inorganic ions, and isotopes of carbon and nitrogen.

MATERIALS AND METHODS

Sampling

Sampling was performed on the roof of a five-story building in urban Kathmandu where air quality likely is influenced mainly by vehicular emissions, as the vehicular traffic in the nearby roads remains heavy throughout the day. The sampling site is located in Sorhakhutte, Thamel, a main tourist area in Kathmandu. The volume of traffic on the roads of Kathmandu is estimated to be 100 to 500 vehicles per hour (CBS, 2009).

Bulk aerosols were collected on quartz fiber filters (Whatman, QM-A) using a pump with a flow rate of 50 liters per minute. To reduce background contamination, all filters were pre-baked at 600°C for 24 hours and Teflon®-sealed in polyethylene dishes prior to sampling. The samples were collected for periods ranging from 18 to 24 hours depending on scheduled power outages and rain events. Collected samples were also stored inside dishes that were Teflon®-sealed. Twenty-five samples and eight field blanks were collected from 26 December 2007 through 30 January 2008. The field blanks were collected after every two subsequent sample collections, and all data described subsequently are corrected by subtracting average values of field blanks. The storage, transportation, and analysis of field blanks were identical to those of samples. All the samples were stored in a freezer prior to shipment to the University of New Hampshire for analysis.

Analyses

EC and OC

Elemental and organic carbon were analyzed by a thermal/optical method using a 1.5-cm² filter punch in a Sunset EC/OC analyzer, as described by Birch and Cary

(1996). Instrumental calibration was performed using succinic and phthalic acid standards. The associated uncertainties, calculated as two times the standard deviation of the eight field blanks using the average volume of air drawn for the sampling, were 0.24 and 0.12 $\mu\text{g}/\text{m}^3$ for OC and EC, respectively.

Secondary Organic Carbon (SOC)

Because EC can be used as an indicator of primary combustion emissions, the smallest observed ratio of OC to EC, $(\text{OC}/\text{EC})_{\text{minimum}}$, provides an estimate of a typical ratio of POC to EC assuming no or very low contribution from non-combustion POC and residual SOC (Castro *et al.*, 1999). This POC/EC ratio is assumed to be constant for a specific location for a specific period of time (Turpin and Huntzicker, 1991). The secondary organic carbon (SOC) is then defined as:

$$\text{SOC} = \text{OC} - \text{EC} \times (\text{OC}/\text{EC})_{\text{minimum}} \quad (1)$$

where POC is the product of the observed EC and $(\text{OC}/\text{EC})_{\text{minimum}}$. The contribution of SOC in the sample with minimum OC/EC is assumed to be negligible; the main source for EC and POC in this sampling site is assumed to be the emissions from fossil fuel combustion. Non-combustion related POC is assumed to be negligible (Castro *et al.*, 1999).

Water Soluble OC (WSOC)

Three punches, each 1.5 cm², were cut from each filter and extracted with 15 mL of milli-Q water. The extract was shaken manually, allowed to sit passively for 10 minutes, and centrifuged for 10 minutes to separate the filter and aqueous solution. The aqueous solution was divided into aliquots, each of 5 mL. One aliquot was used to analyze WSOC using a total organic carbon analyzer (Model 800 TOC, Sievers). The related uncertainty, calculated as two times the standard deviation of the eight field blanks, using the average volume of air drawn for the sampling was 0.65 $\mu\text{g}/\text{m}^3$.

Water-Soluble Ions

Sulfate, NO_3^- , nitrite (NO_2^-), chloride (Cl^-), and oxalate ($\text{C}_2\text{O}_4^{2-}$) anions and ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) cations were analyzed from one of the aliquots. Analysis was performed by ion chromatography (Dionex 500, Dionex Corp, Sunnyvale, California). Anions were analyzed with an AS22, 4X250-mm column equipped with ASRS 300, a 4-mm suppressor, and a 4.5-mM sodium carbonate/1.5-mM sodium bicarbonate eluent. Cations were analyzed with a CS12A, 4X250-mm column equipped with CSRS 300, a 4-mm suppressor, and an 18-mM methanesulfonic acid eluent. A conductivity detector was used for both anion and cation analysis. Sodium (Na^+) data were discarded due to probable contamination. Calibration was performed using mixed standards. The associated uncertainty values, calculated as two times the standard deviation of the field blanks using the average volume of air for sampling, were

0.01, 0.01, 0.06, and 0.03 $\mu\text{g}/\text{m}^3$ for Cl^- , NO_2^- , NO_3^- , and SO_4^{2-} , respectively, and 0.08, 0.16, 0.05, and 0.15 $\mu\text{g}/\text{m}^3$ for NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} , respectively.

Molar hydrogen ion (H^+) concentration was calculated from an ion balance assuming that SO_4^{2-} , NO_3^- , and NH_4^+ , and H^+ are the dominant ions that control the charge balance, particularly in fine particles (Schwab et al., 2004; Ziemba et al., 2007):

$$[\text{H}^+] = 2[\text{SO}_4^{2-}] + [\text{NO}_3^-] - [\text{NH}_4^+] \quad (2)$$

where the brackets represent molar concentrations. Assuming $[\text{NH}_4^+]$ is the only buffer counteracting the acidity in the aerosol, a neutralization ratio also was calculated by (Stevens et al., 1980; Ziemba et al., 2007):

$$f = \frac{[\text{NH}_4^+]}{2[\text{SO}_4^{2-}] + [\text{NO}_3^-]} \quad (3)$$

Carbon and Nitrogen Isotopes

For isotopic analyses, two punches cut from each filter were analyzed using a Costech Elemental Analyzer coupled to a Delta Plus XP Mass Spectrometer. The isotopic analysis was performed for the following eight samples in order to characterize a wide range of aerosol conditions (Total carbon (TC) is the sum of OC and EC.): maximum EC (12/27/07), minimum EC/TC and maximum OC and WSOC (01/05/08), maximum WSOC/OC (01/08/08), minimum WSOC/OC (01/19/08), maximum EC/TC (01/20/08), minimum EC, OC, and WSOC (01/30/08), and two randomly chosen (01/04/08 and 01/26/08). Carbon and nitrogen isotope ratios are calculated in per mil (‰) as follows (Turekian et al., 1998):

$$\delta Y = \left[\frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right] \times 1000 \quad (4)$$

where $Y = {}^{13}\text{C}$ and $R = \frac{{}^{13}\text{C}}{{}^{12}\text{C}}$ for carbon and $Y = {}^{15}\text{N}$ and

$R = \frac{{}^{15}\text{N}}{{}^{14}\text{N}}$ for nitrogen. The standard material was NIST 1515.

Statistical Analyses

The statistical software package JMP version 7.0.2 was used for statistical analyses. These analyses included linear regression and a principal component analysis (PCA) including factor rotation.

Meteorological Data

Meteorological data (maximum and minimum temperature and relative humidity (RH)) were taken from the archived report of the meteorological forecasting division of the Nepalese government (MFD, 2008). These parameters are included in the PCA. Temperature data are included in Fig. 1.

RESULTS

OC and EC

The daily concentrations of EC and constituents of OC during the sampling campaign are shown in Fig. 1 and summarized in Tables 1 and S1. Mean concentrations of OC and EC (with its standard deviation) were 20.02 ± 6.59 and $4.48 \pm 1.17 \mu\text{gC}/\text{m}^3$, respectively. On average, OC accounted for approximately 81% of the carbonaceous aerosol. Overall, there was a decreasing trend for both EC and OC during the sampling period. Despite a stronger decreasing overall trend (Fig. 1) in OC, OC and EC showed a correlation with R^2 of 0.56 (Fig. 2), suggesting a common source for EC and OC. The OC/EC ratio ranged between 3.01 and 6.59, with an average of 4.47 ± 0.93 .

SOC

Using the observed $(\text{OC}/\text{EC})_{\text{minimum}}$ of 3.01, which occurred on the day following the one significant rain event during the sampling period, Eq. (1) yields SOC concentrations in the range of 0 to $18.45 \mu\text{gC}/\text{m}^3$, with an average of $6.81 \pm 4.48 \mu\text{gC}/\text{m}^3$. Daily POC and SOC concentrations are also shown in Fig. 1 and Tables 1 and S1. On average, SOC constituted 31% of OC, with POC accounting for the remaining 69%. Overall SOC also has a decreasing trend during the sampling campaign. Total organic aerosol mass concentrations were calculated by summing the POC and SOC after multiplying each by 1.2 and 2.0, respectively (Turpin and Lim, 2001). The mean organic aerosol mass concentration was $29.26 \pm 11.24 \mu\text{g}/\text{m}^3$.

WSOC

The mean concentration of WSOC was $10.09 \pm 3.64 \mu\text{g}/\text{m}^3$ (Fig. 3 and Tables 1 and S1). Throughout the study period, WSOC accounted for a large portion of OC, with WSOC/OC ranging from 0.39 to 0.60, with an average of 0.50 ± 0.06 . A scatter plot of WSOC versus SOC shows significant correlation ($R^2 = 0.66$, $p < 0.0001$) (Fig. 4).

Water Soluble Ions

The dominant anions were SO_4^{2-} , NO_3^- , Cl^- , and $\text{C}_2\text{O}_4^{2-}$ with average concentrations of 3.16 ± 1.04 , 1.80 ± 0.63 , 1.70 ± 0.38 , and $0.12 \pm 0.08 \mu\text{g}/\text{m}^3$, respectively (Fig. 5 and Tables 1 and S1). Nitrite contributed negligibly overall, with an average concentration of $0.02 \pm 0.01 \mu\text{g}/\text{m}^3$. The dominant cations were Ca^{2+} and NH_4^+ , with average concentrations of 1.16 ± 0.58 and $0.81 \pm 0.46 \mu\text{g}/\text{m}^3$, respectively (Fig. 5 and Tables 1 and S1). Potassium and Mg^{2+} were found to have smaller concentrations, with averages of 0.32 ± 0.47 and $0.07 \pm 0.04 \mu\text{g}/\text{m}^3$, respectively. Note again that Na^+ was not considered in this discussion.

The average ionic concentration was $9.06 \pm 2.49 \mu\text{g}/\text{m}^3$, and the mass of NH_4^+ , SO_4^{2-} , and NO_3^- accounted for 64% of the total observed ionic mass concentration. Ammonium was correlated to both SO_4^{2-} ($R^2 = 0.48$, $p < 0.005$) and NO_3^- ($R^2 = 0.39$, $p < 0.001$). There was very little difference between median and mean. On average, ions accounted for 23% of the total observed aerosol concentration (ions and OM).

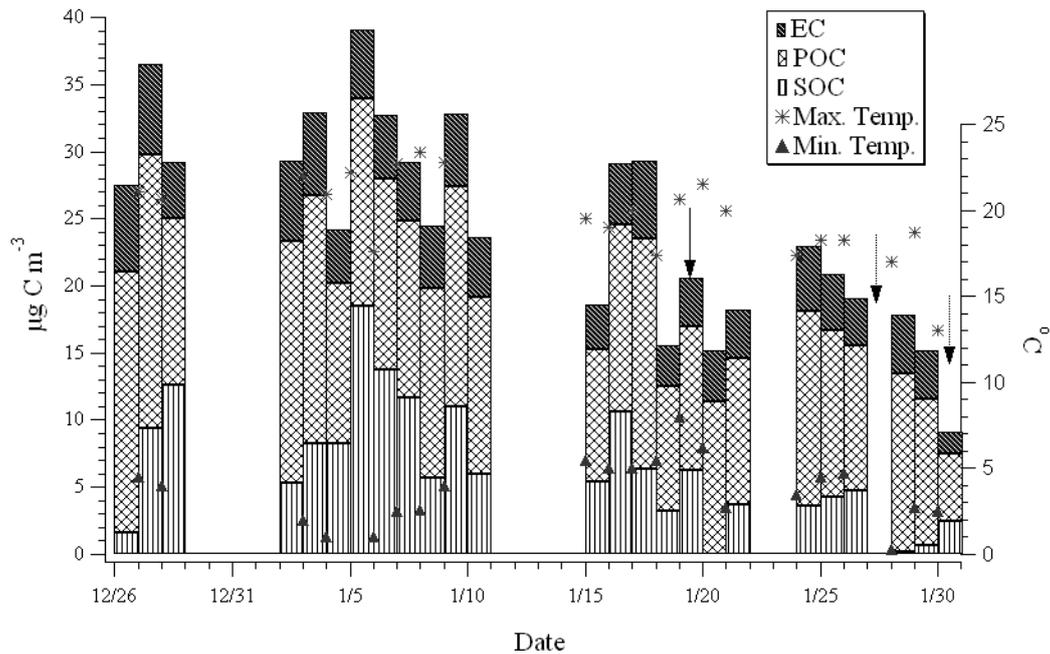


Fig. 1. Time series of EC, POC, SOC, and minimum and maximum temperature. Arrows indicate rainfall (4.9 mm on 1/19, trace amounts on other days).

Table 1. Statistics for aerosol concentrations of carbonaceous species, inorganic ions, and carbon and nitrogen isotopes and for derived parameters in Kathmandu during winter.

Parameter	Mean	Median	1σ	5 th percentile	95 th percentile	n*
OC ($\mu\text{gC/m}^3$)	20.02	19.79	6.59	11.39	29.38	25
OM ($\mu\text{g/m}^3$)	29.26	27.77	11.24	13.78	44.24	25
EC ($\mu\text{gC/m}^3$)	4.48	4.40	1.17	3.12	6.41	25
TC ($\mu\text{gC/m}^3$)	24.51	24.14	7.51	15.15	35.77	25
OC/EC	4.47	4.36	0.93	3.08	6.03	25
SOC ($\mu\text{gC/m}^3$)	6.81	5.84	4.48	0.77	13.54	25
POC ($\mu\text{gC/m}^3$)	13.48	13.23	3.52	9.37	19.26	25
SOC/OC	0.31	0.31	0.14	0.06	0.50	25
WSOC ($\mu\text{gC/m}^3$)	10.09	10.49	3.64	5.01	14.71	25
WSOC/OC	0.50	0.51	0.06	0.39	0.57	25
WSOC/TC	0.41	0.41	0.05	0.32	0.47	25
Cl^- ($\mu\text{g/m}^3$)	1.70	1.78	0.38	1.06	2.29	24
NO_2^- ($\mu\text{g/m}^3$)	0.02	0.02	0.01	0.01	0.03	8
NO_3^- ($\mu\text{g/m}^3$)	1.80	1.69	0.63	1.07	3.06	24
SO_4^{2-} ($\mu\text{g/m}^3$)	3.16	2.85	1.04	1.88	4.95	24
$\text{C}_2\text{O}_4^{2-}$ ($\mu\text{g/m}^3$)	0.12	0.12	0.08	0.01	0.25	16
NH_4^+ ($\mu\text{g/m}^3$)	0.81	0.64	0.46	0.29	1.69	24
K^+ ($\mu\text{g/m}^3$)	0.32	0.12	0.47	0.01	0.85	21
Mg^{2+} ($\mu\text{g/m}^3$)	0.07	0.07	0.04	0.02	0.12	23
Ca^{2+} ($\mu\text{g/m}^3$)	1.16	1.08	0.58	0.41	2.39	24
H^+ (nmol/m^3)	49.99	49.53	18.66	20.71	72.31	24
f	0.45	0.43	0.19	0.23	0.75	24
Total speciated aerosol ($\mu\text{g/m}^3$)	39.08	35.42	11.91	23.69	54.89	24
$\delta^{15}\text{N}$ (‰)	9.45	9.53	0.87	8.18	10.47	8
$\delta^{13}\text{C}$ (‰)	-25.74	-25.70	0.19	-26.01	-25.53	7

* Number of samples. For those less than 25, see Table S1 to see if samples were below detection limit or if analyses were not performed. For statistics, only those samples for which measured values were above detection limits are included.

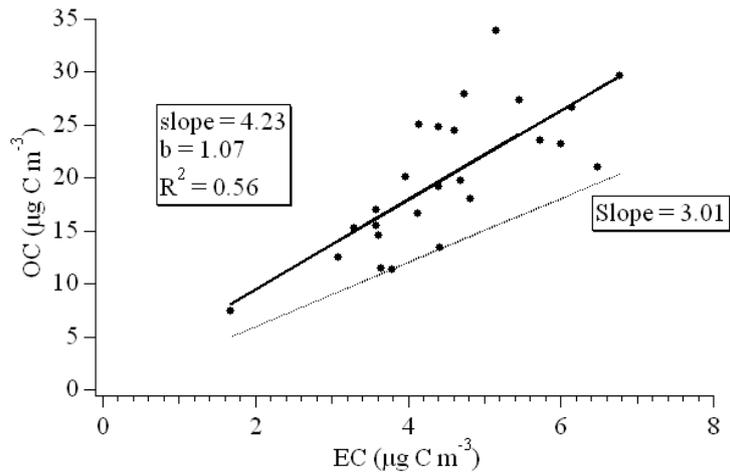


Fig. 2. Regression of EC versus OC during the sampling period. The darker line indicates the regression through the observed values, while the lighter line indicates the minimum ratio of OC/EC used for estimating SOC.

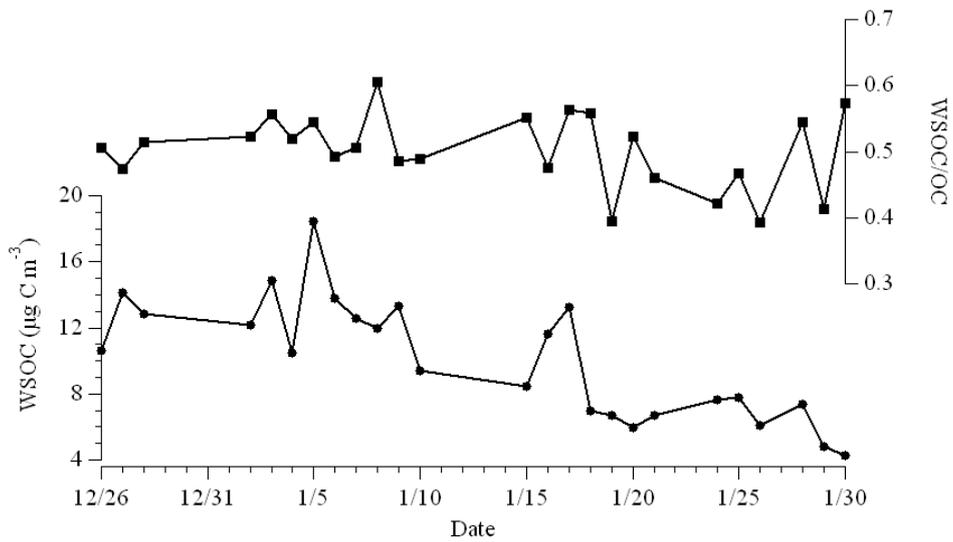


Fig. 3. Time series of WSOC concentrations and WSOC/OC in Kathmandu during the sampling period.

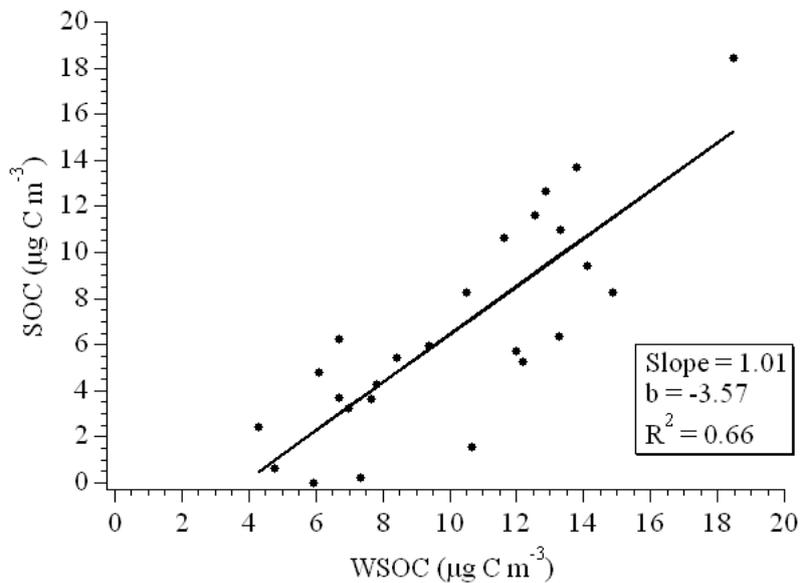


Fig. 4. Regression of WSOC versus SOC during the sampling period.

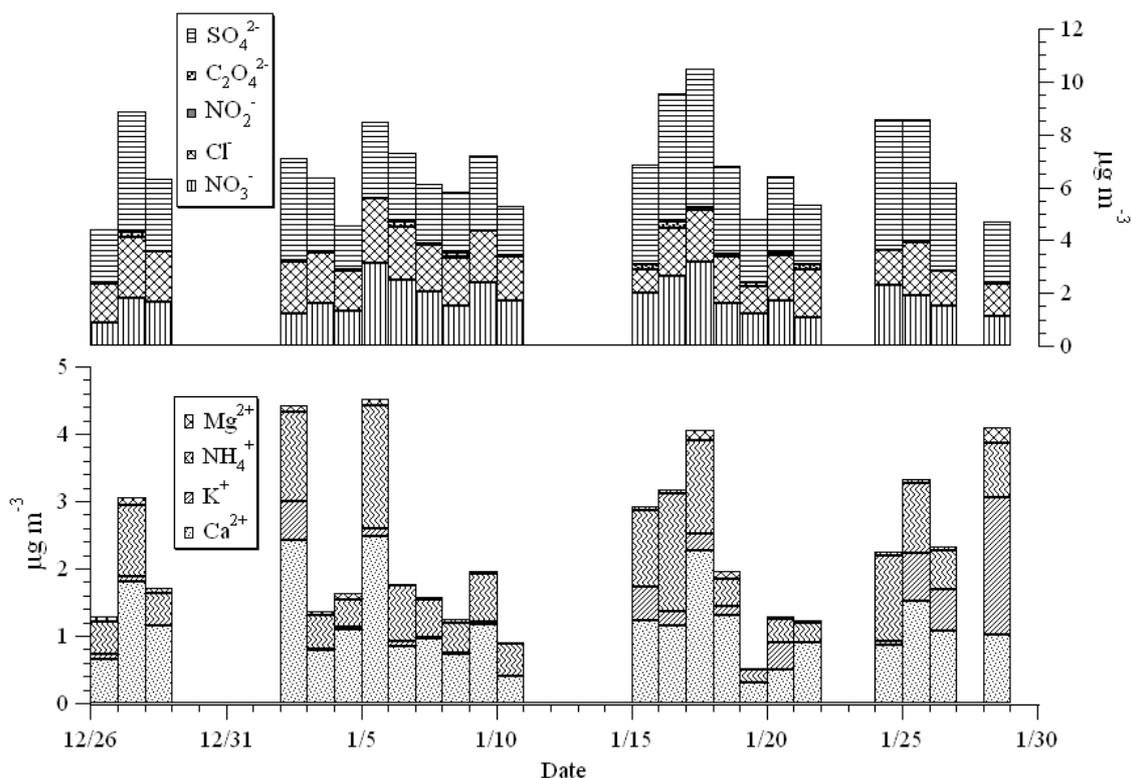


Fig. 5. Anion (top) and cation (bottom) concentrations observed in aerosols of Kathmandu during the sampling period.

On average, the aerosol $[H^+]$ (Fig. 6) was calculated to be $49.99 \pm 18.66 \text{ nmol/m}^3$ and exhibited a large range of 9.14 to 84.32 nmol/m^3 .

Carbon and Nitrogen Isotopes

The average $\delta^{13}C$ in the samples was $-25.74 \pm 0.19\%$, and ranged from -26.05 to -25.51% . The average $\delta^{15}N$ was $9.45 \pm 0.87\%$, and it varied from 8.13 to 10.56% (Tables 1 and S1, Fig. 7). Isotopic content is compared to that measured elsewhere in Table 2.

DISCUSSION

OC and EC

During the study period, OC exhibited greater temporal variability than EC, where Fig. 1 indicates an overall decreasing trend in OC. A small decreasing trend in EC suggests, in general, consistent local primary emissions sources of aerosols and boundary layer dynamics. Because the majority of OC is POC, total OC follows trends similar to those for POC and EC. The strong correlation between EC and OC ($R^2 = 0.56$, $p < 0.0001$) at the sampling site likely indicates a common source for EC and OC including the precursors that lead to SOC.

The average EC and OC of 4.48 and $20.02 \text{ } \mu\text{gC/m}^3$, respectively, in Kathmandu are comparable to those measured during winter in other urban Asian cities. Average EC and OC during winter of 2005 in Guangzhou, China, were 4.2 and $23.9 \text{ } \mu\text{gC/m}^3$ and in Hong Kong were 2.5 and $12.4 \text{ } \mu\text{gC/m}^3$, respectively (Duan et al., 2007), and during winter of 2006 in Xi'an, China were 23.7 and $4.6 \text{ } \mu\text{g/m}^3$,

respectively (Shen et al., 2009). Carrico et al. (2003) observed EC of $1.0 \pm 0.7 \text{ } \mu\text{gC/m}^3$ during October 1999 to January 2000 in Nagarkot, a site inside Kathmandu valley that is approximately 20 kilometers from the site of the current study.

In general, OC to EC ratios depend on emission sources and secondary organic aerosol formation. Hildemann et al. (1991) found OC/EC in fine particles of 2.2 for light-duty gasoline vehicles and 0.8 for heavy-duty gasoline vehicles. The OC/EC values in Kathmandu were larger than these ratios on all days. Cao et al. (2005) found an average OC/EC ratio of 4.1 for vehicle exhaust, a value close to that observed in Kathmandu. Thus, the common source is most likely vehicular emissions. The variation of OC/EC during the sampling period and the values larger than 3.01 indicate the importance of SOC, assuming no fluctuations in emission ratios.

Emission from vehicles appears to be one of the most important sources of aerosols. Kondo et al. (2005) also concluded that the transportation-related emissions are the main sources of air pollution in Kathmandu valley, which is further corroborated by the observations of Panday and Prinn (2009) that showed peaks in concentrations of PM_{10} during the mornings from 2004 to 2005. Further, they observed more concentrated air pollution during winter compared to summer. In Kathmandu, numerous poorly maintained and old vehicles and low-grade and adulterated fuel are often the norms (Faiz et al. 2006). Poor road conditions also contribute to emissions related to vehicle use. The total length of road in Kathmandu is 1279.09 km, of which only about 40% is paved (CBS 2009). In 2005, PM_{10}

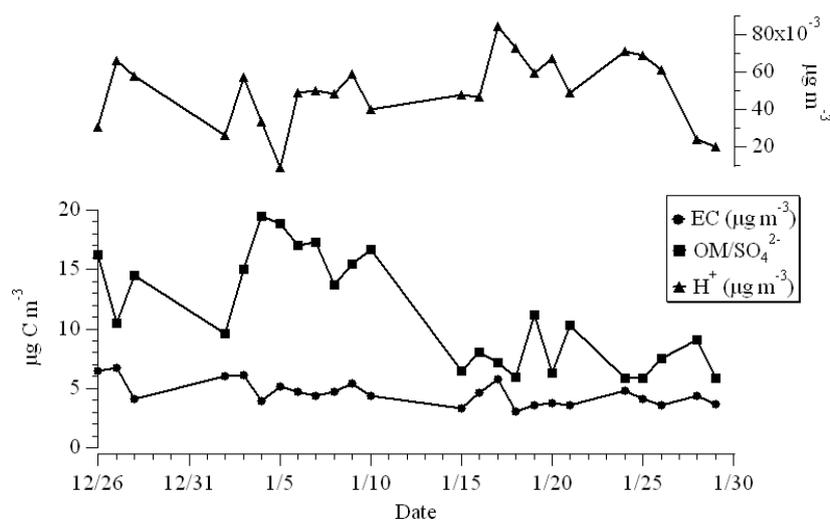


Fig. 6. Time series of EC ($\mu\text{g}/\text{m}^3$), $[\text{H}^+]$ ($\mu\text{g}/\text{m}^3$), and the ratio of OM to SO_4^{2-} (dimensionless) during the sampling period.

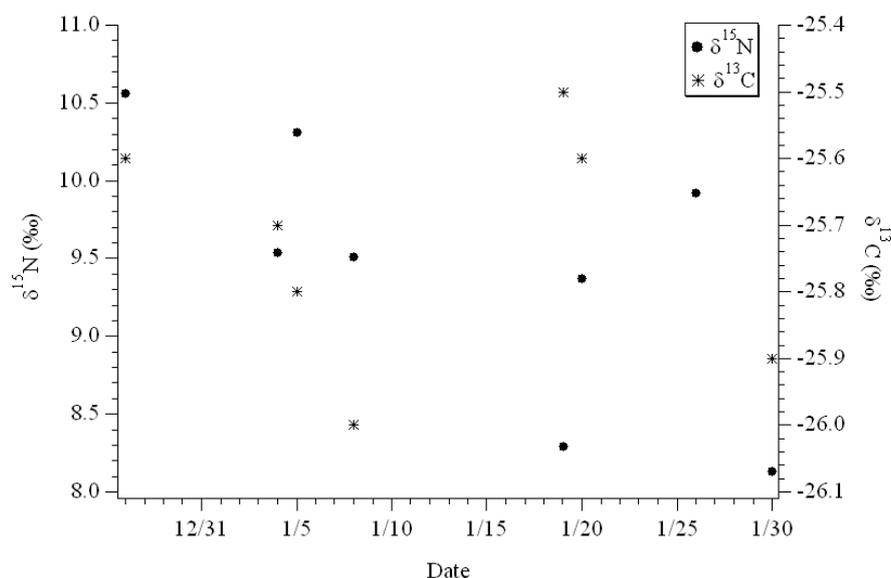


Fig. 7. Carbon and nitrogen isotope ratios in aerosols in Kathmandu during the sampling period.

emission from vehicular activities and suspension of road dust in Kathmandu valley is estimated to be 7890 tons/year (62% of total PM_{10}). The contribution from industrial sources was estimated to be approximately 17% (ICIMOD, 2007). In comparison, Cao *et al.* (2005) attributed approximately 73% and 23% of TC in Xi'an, Shaanxi Province, China during fall 2003 to gasoline and diesel engine exhaust, respectively, while only 44% and 3% of TC during winter 2003–2004 to gasoline and diesel engine exhaust, respectively.

Open waste burning practices are also an important source contributing to the aerosol loadings in Kathmandu. Refuse burning was estimated to emit approximately 172 tons of PM_{10} in 2005 in Kathmandu valley (ICIMOD, 2007). In addition, protests called by various groups often include the burning of vehicle tires on the streets, emitting CO, SO_2 , and NO_2 (Shakya *et al.*, 2008); uncontrolled tire fires may also be significant aerosol sources in Kathmandu.

SOC

The average observed percent contribution of secondary OC to carbonaceous aerosol in Kathmandu (31%) is smaller than but comparable to values observed in other urban Asian cities, though it should be noted here that the values presented in this study likely represent a lower bound because some SOC could have been present during the period associated with the minimum OC/EC ratio. Lin and Tai (2001) reported that the SOC contribution to OC was larger in $\text{PM}_{2.5}$ (40%) compared to PM_{10} (32.4%) during November 1998 to April 1999 in Kaohsiung City, Taiwan. In Guangzhou, China, the average SOC concentration during winter 2005 was $11.5 \mu\text{g}/\text{m}^3$ (Duan *et al.*, 2007), which is larger than that observed in Kathmandu. During winter 2006–2007 in Tianjin, China, Li *et al.* (2009) observed SOC contribution to OC of 37.3–50.3% compared to mean of ~34% observed in Kathmandu. The majority of OC was primary in nature in Kathmandu, comparable to the

measurements made in the San Joaquin Valley of California, where secondary contributions to OC were smaller in winter due to decreased mixing heights and photochemistry (Strader *et al.*, 1999). The smaller percentage of SOC relative to OC suggests that motor vehicles and other local emissions (as opposed to transport and processing) are the major factors controlling concentrations of carbonaceous aerosols. However, the strong relationship between OC and EC ($R^2 = 0.56$) indicates that any SOC likely was derived from volatile organic compounds co-emitted with POC and EC.

WSOC

The correlation of WSOC with SOC ($R^2 = 0.66$ and slope of approximately unity, Fig. 4) indicates the likelihood that a large fraction, if not all, of the SOC is WSOC. Like OC, there was an overall decreasing trend in WSOC during the sampling; no such trend was observed for WSOC/OC. WSOC/OC was observed to be the smallest (0.39) during the rain event (4.9 mm) on 19 January 2008, likely indicating favorable wet deposition of WSOC and decreased photochemical processing. WSOC did not show any significant correlation with SO_4^{2-} and only a weak correlation with NO_3^- ($R^2 = 0.31$, $p < 0.005$). The lack of significant correlation of WSOC with SO_4^{2-} and NO_3^- indicates that WSOC likely is formed primarily via pathways that are different than those for SO_4^{2-} and NO_3^- . This is in stark contrast to the strong correlation between WSOC and SO_4^{2-} and NO_3^- observed in urban and suburban sites in Nanjing, China (Yang *et al.*, 2005).

The non-zero intercept (i.e. -3.57) in Fig. 4 underscores that some fraction of the POC in Kathmandu is likely water-soluble. If it is assumed that all SOC is WSOC, the fraction of POC that is WSOC can be found by (WSOC-SOC)/POC. This value, on average, is 0.26, likely a lower bound because not all SOC will definitively be WSOC. In Houston, Anderson *et al.* (2008) also noted an increase in particulate WSOC associated with rush hour, suggesting a primary source for WSOC. A large WSOC fraction is usually assumed to be indicative of processed aerosol or SOA (Sullivan *et al.*, 2004; Weber *et al.*, 2007). The average ratio of WSOC to OC (~ 0.18) in Lahore, Pakistan during spring 2006 with very large average PM_{10} concentrations ($459 \mu\text{g}/\text{m}^3$) mainly as a result of vehicular activities (Zhang *et al.*, 2008) was smaller than the observed ratio of ~ 0.50 in the present study.

Water Soluble Inorganic Ions

Because K^+ , a tracer of biomass burning, was found in small concentrations, biomass burning seems to have a small influence on aerosol mass loadings in Kathmandu in winter. However, K^+ increased significantly after 25 January 2008, possibly because of the influence of biomass burning after this day. The average K^+/EC before 01/25/08 was very small (0.03). A K^+/EC ratio of 0.03 was also observed in a location influenced by vehicular emissions in Auckland, New Zealand (Wang *et al.*, 2005). The average ratio of K^+ to total ionic aerosols was less than 0.14%, compared to 7.3% observed during winter 2006–2007 in Tianjin, China (Li *et*

al., 2009). However, the ratio increased unusually to $\sim 24\%$ on 28 January 2008. Fires made by street vendors for heat during winter and open refuse burning may have played a role in increased K^+ concentrations at the end of the campaign.

The strong correlation of Ca^{2+} with Mg^{2+} ($R^2 = 0.59$, $p < 0.0001$) suggests crustal sources of aerosols in Kathmandu. Carrico *et al.* (2003) also reported the influence of dust transport inside Kathmandu valley from a Saharan region. The influence of dust transport was highly variable, with Ca^{2+} and Mg^{2+} contribution to total ionic aerosols ranging from 6 to 22%.

Sulfate was significantly correlated with NH_4^+ ($R^2 = 0.48$, $p < 0.005$). The average winter SO_4^{2-} concentration in Kathmandu ($3.16 \mu\text{g}/\text{m}^3$) was smaller than the annual mean SO_4^{2-} observed in Seoul ($8.70 \mu\text{g}/\text{m}^3$) (Lee *et al.*, 1999) and larger than in Nagarkot, Kathmandu valley ($2.5 \mu\text{g}/\text{m}^3$) (Carrico *et al.*, 2003). The neutralization ratio ranged from 0.15 to 0.92 during the campaign and had a mean of 0.45 ± 0.19 . Clearly, NH_4^+ was not sufficient to neutralize the aerosols, which were most likely acidic unless they were neutralized by compounds other than NH_4^+ .

Daily aerosol acidity ranged from 9.14 to $84.32 \text{ nmol}/\text{m}^3$ in Kathmandu during winter. This is larger than the mean H^+ concentration observed in Seoul during fall ($5.19 \text{ nmol}/\text{m}^3$) (Lee *et al.*, 1999). Peak $[\text{H}^+]$ concentration coincided with those of SO_4^{2-} and NO_3^- . The molar ratio of H^+ to SO_4^{2-} was found to range from 0.31 to 2.35. Lee *et al.* (1999) observed a range for the H^+ to SO_4^{2-} ratio of 0.013 to 0.184 during fall in Seoul with the presence of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$.

Organic mass (OM) to SO_4^{2-} ratios are compared to H^+ and EC concentrations in Fig. 6. The maximum OM/ SO_4^{2-} (19.31) occurred on 5 January 2008, which also had the smallest $[\text{H}^+]$ ($9.15 \text{ nmol}/\text{m}^3$) and the largest OC, SOC, WSOC, OC/EC, and OM. The minimum OM/ SO_4^{2-} ratio (4.53) was observed on 30 January 2008, associated with $[\text{H}^+]$ of $67.53 \text{ nmol}/\text{m}^3$. The largest H^+ (nmol/m^3) was observed on 17 January 2008 with the largest ionic aerosol concentration. During the day (20 January 2008) with one of the smallest OM to SO_4^{2-} ratios (4.74), one of the highest $\delta^{13}\text{C}$ (-25.6%) also was observed. In a rural location with biogenic influence, Ziemba *et al.* (2007) reported larger OM/ SO_4^{2-} (6.4) and smaller H^+ ($1.7 \text{ nmol}/\text{m}^3$), attributed to stronger biogenic influence and less photochemical aging, and a smaller OM/ SO_4^{2-} (0.4 and 0.6) and larger H^+ (69 and $56 \text{ nmol}/\text{m}^3$), attributed to anthropogenic influence and photochemical aging.

Carbon and Nitrogen Isotopes

The aerosol data indicate that Kathmandu is polluted and that the dominant source most likely is fossil fuel combustion. In such an area, smaller $\delta^{13}\text{C}$ values are expected (Cachier 1989). Furthermore, Cachier (1989) found mean $\delta^{13}\text{C}$ values of -25.5 and -26.5% for industrial and vegetation combustion, respectively, compared to -22.5% for vegetative emission. The mean $\delta^{13}\text{C}$ of -25.74% in the samples is consistent with a dominant fossil fuel combustion source, and is comparable

to the values observed in aerosols collected from urban areas (Table 2). The minimum $\delta^{13}\text{C}$ (-26.05‰) was observed on 8 January 2008, with the maximum WSOC/OC, while the maximum $\delta^{13}\text{C}$ (-25.51‰) was observed on 19 January 2008, with the minimum WSOC/OC. Though $\delta^{13}\text{C}$ was not correlated to WSOC, it had a strong correlation with WSOC/OC ($R^2 = 0.79$; $p < 0.01$) indicating its association with water-soluble fraction of OC and that the variation in $\delta^{13}\text{C}$ may be linked to processing. The little variation in these samples, however, indicates the consistent source of carbonaceous material. The mean $\delta^{13}\text{C}$ observed in Kathmandu is comparable to the observations made in other urban and anthropogenically influenced locations around the world (Table 2).

The mean $\delta^{15}\text{N}$ ($9.45 \pm 0.87\text{‰}$) observed in this study is comparable to the aerosol samples collected from Paris during winter ($10.00 \pm 3.4\text{‰}$) (Widory, 2007). The maximum $\delta^{15}\text{N}$ (10.56‰) was observed on 27 December 2007, associated with maximum EC and POC. The minimum $\delta^{15}\text{N}$ (8.13‰) was observed on 30 January 2008 with minimum EC, OC, and WSOC. There was a strong correlation of $\delta^{15}\text{N}$ with $\text{NH}_4^+/\text{NO}_3^-$ ($R^2 = 0.84$, $p < 0.005$) (Fig. 8). Yeatman *et al.* (2001) observed the larger $\delta^{15}\text{N}$ (-1 – 7‰) in aerosol NO_3^- (10 – 12‰) compared to that in aerosol NH_4^+ from the samples collected next to vehicle sources in London. The correlation of $\delta^{15}\text{N}$ with crustal cations such as Ca^{2+} ($R^2 = 0.74$, $p < 0.05$) and Mg^{2+} ($R^2 = 0.71$, $p < 0.05$) indicates that heavier nitrogen isotopes and

some associated nitrates may have originated from distant sources related to dust. Because larger $\delta^{15}\text{N}$ values in aerosols indicate residual material from the combustion of vegetation (Turekian *et al.*, 1998), the smaller $\delta^{15}\text{N}$ values observed in this study indicate the lack of an influence of biomass burning. Further, the aerosol sources from fuel oil and coal ($\delta^{15}\text{N} < 0\text{‰}$) are less likely because the aerosols in this study were enriched in ^{15}N (Widory, 2007).

Principal Component Analysis (PCA)

The PCA found four factors with Eigenvalues greater than unity that explained a combined 82.2% of the variance in the data (Table 3). Factor 1 explained the most of the variance, 38.7%, and had strong loadings of EC, POC, SOC, WSOC, Cl^- , and maximum temperature. Factor 1 is attributed to the primary local sources, mainly from vehicular emissions. Interestingly, it had a high negative loading of K^+ , suggesting the role of biomass burning when local vehicular emission sources decrease. During the end of the sampling campaign, the smallest values for carbonaceous aerosol concentrations were observed, and K^+ values peaked. Factor 2, with strong loadings from NH_4^+ and NO_3^- explained an additional 23.0% of the variance. This factor appears to be associated with secondary aerosol formation via gas-to-particle partitioning. Factor 3, with strong loadings from SO_4^{2-} , RH, and minimum temperature likely represents aqueous processing and accounts for 11.4% of the variance. Interestingly, minimum temperature and RH

Table 2. Carbon and nitrogen isotope ratios in aerosol collected in different locations.

Location	Type	Date	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	Reference
Kathmandu, Nepal	Urban	Dec. 2007–Jan. 2008	-25.74 ± 0.19 (TC)	9.45 ± 0.87	This work
Downtown LA, USA	Urban	Fall 1987	-23.41 (TC)		Kaplan and Gordon (1994)
Stockholm, Sweden	Urban	Oct.–Nov. 2005	-27.3 ± 0.1 (TOC)		Zencak <i>et al.</i> (2007)
Hong Kong, China	Urban	Nov. 2000–Feb. 2001	-26.9 ± 0.6 (OC) -25.6 ± 0.1 (EC)		Ho <i>et al.</i> (2006)
Cassier Tunnel, Canada	Anthropogenic	Aug. 2001	-27.13 (OC) -26.97 (EC)		Huang <i>et al.</i> (2006)
Rio de Janeiro, Brazil	Urban	Jun.–Jul. 1985	-24.1 to -25.6 (OC) -23.3 to -26.4 (EC)		Tanner and Miguel (1989)
Pracicaba, Brazil	C ₄ plantations	Aug. 1999–Sep. 2000	-20.9 ± 0.8 (TC)	10.6 ± 2.8	Martinelli <i>et al.</i> (2002)
Paris, France	Urban	Feb.–Apr. 2003 Jun.–Aug. 2003		3.9 – 5.4 (diesel–vehicles) 2.9 – 15.4 (natural gas–heating source) -19.4 – 2.9 (fuel oil–heating source) -5.3 (coal–heating source) 5.5 – 8 (waste incinerators)	Widory (2007)

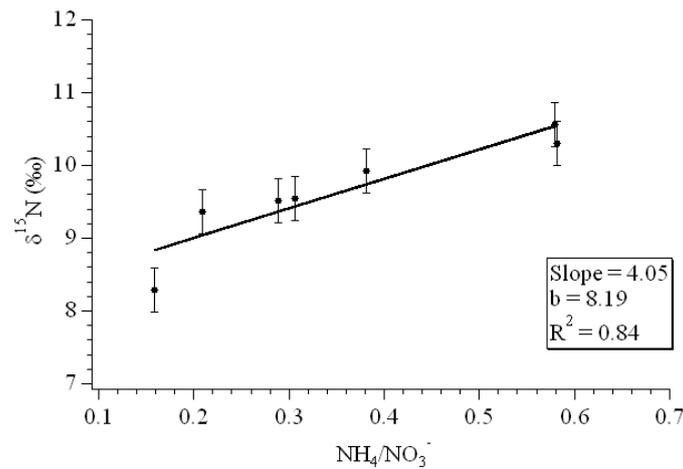


Fig. 8. Regression of $\text{NH}_4^+/\text{NO}_3^-$ versus $\delta^{15}\text{N}$ during the sampling period.

Table 3. Principal component analysis of carbonaceous components, water-soluble organic, water-soluble inorganic ions, and meteorological data. Only factors with eigenvalues exceeding unity were included. The largest absolute factor loading for each variable is shown in bold (if the original loading was positive).

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Communality
EC	0.87	0.13	0.19	0.22	0.87
POC	0.87	0.13	0.19	0.22	0.87
SOC	0.63	0.55	-0.39	-0.24	0.91
WSOC	0.87	0.37	-0.27	0.01	0.96
Cl^-	0.74	0.28	-0.13	0.23	0.69
NO_3^-	0.34	0.86	0.15	0.03	0.88
SO_4^{2-}	-0.16	0.42	0.70	0.43	0.88
NH_4^+	-0.07	0.88	0.11	0.26	0.86
K^+	-0.77	0.05	0.09	0.24	0.66
Mg^{2+}	0.09	0.06	0.08	0.89	0.82
Ca^{2+}	0.16	0.56	-0.04	0.72	0.86
MaxT	0.72	-0.17	-0.27	-0.08	0.63
MinT	-0.33	-0.09	0.85	0.18	0.87
RH	0.24	0.13	0.74	-0.36	0.75
Eigenvalue	5.42	3.22	1.60	1.27	
Cumulative% variance	38.74	23.00	11.43	9.05	
Estimated Source	Local/ Vehicles	Secondary Gas-to- Particle	Aqueous Processing	Dust transport	

fall in this category, possibly suggesting the sensitivity of aqueous phase oxidation of SO_2 to RH levels and the relationship between minimum temperature and RH. Moreover, the dominance of SO_4^{2-} together with RH in factor 3 may mean that the major pathway for SO_4^{2-} formation in this locality is mainly through heterogeneous reactions (Kai *et al.*, 2007). The strong loadings of mineral aerosols (Ca^{2+} and Mg^{2+}) indicate that Factor 4 is associated with transport of dust. This factor explained an additional 9.1% of the variance. However, the loading of NH_4^+ in this factor is minor, and thus, the transport of NH_4^+ with dust also appears to be minor. In summary, the PCA performed on this data shows that primary local emissions from vehicular activity had the strongest influence on particle concentrations at this site during winter, followed by secondary processing and long-distance dust transport.

CONCLUSIONS

Kathmandu, the capital of Nepal, experiences very large levels of air pollution due to urbanization and being located inside a valley. In winter, the capacity of aerosols to accumulate in ambient air increases in the absence of major deposition processes such as precipitation. Thus, this study was carried out to gain information regarding the composition, concentration, and sources of aerosols in Kathmandu winter. The daily OC/EC ratio varied between 3.01 and 6.59. Correlation of EC and OC ($R^2 = 0.56$), large POC contribution to carbonaceous aerosol, and smaller $\delta^{13}\text{C}$ ($-25.74 \pm 0.19\text{‰}$) all imply that local vehicular emission is the single most important source in Kathmandu. Principal component analysis revealed that other important sources/pathways include dust transport and secondary

processing. The strong correlation of Ca^{2+} and Mg^{2+} ($R^2 = 0.59$) supports some crustal aerosol sources for the transported dust. Biomass burning did not play a significant role in aerosol formation/emissions, except at the end of the sampling period.

Most (69%) of the observed OC was estimated to be primary. About half of the OC observed in Kathmandu was water-soluble, with contributions from both SOC and POC. Ionic concentrations are approximately a factor of two smaller than those of organic carbon and are dominated by SO_4^{2-} , NO_3^- , and NH_4^+ . The neutralization ratio indicated that the aerosols in Kathmandu are acidic in nature, as NH_4^+ was not sufficient to neutralize the acidity in fine particles. Sulfates were the dominant ion, confirming the anthropogenic source of aerosols. Analysis of carbon isotopes indicates fossil fuel combustion sources, while nitrogen isotopes indicate transport from distant sources and minimal influence from biomass burning.

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SUPPLEMENTARY MATERIALS

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

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