



Chemical Characterization of Airborne Particulates of Kathmandu, Nepal

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Abstract

Particulate matters of different aerodynamic diameter were collected on 47mm quart filter using Omni frm Ambient air Sampler from 9th March 2010 to 28th April 2010. The collected particulate matter 24-h samples were analyzed for 13 nonionic and 9 ionic components. Black Carbon concentration was also monitored for the same duration using AE 31 Magee Scientific Aethalometer. The chemical analysis shows dominating concentration of silicon in all the samples followed by Na⁺, Fe, SO₄²⁻, Ca²⁺, NH₄⁺ and Cl⁻ with common radicals NO₃⁻, NO₂⁻, K⁺, Mg²⁺ and metals Ni, Pb, Al, Ag, Ti, V, Mn, Cd, Cr, Cu and Zn. Only four samples out of all the analyzed samples has shown the presence of F. PM₁₀ with 105.16 μg/m³ was the highest value of particulate matter while black carbon for the same duration was 12.97 μg/m³. The variation of particulate matters for the observed period was from 105.16 - 56.47 μg/m³ and that for black carbon 21.8 - 4.7 μg/m³. The present observation shows that major contributor in the particulate matter are derived from roadsuspension, vehicular emission and domestic activities. Irrespective to the nature of particulate matters of different aerodynamic diameter analyzed most of the ionic and metallic components are common in all the analyzed samples reflecting their common impact on human health.

Keywords: Particulate matter, black carbon, air sampler, aethalometer.

Introduction

Particulate matter (PM) is the general term used for the mixture of solid particles and liquid droplets suspended in the air. Individual particles vary in size, geometry, mass, concentration; chemical composition and physical properties. PM may be produced as a direct or indirect result of human activities. Atmospheric particles-aerosol-are some of the key components of the atmosphere. PM the solid aerosols are emitted from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, wind driven or traffic-related suspensions of road, soil, mineral dust, sea salt and biological materials. The aerosols emitted by the fixed and mobile sources have a variety of health effects that are known for a long period of time¹. Ambient concentration of particulate matter and its chemical components depend strongly on wind dynamics in a study area². It has been estimated that urban air pollution causes ~360000 premature deaths each year in Asia³. Chemical composition of particulates, especially the presence of small amount of toxic chemicals, is a more appropriate parameter for the assessment of particulate health effects rather than their mass concentration⁴. The presence of major and minor elements in ambient particulate matter is frequently related to emission from specific source^{5, 6}. Monitoring of both PM mass and chemical composition is important for identification of the emission source, determination of compliance with the set air quality standards, bridging the knowledge gap between air quality and its health effects, and establishment of effective pollution control programs⁷. Anthropogenic elements are

originated from different sources. Those emitted during the burning of fossil fuels (V, Co, Mo, Pb, Ni, and Cr) were mostly associated with particles smaller than PM_{2.5}^{8,9}. Traffic pollution involves a wide range of trace element emission that include Fe, Ba, Pb, Cu, Zn and Cd^{8,10}. As trace elements associated with fine particles are nonvolatile in nature, they are less prone to chemical transformations and remain in the form as they were emitted, even though they tend to undergo long range atmospheric transport¹¹. Particulate heavy metals can have severed toxic and carcinogenic effects on human when inhaled in higher concentration. Some of the well known anthropogenic processes contributing to the airborne particulate pollution include transportation, industrial activities, biomass burning and agricultural activities¹²⁻¹⁵. Particulate Matter (PM) has adverse effects on human health^{16,17}. The health risk posed by PM is due to a number of factors, namely, particle size, surface area and chemical composition^{18,19}.

In the past, government of Nepal and the Danish International Development Agency (DANIDA) had initiated air quality management of Kathmandu valley as the fifth Component of the Environment Sector Programme Support (ESPS) from 2002-2004. The pollutants measured were total suspended particles (TSP), particulate matter of 10 micrometer or less in diameter (PM₁₀), PM_{2.5}, NO₂, SO₂, and benzene. This programme had only quantified the physical components of the particulate matter and had not attempted for the chemical analysis of the monitored samples during the observation period. In 1993, the Environment and Public Health Organization (ENPHO)

measured the average 24-hour lead concentration in the Valley and found an average value of $0.32 \mu\text{g}/\text{m}^3$, with a range from $0.18 \mu\text{g}/\text{m}^3$ to $0.53 \mu\text{g}/\text{m}^3$.²⁰ Due to the phase-out of leaded gasoline it was assumed that the lead concentration would decrease. Since 26 December 1999, only unleaded gasoline has been distributed in Nepal. Recently some papers had been published by monitoring black carbon (BC) aerosol in Kathmandu valley. Distinct diurnal, monthly and seasonal variation of BC was observed in Kathmandu Valley²¹. About fifty percent of BC aerosol in the valley is contributed by vehicles and industries²². Long-term exposure to particulate matter shows decreased lung function, chronic bronchitis, premature deaths, and heart attacks. The health impact of air pollution depends on the pollutant type, its concentration in the air, length of exposure and individual susceptibility. This paper for the first time has attempted to analyze the chemical components like ionic and nonionic present in the particulate matter and their possible impacts on human health. In addition to this an attempt was also done to know the variation of BC during the monitored period.

Material and Methods

Study Area: Kathmandu valley located between $27^{\circ}37'30''$ N and $27^{\circ}45'0''$ N Latitude and $85^{\circ}15'0''$ E and $85^{\circ}22'30''$ E Longitude is about 1500 meters above sea level and covers about 340 sq.km. The cross section of the valley is about 20 km north to south and 30 km east to west. Kathmandu valley has a bowl like structure surrounded by four major mountains namely Shivapuri, Phulchowki, Nagarjun and Chandragiri at an elevation of more than 500m from its base. Figure 1 is showing Kathmandu valley surrounded by major mountains with the Himalayas in the north side and the three major cities Kathmandu, Bhaktapur and Lalitpur with the location of study site Pulchowk Campus.

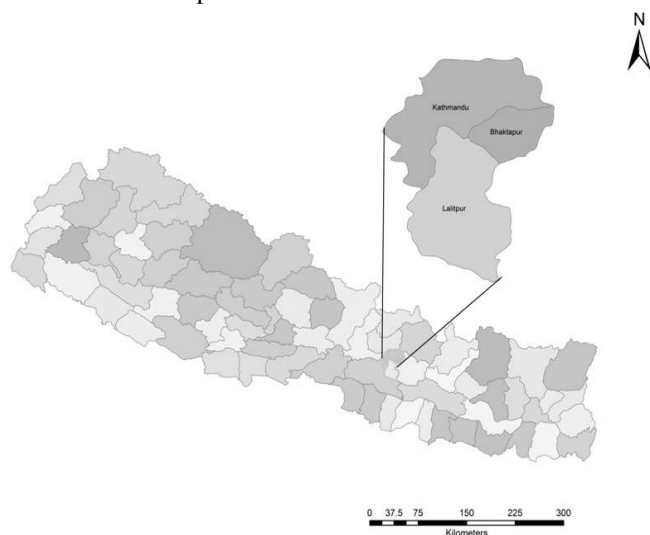


Figure-1
Kathmandu Valley map showing three districts Kathmandu, Lalitpur and Bhaktapur with study site

Instruments Used: *frmOmni* Ambient Air sampler was used for the measurement of particulate matters like TSP, PM_{10} , $\text{PM}_{2.5}$ and PM_1 by changing jet for each type for the time duration of 24 hours. A constant flow rate of 5 liter per minute was maintained at the system through the use of interchangeable single jet impaction nozzles. The particles penetrating the impactor stage were collected on a standard 47 mm quartz filter for subsequent gravimetric and chemical analysis. The suction hour, time, date and total volume of air suctioned in that time duration can be easily downloaded from the instrument when connected with the computer having its software. The initial weight of the filter paper (standard paper), the weighed paper with particulate matter and volume of air suctioned during that time is used in the calculation of particulate matters in $\mu\text{g}/\text{m}^3$.

A microwave pre-treatment method under Clean Water Act issued by USEPA and a HNO_3 -HCl pre-treatment method with Questron's Model Q-15 Micro Prep were used to analyze inorganic elements in PM. To do this, each filter was cut to several pieces with fixed size by a stainless steel cutter, and one of pieces was soaked by HNO_3 (61%) and HCl (35%) solution and heated for 5 minutes. After extraction the solution was filtered by a filter paper (No. 5B, 110 mm, Advantec MFS Inc.), and diluted to 50 ml with deionized water. Each filtrate was analyzed to determine 13 inorganic elements (Ni, Pb, Al, Ag, Ba, Si, Ti, V, Mn, Cd, Cr, Cu, and Zn) by inductively coupled plasma atomic emission spectroscopy (ICP-AES, DRE ICP, Leeman Labs Inc., USA). Further a piece of the filter was soaked in ultra pure water and ionic components were ultrasonically extracted. After passing through micro porous membrane filters (pore size, $0.45 \mu\text{m}$; diameter, 25 mm), each filtrate was used to analyze 5 cations (Na^+ , K^+ , NH_4^+ , Mg^{2+} , and Ca^{2+}) and 3 anions (F^- , NO_2^- , NO_3^- , SO_4^{2-} , and Cl^-) by ion chromatography (Dionex, Model DX-400), which consists of a separation column (Dionex Ion pac AS12A for anion and CS12 for cation) and a guard column (Dionex Ion pac AG 11 for anion and AG12A for cation). Prior to use ICP-AES and IC, several standard solutions with similar level of sample concentration were injected to examine quality assurance. An accuracy check was performed by calculating a relative error (RE) resulting from standard solutions and a precision check was performed by obtaining relative standard deviation and a coefficient of variation (CV) based on 3 repetitive measurements. REs for Si by ICP-AES and for NH_4^+ by IC were 17.6% and 9.6% in terms of measurement accuracy, respectively. Similarly, CVs for Si by ICP-AES and for NO_3^- by IC were 11.1% and 12.5% in terms of measurement precision, respectively.

Black carbon for the same duration (24 hours) was measured by using An aethalometer AE 31 manufactured by Magee Scientific USA is a seven wave length instrument to monitor BC. It was placed for operation on the second floor of G block, Pulchowk Campus for continuous monitoring of BC. The aethalometer is an instrument that provides a real time

read out of the concentration of BC or EC aerosol particles in air stream. The instrument was set into operation at a time interval of 5 minutes round the clock with a flow rate of 2 liters per-minutes (2LMP). It shows BC concentration in the display screen in an interval of five minutes. These data are automatically recorded in the flash card memory of the instrument. The instrument using its inlet tube aspirates ambient air from an altitude of ~8m above the ground level. Black carbon mass concentration is estimated by measuring the change in the transmittance of a quartz filter tape on to which particles impinge. The detail of the working of aethalometer is found in the operation manual.

Results and Discussion

Different samples of particulate matters from 9th March 2010 to 28th April 2010 for 24 hours duration collected by frm Omni ambient air sampler were analyzed. The data reveal that Si has a maximum mean concentration of 19.62 $\mu\text{g}/\text{m}^3$, followed by Fe, at 6.19 $\mu\text{g}/\text{m}^3$. These results are quite expected since levels of these elements in the atmosphere are normally soil derived. of the remaining metals Cr, V, Ni, Zn and Cd showed mean level 0.86, 0.85, 0.76, 0.74, and 0.43 $\mu\text{g}/\text{m}^3$ respectively. Al, Cu, Pb, Ag, Mn and Ti were comparatively in low concentration 0.30, 0.26, 0.16, 0.08, 0.05 and 0.02 respectively. The overall increasing order of metals concentration as Si>

Fe> Cr> V> Ni>Zn>Cd>Al>Cu>Pb>Ag>Mn>Ti. While in the case of ionic components the over all increasing order is $\text{Na}^+ > \text{SO}_4^{2-} > \text{Ca}^{2+} > \text{NH}_4^+ > \text{Cl}^- > \text{K}^+ > \text{NO}_2^- > \text{NO}_3^- > \text{Mg}^{2+}$. Further result is reflecting higher concentration of ionic components in the samples S18, S6, S11, S9 and S10 because the mass of particulate matters in these samples is also comparatively higher. On the basis of variation in the average concentration of nonionic and ionic components of particulate matters analyzes they can be categorized into 3 and 2 categories respectively.

Type-1 Nonionic components of range 6.19-19.62 $\mu\text{g}/\text{m}^3$ (higher concentration category) Fe and Si.

Type-2 Nonionic components of range 0.43-0.86 $\mu\text{g}/\text{m}^3$ (moderate concentration category) Cd, Zn, Ni, V and Cr.

Type-3 Nonionic components of range 0.02-0.30 $\mu\text{g}/\text{m}^3$ (low concentration category) Ti, Mn, Ag, Pb, Cu and Al.

Type-1 Ionic components of range 5.77-7.28 $\mu\text{g}/\text{m}^3$ (higher concentration category) Cl^- , NH_4^+ , Ca^{2+} , SO_4^{2-} and Na^+ .

Type-2 Ionic components of range 1.29-2.79 $\mu\text{g}/\text{m}^3$ (moderate concentration category) Mg^{2+} , NO_3^- , NO_2^- , and K^+ .

Table-1

Descriptive statistics of the ionic components present in the different particulate matter analyzed

Radicals present in PM	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Average in $\mu\text{g}/\text{m}^3$	5.77	2.60	2.29	6.18	7.28	5.90	2.97	1.29	6.0
St deviation	3.70	1.23	2.03	2.65	2.78	1.45	1.34	0.52	2.04
Maximum	16.60	5.39	7.72	12.47	15.82	8.27	7.12	2.86	11.8
Minimum	2.88	1.43	0.69	2.21	5.27	2.68	1.75	0.78	3.73

The maximum, minimum, average and standard deviation for ionic components from different samples analyzed show maximum value of Cl^- followed by Na^+ , SO_4^{2-} and Ca^{2+} inferring their origin from biomass burning and traffic pollution.

Table-2

Descriptive statistics of the nonionic present in the different particulate matter analyzed

Metals present in PM	Fe	Ni	Pb	Al	Ag	Si	Ti	V	Mn	Cd	Cr	Cu	Zn
Average in $\mu\text{g}/\text{m}^3$	6.19	0.76	0.16	0.30	0.08	19.62	0.02	0.85	0.05	0.43	0.86	0.26	0.74
St deviation	0.75	0.08	0.09	0.13	0.07	3.36	0.01	0.06	0.01	0.25	0.13	0.04	0.41
Maximum	7.81	0.92	0.37	0.58	0.25	32.33	0.03	0.96	0.07	1.17	1.05	0.35	2.02
Minimum	5.17	0.63	0.04	0.09	0.01	17.58	0.01	0.76	0.03	0.19	0.63	0.20	0.48

The maximum, minimum, average and standard deviation of nonionic components present in different samples of particulate matters shown in table 2 show maximum value for Si followed by Fe, Zn, Cd and Cr suggesting their origin from road suspension and traffic pollution.

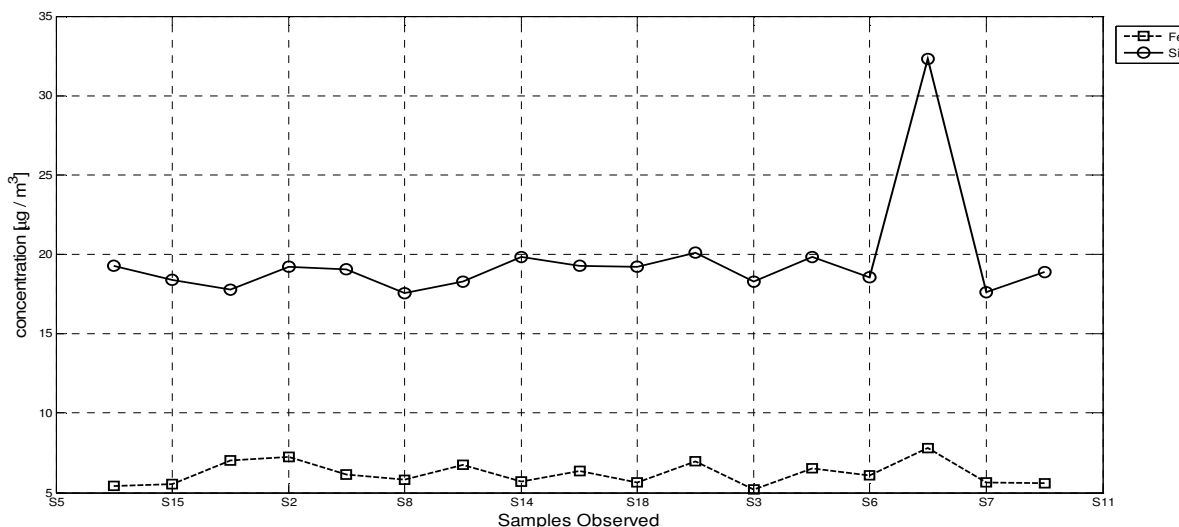


Figure-2(a)
 Variation of Si and Fe in different samples of particulate matter analyzed

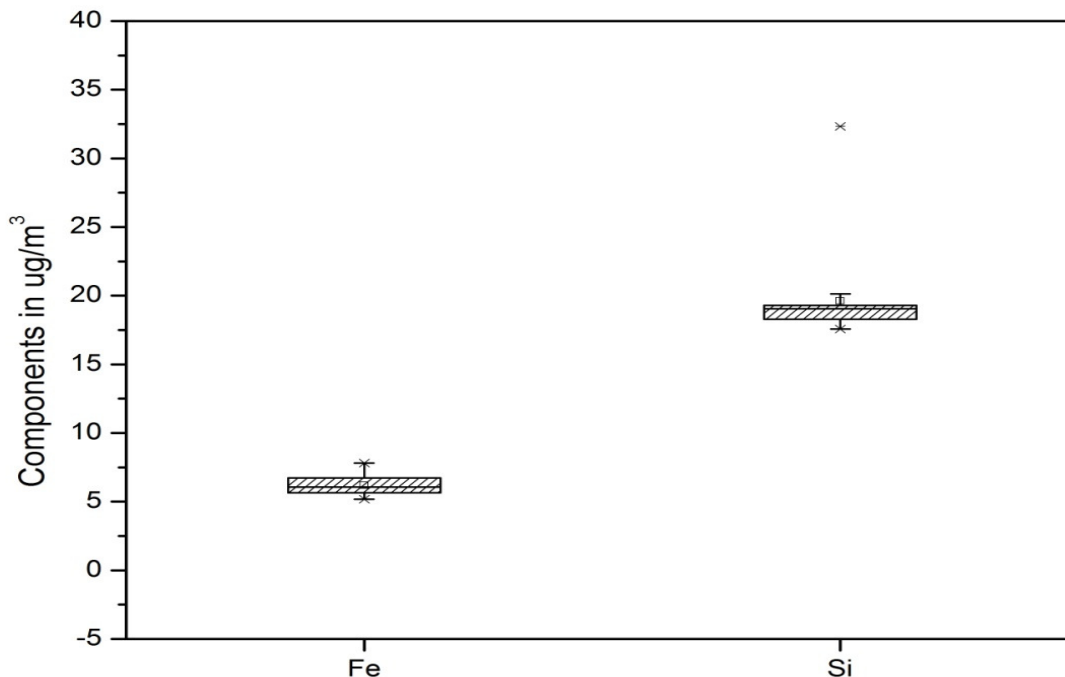


Figure-2(b)
 Distribution Fe and Si in different particulate matters as displayed in box and whisker plot

The concentration variations of nonionic and ionic components present in the particulate matters are presented in figure 2(a, b), 3(a, b), 4(a, b) and 5(a,b). Since, their concentration variation is fluctuating from very low value to high so they are separately represented in different figures on the basis of their concentration as type 1,2,3 for nonionic and type 1,2 for ionic. The highest value of Si was observed in sample S10 of total suspended particulate matter (TSP) and its mass is also comparatively high. Interestingly the concentration of iron is

also highest when the value of Silicon is maximum as shown in figure 2(a). Further it has been found that the correlation between Fe and Si is 0.6, inferring their common source of origin. Further it has been found that the variability in Silicon is more than iron in different samples

Figure 2(b) shows the distribution of Si and Fe in total samples analysed. The maximum value of Si is characterized by highest outlier's value while iron shows homogenous distribution.

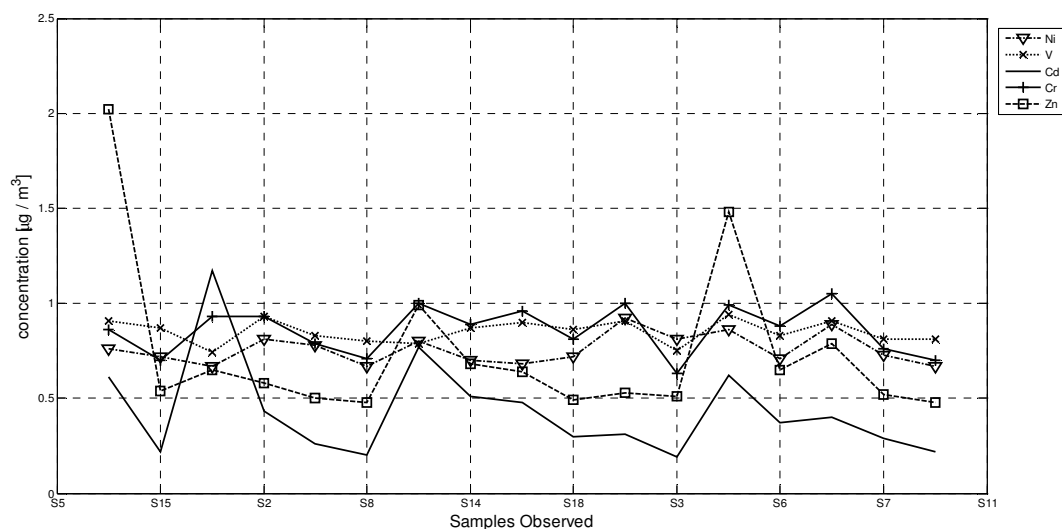


Figure-3(a)
 Ni, V, Cd, Cr, and Zn metal concentration variation in different samples of particulate

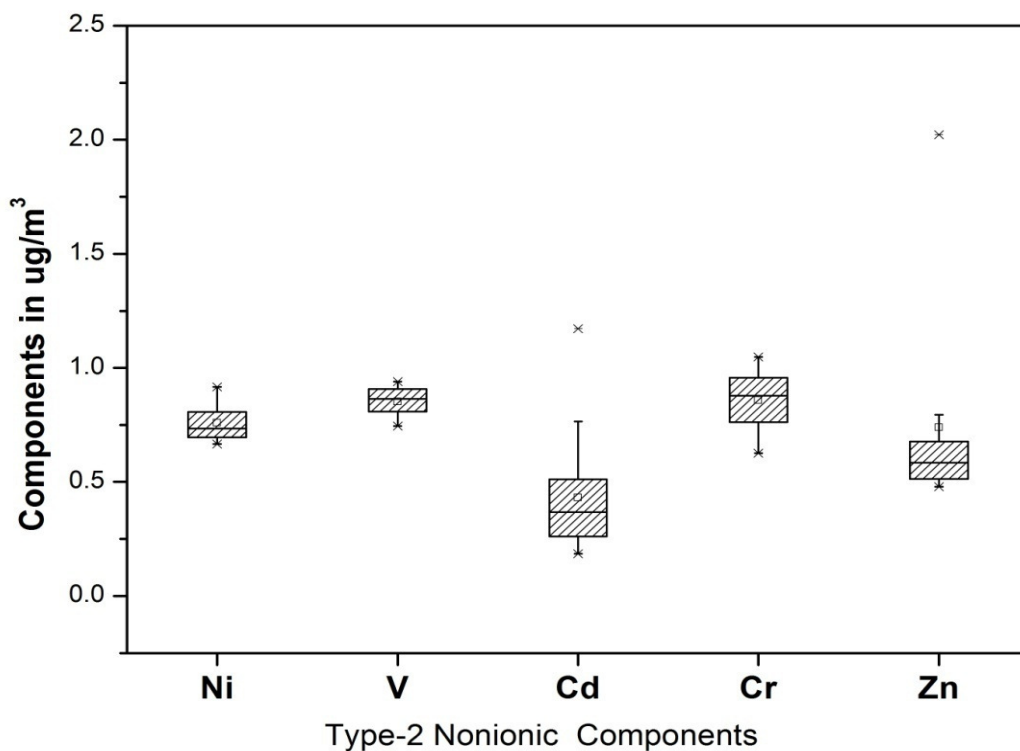


Figure-3(b)
 Distribution of type 2 nonionic components in different particulate matters as displayed in box and whisker plot

Figure 3 (a) represents variation of type 2(moderate concentration) components in each particulate matter sample. Highest value of Zn is monitored in two different samples followed by Cd in one sample. Ni, V and Cr values in all the samples are remaining below $1.0\mu\text{g}/\text{m}^3$. Figure 3(b) box and whisker plot for the same components shows the variation of

each component in total samples. Higher values with homogenous distribution is observed in Cr, V and Ni where there is more fluctuation in the value of Cd, Zn shows homogenous distribution with greatest outlier value followed by Cd.

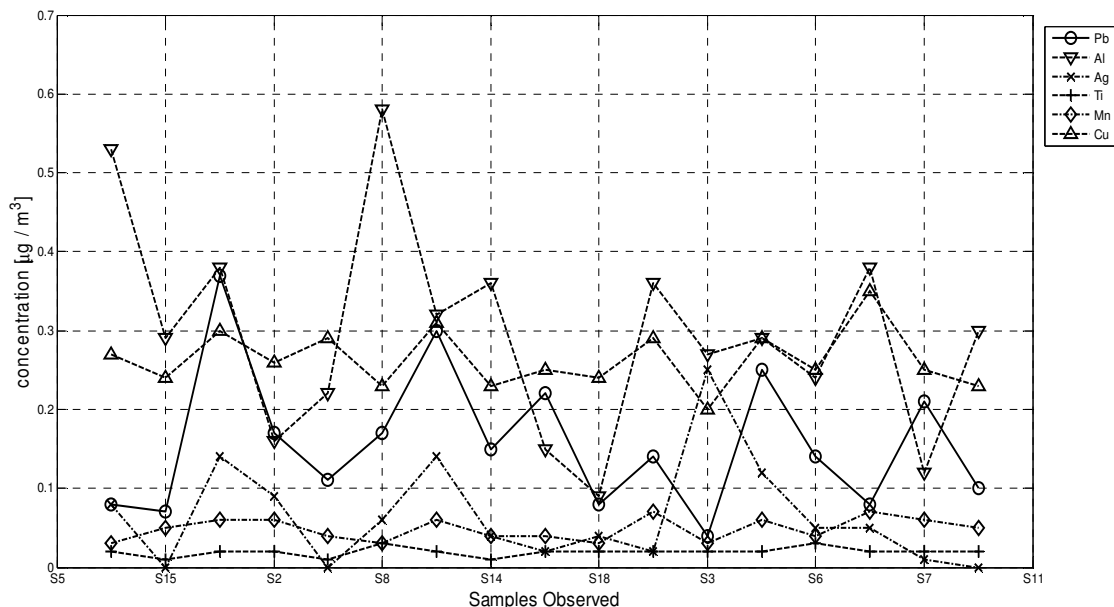


Figure-4(a)

Concentration variations of Pb, Al, Ag, Ti, Mn, and Cu in different samples of particulate matters analyzed

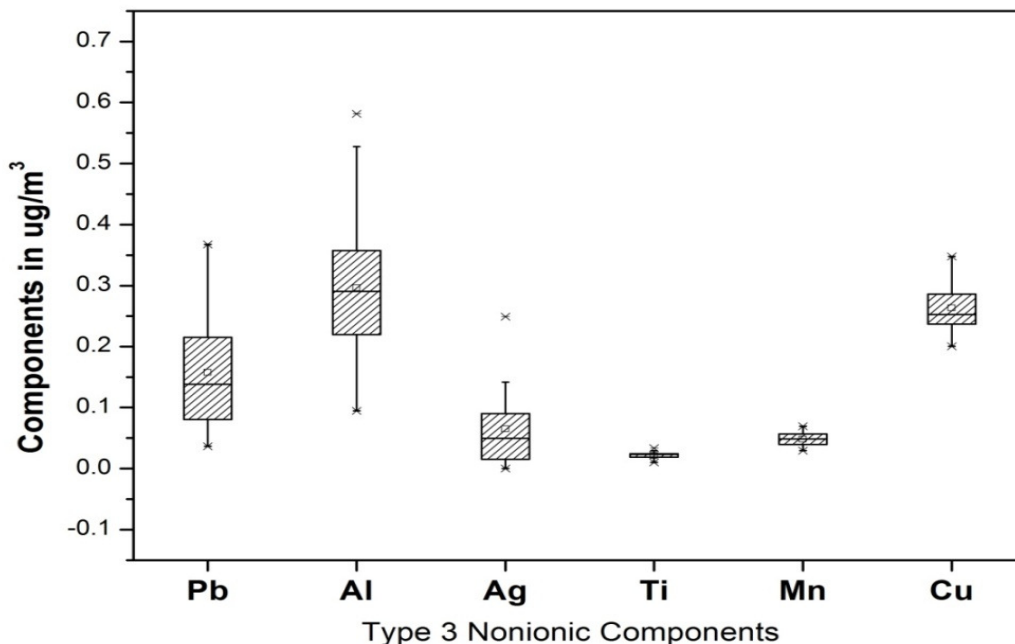


Figure-4 (b)

Distribution of type 3 nonionic components (Pb, Al, Ag, Ti, Mn, and Cu) of different particulate matters are displayed in box and whisker plot

Figures 4(a) show type-3 nonionic components (low concentration category); it shows their variation in different particulate matters. Even the highest value of Al is below $0.6\mu\text{g}/\text{m}^3$ out of rest five components analyzed in this category. Burning of fossil fuel or traffic pollution might be the sources of origin of these analyzed components. Further the box and

whisker plot figure 4(b) shows the individual components variation with mean, median and 25th and 75th percentile in the hatched box. It shows maximum fluctuation in Al followed by Pb, Cu and Ag. Ti with minimum value and homogenous distribution is followed by Mn.

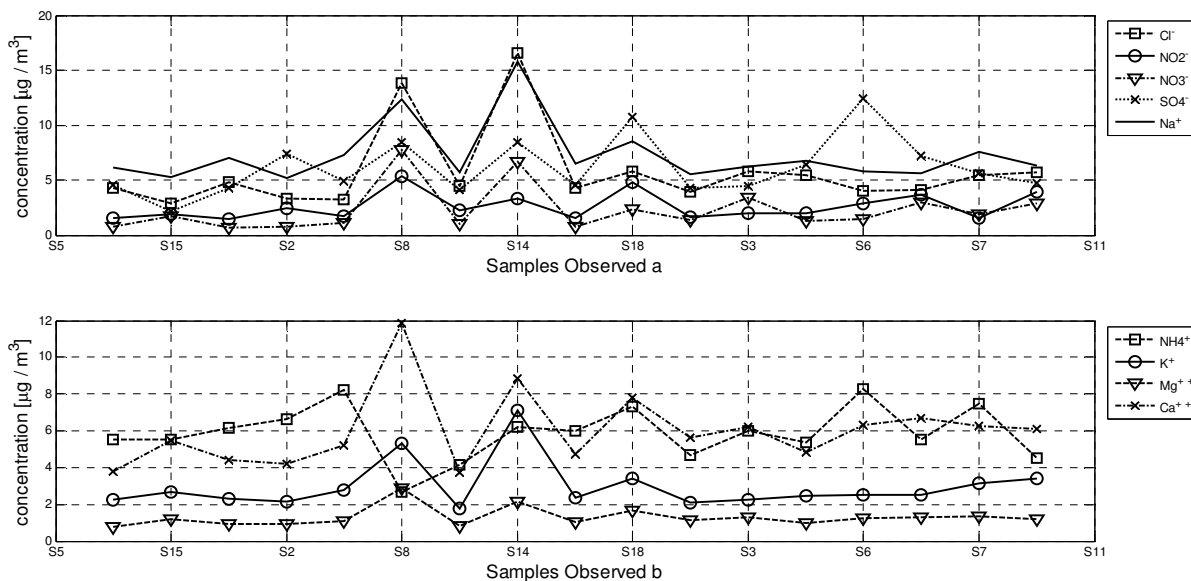


Figure-5(a)

Variation of ionic components Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , Na^+ and NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} in different samples of particulate matters analyzed

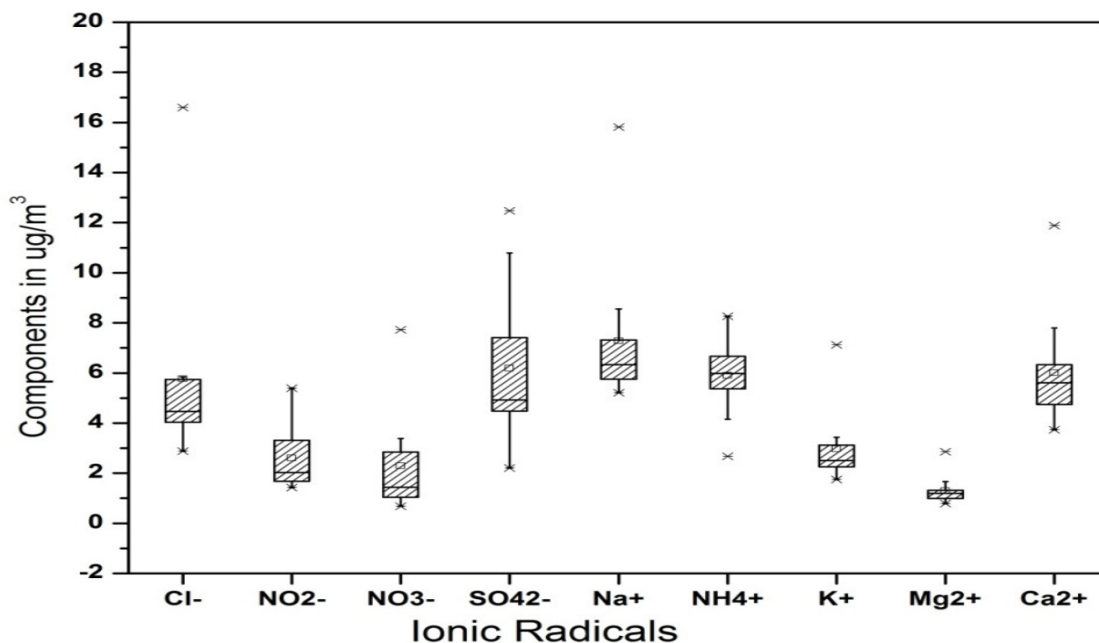


Figure-5(b)

Distribution of ionic radicals present in different particulate matters are displayed in box and whisker plot.

Figure 5(a) shows variation of ionic type-1 and type-2 components in different samples analyzed. The highest concentration peak of Cl^- and Na^+ , NO_3^- and K^+ was distinctly observed in type-1 and type-2 respectively. The distribution of ionic radicals present in different particulate matters in box and whisker plot is represented in figure-5 (b). The square (\square) sign denotes the mean, the horizontal bar represents the median and

the hatched box contains 25th and 75th percentile range of the values in the total samples analyzed. Outliers are shown as (*) asterisk. There is maximum fluctuation in the value of sulphate radical than the rest but chloride radical shows maximum outlier value followed by sodium ion, sulphate ion, calcium ion, nitrate ion and potassium ion.

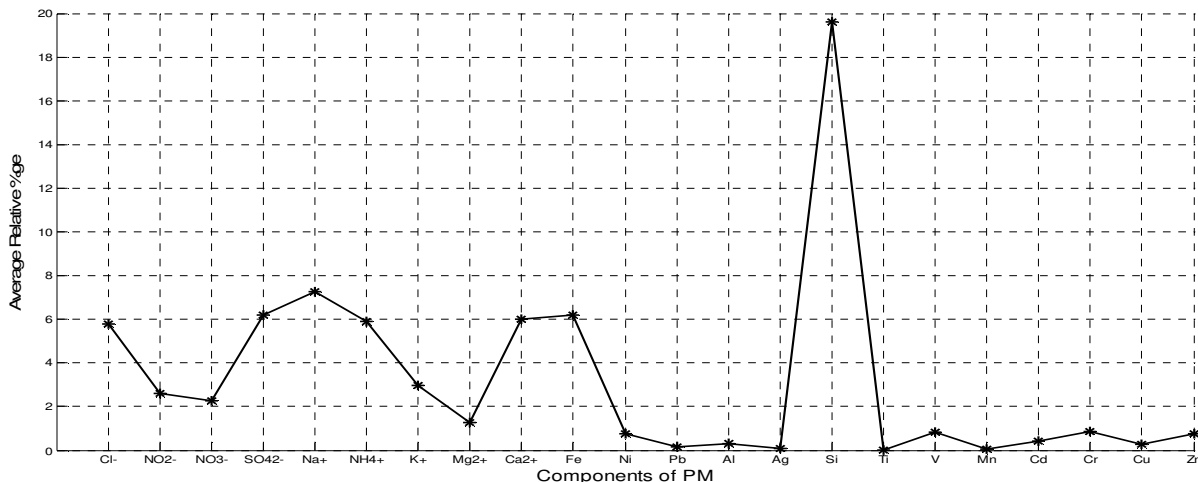


Figure-6

Contribution of average relative percentage of different components present in the particulate matters analyzed

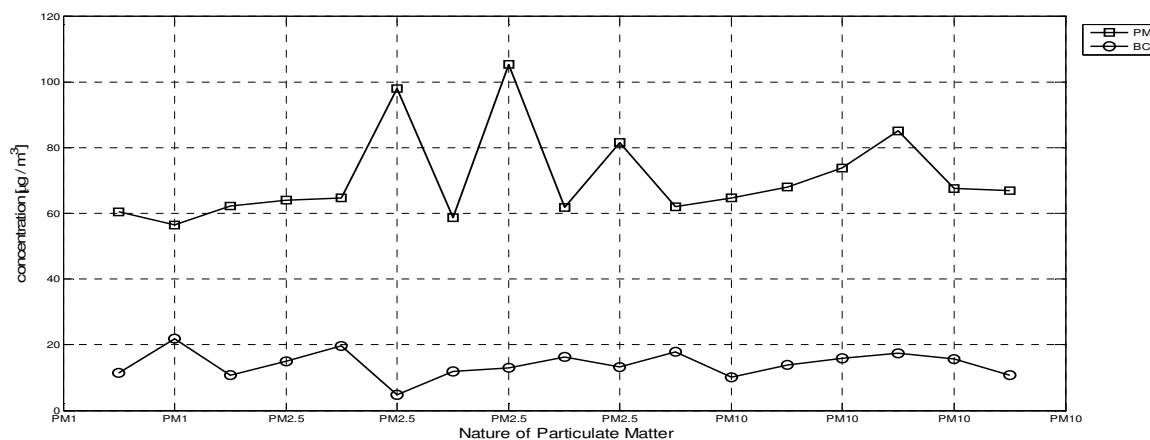


Figure-7

Comparison of concentration variation of black carbon with different samples of particulate matters observed

Contribution of average relative percentage of different components present in the particulate matters is shown in figure 6. Silicon contributes the highest average relative percentage followed by Na⁺, Fe, NH₄⁺, SO₄²⁻, Ca²⁺, Cl⁻ and K⁺. This result suggests that the components present in the particulate matters are derived from road suspension, vehicular emission and domestic activities.

Figure 7 shows the variation of particulate matters and BC for the same duration. Particulate matters of different aerodynamic diameter in the observed period vary from 105.16 to 56.47 µg/m³. This highest value was for PM₁₀ and lowest for PM₁. Black carbon for the same duration varies from 21.8 -4.7 µg/m³. BC and particulate matters are not distinctly correlated in the present analysis.

Conclusions

The chemical analysis of 24-hour samples showed nearly same components in all the analyzed samples except F⁻ only in four

samples and Ag missing in three samples. There is no any relation among these missing components and nature of particulate matters analyzed. The result obtained from the analysis reflects that there is maximum variation in the concentration of almost all the nonionic and ionic components. Moreover the variation is not dependent on the nature and aerodynamic diameter of particulate matters.

Out of 13 nonionic and 9 ionic components analyzed, the components which are the major contributor of the air borne particulate matter of Kathmandu Valley are Si, Na⁺, Fe, NH₄⁺, SO₄²⁻, Ca²⁺ and Cl⁻ while the remaining are the minor one. Nature and type of components analyzed infers that their origin is road suspension, biomass burning and traffic pollution.

Comparisons of 24-hour black carbon with the same duration particulate matters indicate the variation by percentage from 4-38%. Trace metals present in the particulate matters of the valley are toxic so, they may affect human health in different degree on the basis of their concentration.

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