

Chemical Characterization of Atmospheric Particulate Matter for K, Cu, Ni and Zn Metals Collected from Agricultural, Semi-Urban and Commercial Locations in NW India

Nirankar Singh^{1*}, Susheel Mittal², Amit Awasthi³, Ravinder Agarwal⁴ and Prabhat K Gupta⁵¹Department of Chemistry, Maharishi Markandeshwar University, Ambala, Haryana, India²School of Chemistry and Biochemistry, Thapar University, Patiala, Punjab, India³Department of Physics, University of Petroleum and Energy Studies, Dehradun, Uttarakhand, India⁴Department of Electrical and Instrumentation Engineering, Thapar University, Patiala, Punjab, India⁵National Physical Laboratory, New Delhi, India

Abstract

Atmospheric particulate samples (comprising ≤ 100 micron size particles) were collected from different locations in Patiala, India during 2006-2007 covering rural, agricultural, urban, semi-urban, residential and commercial areas. These samples were analysed to measure the concentration of potassium, copper, nickel and zinc metals by using atomic absorption spectrophotometer and flame photometer. Average monthly concentration of particulate matter varied between $100 \pm 30 \mu\text{g m}^{-3}$ - $593 \pm 181 \mu\text{g m}^{-3}$ during the study period with higher levels in the month of April-May during summers and October-November. Around 80% samples were loaded with $\text{SPM} > 200 \mu\text{g m}^{-3}$. Concentration of Cu, Ni and Zn varied between $0.05 \mu\text{g m}^{-3}$ - $1.45 \mu\text{g m}^{-3}$ while K concentration levels varied between $4.5 \mu\text{g m}^{-3}$ - $20.2 \mu\text{g m}^{-3}$ with 60% samples having concentration $> 10 \mu\text{g m}^{-3}$. Monthly averaged SPM concentration levels were compared with the levels of selected metals. Results indicated significant spatial variation in the ambient air levels of SPM, Cu, Ni, Zn and K.

Keywords: Metal pollution; Particulate matter; Crop residue burning; Air quality

Introduction

The urban as well as rural air quality is degrading globally due to upward trends in power consumption, industrialization and vehicle use [1]. Crop residue burning (CRB) has also been identified as a dominating contributor of atmospheric particulate and gaseous pollution in many developing and developed countries [2-4]. Study conducted by [2] has shown that major contributors to the ambient air pollution of urban atmosphere are vehicle exhaust (26%), soil dust (13%) and field burning (4%) whereas Begum et al. in has reported that biomass burning contribute 50% towards the atmospheric particulate pollution [5]. Particulate matter has been linked with human morbidity and mortality and weakening of environmental properties [6-8]. It has been observed that toxic metals remain associated with fine particulates, which remains in ambient air environment for longer duration under the prevailing meteorological conditions [9-11]. A study conducted by Shah et al. for seasonal variations of SPM and selected metals (Na, K, Zn, Cu, Pb, Sb, Sr, Co and Cd) showed high levels during winters and low during summer months [12]. The levels of Ca, Fe, Mg and Mn were recorded with highest concentration during the spring months. These metals transport further from one place to other due to the influence of wind and contaminate other pristine environments [13-17].

Long exposure to heavy metals has adverse effects on the human health and biodiversity [18]. Copper smelters have been reported as the main source of copper emissions in the ambient air in industrial areas but recent studies have indicated that brake wear emissions may also be responsible for copper emissions to the extent of 50-75% of the total copper emissions to the ambient air for most of Western Europe regions [19]. Some studies have also reported particle abrasion from wheels of rail and railway tracks as a source of metal pollution in ambient air [20]. Various studies in India has revealed the presence of Cu in particulate samples collected from different cities [15,16,21].

High levels of zinc in the ambient air have been associated with the increase in hospital admissions for asthma on the following day among children living in an urban area. Pulmonary toxicity from atmospheric dust samples has also been attributed to zinc and copper [4,22,23].

Although, Cu is an essential nutrient for plants and animals in small amounts but high levels can cause gastric problems, vomiting and liver or kidney damage depending on the duration of exposure. Globally, Cu takes the fourth position after Pb, Zn, and Ni in terms of atmospheric emissions from anthropogenic sources [24]. The accurate determination of chemical constituents of particulate matter is very important to understand the sources of its origin and human health effects. The revision of long term consequences of SPM on the environment needs a profound knowledge of particulate concentration, its chemical composition and distribution in the ambient atmosphere. In last many years, concern on airborne particles led to a number of studies on the characterization of SPM with reference to industrial influences. But the data on the metal chemistry of ambient air in absence of large scale industrial units is very scarce.

We have already studied the influence of crop residue burning practices on the air quality of Patiala with respect to suspended particulate matter (SPM), SO_2 and NO_2 in addition to the effect of wind speed and wind direction on the pollutant concentration [25]. The type and amount of emissions changes every year due to changes in the nation's economy, technology, land use pattern, industrial and vehicular activities. Pollution regulations and emission controls also affect the regional air quality. The present study covers the monthly and seasonal variation in the ambient levels of particulate matter and associated metals at four different locations of Patiala, India. It also covers the impact of crop residue burning practices on the air quality at longer distances. The long-term trends and short-term fluctuations in the levels

***Corresponding author:** Dr. Nirankar Singh, Associate Professor, Department of Chemistry, Maharishi Markandeshwar University, Ambala, Haryana, India, Tel: +918950898140; E-mail: nirankarsingh11@gmail.com

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of K, Cu, Ni, Zn and SPM in absence of major industrial facilities in and around Patiala city have been presented here.

Study design and characteristics of sampling sites

Episodic crop residue burning events during April-May and October-November are very usual in and around Patiala. There was no large-scale industry near the vicinity of the city. Rice and wheat crop is harvested during October-November and April-May and the left over residue is burnt in the fields after harvesting. The particulate samples collected during 2006 and 2007 were analysed gravimetrically and chemically for the levels of total suspended particulate matter and selected metals viz. K, Cu, Ni and Zn.

Patiala is located in the south-eastern part of Indian Punjab (latitude between 29°49' and 30°47' N, longitude between 75°58' and 76°54' E). The area around Patiala city is predominantly agricultural (rural) where farmers mainly follow rice-wheat cropping system (Figure 1). It covers a combined cropping area of more than 86% of the total cultivated land. As a result, a large amount of residue is produced in the fields during harvesting season. Farmers usually burn this crop residue after harvesting. During summers, maximum temperature was recorded as $43 \pm 2^\circ\text{C}$ while in winters minimum temperature was recorded as $4 \pm 2^\circ\text{C}$. The annual average rainfall recorded was 650 ± 30 mm. Wind direction of Patiala remained North-West (NW) for most of the time period [25].

The four sampling sites (Table 1) from different locations were carefully selected covering urban, rural (agricultural), semi-urban and commercial areas taking natural wind direction and land use patterns into consideration. Accessibility of logistics, security of sampling instruments and electricity supply during air sampling was also taken

into consideration. All the sampling sites were located in downwind direction within a radius of 10-15 kms. The Baradari Garden was considered as the centre point of the city and distance of the various sampling sites was measured.

A high volume sampler (HVS) was placed on the rooftops of the buildings at each monitoring site to collect samples simultaneously from different locations. The site-1 (PUS), considered as semi-urban site, was about 500 meters away from a very busy state highway (Patiala-Ambala) and close to the agricultural fields (about 1 Km) on its northern side. The Site-2 was located in a village known as Sidhuwal, 7 km away from Patiala city in the North-West (NW) direction. It was completely a rural area around which lots of agricultural fields were present. There was no industry in and around this village. The sampler was placed at the Govt Elementary School in the village. There was a pond in one side of the school while all other sides were covered with agricultural fields. Site -3, considered as commercial area site, was located in the SE direction of the Patiala city with dense population and high vehicular activities. It was a commercial area with 3-4 small units of cotton seed oil mills. There was also a solid waste dumping site in this area spreading over in 0.25 acres of land. It releases foul smell and the intoxicants mix with groundwater and ambient air. The HVS was placed on the second floor of a Secondary School about 8 meters above the ground level. The site was located on the South-East (SE) of Patiala city with large number of shops. The fourth site was located in a Military area approximately 7 kilometres away from the city. The high volume sampler was installed on the rooftop of a central government school building (Kendriya Vidyalaya-3) in the military area. This sampling site was surrounded by a few agricultural fields as most of the land was kept vacant for military trainings. There was no industry in and around its vicinity of 5-10 kilometres.

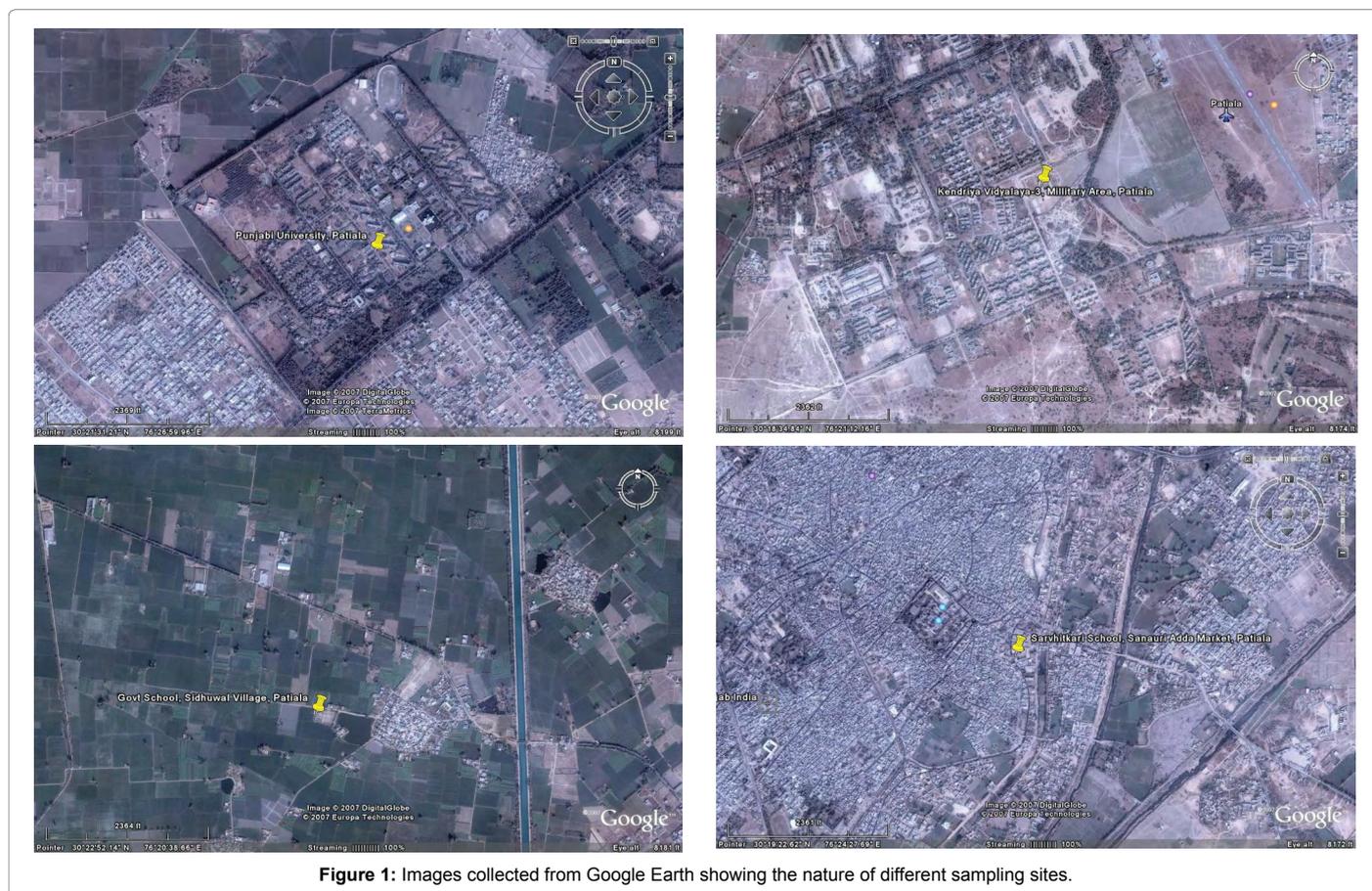


Figure 1: Images collected from Google Earth showing the nature of different sampling sites.

Site No.	Site Name (Abbreviation)	Land use Pattern	Grid Reference	Direction and Distance from the centre of the city	Direction and Distance from the rural area site
1	Punjabi University Site (PUS)	Semi-urban site	Latitude- 30°21'28.10" N Longitude- 76°27'02.57" E	NE, 7 Km	≈15 Kms
2	Sidhuwal Village Site (SVS)	Rural-Agricultural site	Latitude- 30°22'42.14" N Longitude- 76°20'31.52" E	NW, 7 Km	0 Kms
3	Sanauri Adda Site (SAS)	Commercial site	Latitude- 30°19'23.14" N Longitude- 76°24'23.88" E	SE, 2 Km	≈10 Kms
4	Military Area Site (MAS)	Semi-urban site	Latitude- 30°18'41.31" N Longitude- 76°21'12.82" E	SW, 7 Km	≈15 Kms

Table 1: Summary of sampling locations.

Monitoring and collection of SPM samples

The standard procedure for the sampling of particulate matter was followed (IS: 5182, Part XV; Part XIV, 1974). In order to get entire coverage of air particulate matter emanating from crop residue burning and other activities, samplers (APM-430, Envirotech Instruments Pvt. Ltd, India) were installed at four different sites and operated actively during the period 2006-2007 under natural atmospheric conditions at all the selected sites in Patiala. Particulate samples (particles of less than 100 μm size) were collected for 24 hours on pre-weighed Glass Micro Fiber Sheets (GMF/A, 20 \times 25 cm^2 size, Whatmann) at an average air flow rate of 1.5 $\text{m}^3 \text{min}^{-1}$. Mass of particulate matter was estimated gravimetrically for the determination of concentration of aerosols in the ambient air. All the high volume samplers were calibrated and standardized once in six months. Before and after the sampling, each blank and sampled filter sheet was conditioned for 24 hour and then weighed in the weighing chamber with 25°C temperature and 40% humidity. It was done to reduce the weighing errors produced by differences in temperature and humidity between weighing. After 24 hours continuous sampling, each filter sheet was removed from the sampler, folded with the particulate matter inside, placed in a clean polythene bag and carried into the laboratory for conditioning and weighing. Silica gel (Loba Chemie) was used as a conditioning agent in desiccator and electronic balance (Sartorius, BT224S, Germany) was used for pre- and post weighing. After gravimetric estimation, samples were preserved in refrigerator (Samsung) maintained at a temperature of 4°C for further analysis. Weekly sampling was carried out during non crop residue burning period (pre- and post-burning months) while alternate day sampling was carried out consecutively during burning periods.

Quantification of metals in SPM samples

SPM samples were analyzed for the determination of potassium (K), copper (Cu), nickel (Ni) and zinc (Zn) concentration in the ambient air of Patiala. The collected SPM samples were prepared by digesting $\frac{1}{4}$ portion of each filter sheet in a mixture (3:1 ratio) of conc. HNO_3 (AR grade, Sdfine Chem, India) and conc. HCl (35-40%, GR, Lobachemie, India) at 70°C temperature for one and half hour using hot plate digestion system placed in a fuming hood (Method IO-3.2, 1999; NIOSH Method-7300, 1984, US EPA, 1999 b). The extract was filtered through Whatman filter sheets and final volume was made up to 100 mL in a volumetric flask by adding deionised water. Metals concentration was determined in the flask. The potassium (K) concentration was determined by Flame Photometer at an airflow rate of 15 lpm [2,21,26] while Cu, Ni and Zn concentrations were determined by the Atomic Absorption Spectrophotometer (AAS) (Elementa's, AAS4129, ECIL, India) with the analytical conditions as shown in Table 2. Metals concentrations were also measured in solutions of blank filters and were treated in a similar way as the filters loaded with SPM to establish a baseline and the concentration was subtracted from the concentration of true samples (Marrero et al.).

S. No.	Metal	Analytical conditions
1	Copper (Cu)	Lamp current 3.5 mA, Air flow 12 lpm, Acetylene 1.8 lpm, Wavelength 324.8 nm, Slit 0.5 nm, Relative sensitivity 1.
2	Nickel (Ni)	Lamp current 3.5 mA, Air flow 12 lpm, Acetylene 1.8 lpm, Wavelength 232.0 nm, Slit 0.2 nm, Relative sensitivity 1.
3	Zinc (Zn)	Lamp current 5 mA, Air flow 12 lpm, Acetylene 1.8 lpm, Wavelength 213.9 nm, Slit 1.0 nm, Relative sensitivity 1.

Table 2: Analytical conditions of atomic absorption spectrophotometer during the analysis of Cu, Ni and Zn.

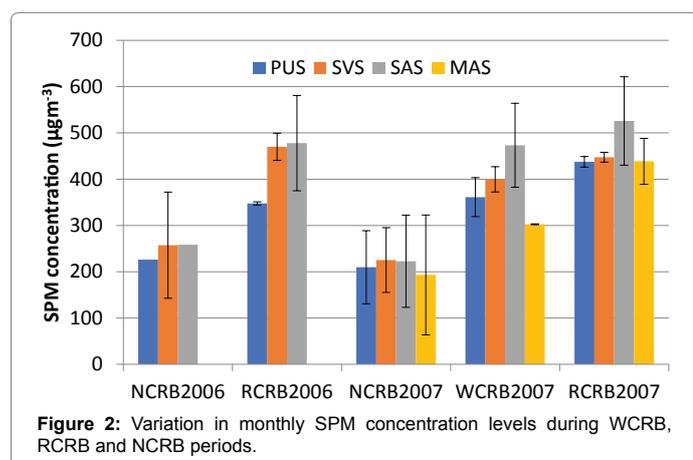
Results and Discussion

The concentration of copper (Cu), Nickel (Ni) and Zinc (Zn) metals varied between 0.05-1.45 $\mu\text{g m}^{-3}$ in the collected particulate samples. The potassium (K) levels varied between 4.5-20.2 $\mu\text{g m}^{-3}$ with 60% samples having concentration greater than 10 $\mu\text{g m}^{-3}$. Monthly SPM levels varied between 117 $\mu\text{g m}^{-3}$ to 488 $\mu\text{g m}^{-3}$. Out of the collected samples, about 80% samples were loaded with the particulate concentration greater than 200 $\mu\text{g m}^{-3}$ (standards set by the CPCB for residential areas, NAAQS India, 1999). In order to find out the emissions of selected metals, the levels of SPM, K, Cu, Ni and Zn obtained during crop residue burning episodes were compared with those obtained during non-burning episodes. The monthly variations in the levels have also been plotted and trends have been discussed in the following paragraphs.

Levels of Suspended Particulate Matter (SPM) in the ambient air

The monthly SPM levels (average of different sites) varied between 117-488 $\mu\text{g m}^{-3}$ during the study period in Patiala. Higher SPM levels were obtained during the months of October and November ($345 \pm 37 \mu\text{g m}^{-3}$ - $491 \pm 173 \mu\text{g m}^{-3}$ in 2006; $429 \pm 166 \mu\text{g m}^{-3}$ - $455 \pm 149 \mu\text{g m}^{-3}$ in 2007) and during April and May ($331 \pm 103 \mu\text{g m}^{-3}$ - $419 \pm 208 \mu\text{g m}^{-3}$ in 2007) at all the sites as compared to the concentration in other months (Tables 1 and 2). This clearly indicates the effect of crop residue burning activities performed by the farmers during these months. Periodic trends of SPM variation as shown in 2D column plots also revealed the higher levels during crop residue burning periods at all the sites (Figure 2). Among the different sampling sites, higher levels of SPM were obtained at commercial site, SAS ($593 \pm 181 \mu\text{g m}^{-3}$ in November 2007). This could be due to the mixed influence of CRB and commercial activities (vehicular and small mills). The overall levels of SPM were high during the burning months and exceeded the maximum permissible limit set by the National Ambient Air Quality Standards (NAAQS), India.

A significant increase in the levels of SPM were observed at agricultural site (SVS) during April-May and October-November as compared to other sampling months due to crop residue burning activities in these months. Though, levels of SPM were higher during both the burning periods but levels were comparatively higher during October-November. During April-May, wheat crop is harvested and during thrashing (a process of grain segregation from stalk) the other plant material is converted into fodder which is a popular cattle feed



in North India. Most of the farmers use wheat crop residue in the form of fodder for their cattle and due to this reason lesser amount of crop residue is burnt in fields during clearing process. In the case of rice crop residue, most of the plant material is burnt by farmers in the field only due to lesser utilization as cattle feed.

Levels of potassium (K) in the ambient air

The balanced amount of mineral fertilizers plays an important role in improving crop yields. During cultivation of wheat and rice crops, nitrogen (N), phosphorus (P) and potassium (K) are supplemented in the soil in the form of chemical fertilizers (N-P-K) to increase the crop yield [27-31]. These elements are up taken by the plants from the soil and remain present in the plant material after harvesting of crops. Potassium (K) is one of the important elements in particulate matter emanated from open burning of crop residues [32]. Potassium (m.p. 63.38 °C) is released into the atmosphere at higher temperature when these crop residues are burnt [5,6]. Tracking of potassium as a marker element is the most convenient and reliable method to estimate the contribution of agricultural residue burnings [15,26]. In this study, increase in the levels of K concentration at different monitoring sites during crop residue burning months clearly indicates that residue burning was the dominating source of particulate pollution in this region. Monthly data is shown in Tables 3 and 4 and periodic variations in the concentrations of K levels are presented in Figure 3.

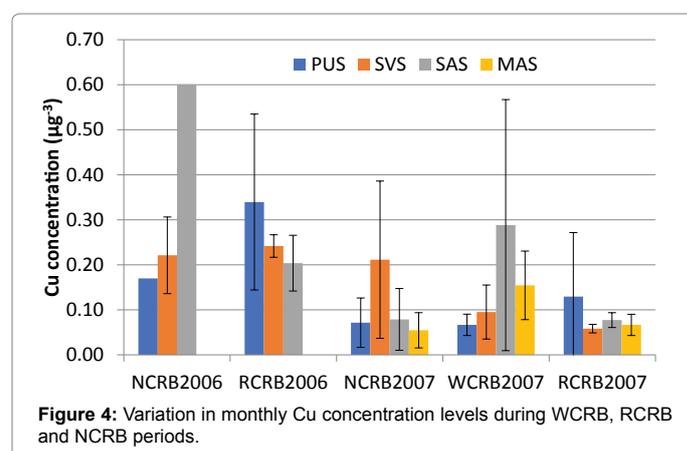
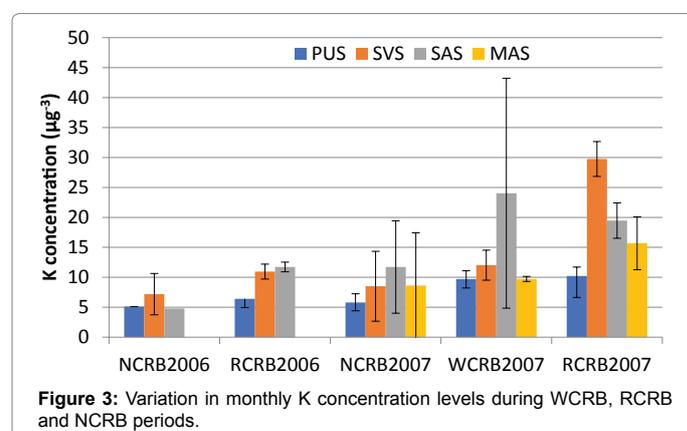
Overall monthly average K concentration varied between 0.53-38.0 µgm⁻³ during the sampling period at all the sites. The trend of periodic variation in K levels showed a clear increase during rice crop residue burning (RCRB) months (October-November) and wheat crop residue burning (WCRB) months (April-May). Around 40% increase was observed during crop residue burning (CRB) months as compared to the non-crop residue burning (NCRB) months. Though, K concentrations during burning months were higher at all the sampling sites but a smooth trend was obtained at rural-agricultural site (SVS). Increment in the levels was observed higher in 2007 during October-November as compared to the levels in corresponding months in 2006, indicating a higher production of rice crop residue as well as its burning. The highest K concentration (37.59 µgm⁻³, April 2007) was obtained at commercial site (SAS, Table 4) followed by rural-agricultural area site (SVS) in (31.81 µgm⁻³, October 2007 and 27.69 µgm⁻³, November 2007).

Levels of Cu, Ni, and Zn in the ambient air of Patiala

In the present study, the overall monthly average concentrations of the three heavy metals Cu, Ni and Zn ranged between 0.04-1.84 µgm⁻³ without any specific order or trend of variation. However, the levels of SPM and K were found associated with a similar trend of variation

($r=0.56$). Though, ambient levels of copper varied between 0.04 ± 0.01 µgm⁻³ and 0.49 ± 0.19 µgm⁻³ (Figure 4) but an increase was observed during September 2006 to April 2007. Peak concentration was obtained in the month of December 2006 while the lowest concentration was obtained in the month of December 2007. No significant association was found in the monthly or periodic variation of copper with crop residue burning activities. The individual variability in airborne copper concentrations could be examined through either respective ranges or standard deviation (SD) values listed in Tables 3 and 4. At agricultural area site (SVS), peak Cu concentrations were obtained in January and February 2007, whereas, lower Cu levels were obtained in April, November and December in 2007. In spite of the higher levels of SPM in December 2007, a gradual increase in the Cu concentration was observed from September 2006 to February 2007 (Table 3). The 2D column plot indicates that there was no association in Cu levels and crop residue burning. Railway tracks and vehicular brake abrasion might be a potential source of copper in the ambient air of Patiala as there is no major industrial unit in the vicinity of the city. Copper fibres are generally used in brake linings to provide mechanical strength and structure to the linings.

The monthly concentration of nickel varied between 0.13 ± 0.10 µgm⁻³ and 2.07 ± 1.20 µgm⁻³ (Tables 3 and 4) with maximum concentration in November 2006 (Figure 5). Levels were quiet higher than the copper levels. Similarly, zinc concentration varied between 0.89 µgm⁻³ and 1.84 µgm⁻³. The levels increased in September 2006 till April 2007 and after that remained almost in a range of 1 µgm⁻³ till the end of the study period. No significant increase was observed in Zn concentration in association with CRB activities. However, the background concentration level of Zn seems to decrease in 2007 as compared to that of 2006 (Figure 6).



Year	Period	Month	Concentration levels in $\mu\text{g m}^{-3}$									
			PUS					SVS				
			PM	K	Cu	Ni	Zn	SPM	K	Cu	Ni	Zn
2006	NCRB	Sep	--	--	--	--	--	339 ± 4	4.75 ± 0.29	0.16 ± 0.03	0.32 ± 0.06	0.98 ± 0.34
	RCRB	Oct	345 ± 37	7.44 ± 5.82	0.48 ± 0.02	0.43 ± 0.26	1.38 ± 0.38	491 ± 173	10.08 ± 3.17	0.22 ± 0.06	0.84 ± 0.38	1.68 ± 0.44
		Nov	350 ± 115	5.38 ± 1.20	0.20 ± 0.01	1.09 ± 0.54	1.83 ± 0.21	449 ± 132	11.84 ± 2.80	0.26 ± 0.16	0.57 ± 0.24	1.52 ± 0.09
	NCRB	Dec	226 ± 16	5.10 ± 1.60	0.17 ± 0.01	0.99 ± 0.48	1.99 ± 0.55	176 ± 30	9.62 ± 7.27	0.28 ± 0.27	1.97 ± 0.04	1.22 ± 0.83
2007	NCRB	Jan	244 ± 68	6.58 ± 0.42	0.19 ± 0.10	0.75 ± 0.62	1.59 ± 0.04	244 ± 68	6.60 ± 2.50	0.43 ± 0.18	1.09 ± 0.73	1.46 ± 0.56
		Feb	249 ± 123	5.49 ± 0.37	0.12 ± 0.06	0.39 ± 0.19	1.72 ± 0.40	283 ± 103	6.87 ± 1.40	0.47 ± 0.08	1.97 ± 0.47	1.18 ± 0.39
		Mar	252 ± 109	7.91 ± 7.19	0.06 ± 0.04	0.60 ± 0.31	1.05 ± 0.63	268 ± 96	7.25 ± 2.50	0.34 ± 0.21	1.50 ± 1.20	0.99 ± 0.12
	WCRB	Apr	391 ± 87	10.77 ± 8.79	0.05 ± 0.01	0.54 ± 0.30	0.91 ± 0.35	419 ± 208	13.80 ± 4.63	0.05 ± 0.03	1.25 ± 0.08	1.22 ± 0.23
		May	331 ± 103	8.65 ± 4.15	0.08 ± 0.03	0.40 ± 0.11	0.82 ± 0.09	380 ± 65	10.24 ± 7.26	0.14 ± 0.11	0.36 ± 0.32	1.03 ± 0.54
	NCRB	Jun	277 ± 253	5.64 ± 3.61	0.04 ± 0.02	0.50 ± 0.26	0.77 ± 0.11	296 ± 278	5.19 ± 3.23	0.08 ± 0.06	0.49 ± 0.36	0.97 ± 0.04
		Jul	130 ± 28	3.32 ± 0.58	0.04 ± 0.01	0.60 ± 0.05	0.82 ± 0.06	267 ± 139	3.42 ± 1.33	0.12 ± 0.01	0.86 ± 0.14	1.14 ± 0.87
		Aug	122 ± 22	6.22 ± 6.65	0.04 ± 0.03	0.72 ± 0.16	0.84 ± 0.06	111 ± 22	7.39 ± 1.75	0.08 ± 0.02	0.60 ± 0.09	0.56 ± 0.13
		Sep	100 ± 30	4.64 ± 0.10	0.04 ± 0.01	0.18 ± 0.08	0.75 ± 0.05	133 ± 48	8.96 ± 5.78	0.14 ± 0.03	0.55 ± 0.13	1.03 ± 0.76
	RCRB	Oct	446 ± 94	7.68 ± 2.10	0.03 ± 0.01	0.59 ± 0.31	0.61 ± 0.51	440 ± 116	31.81 ± 14.19	0.07 ± 0.04	0.65 ± 0.57	1.50 ± 0.67
		Nov	429 ± 166	12.74 ± 4.82	0.23 ± 0.09	0.82 ± 0.61	0.82 ± 0.28	455 ± 149	27.69 ± 4.53	0.05 ± 0.01	1.09 ± 1.05	1.27 ± 0.35
	NCRB	Dec	303 ± 12	6.50 ± 2.12	0.04 ± 0.01	0.28 ± 0.04	0.58 ± 0.21	201 ± 103	22.37 ± 7.94	0.04 ± 0.01	0.49 ± 0.32	1.02 ± 0.33

Table 3: Monthly concentration of SPM and metals at PUS and SVS. Note: (--) Data not available, Bold indicates concentration during crop residue burning (WCRB, RCRB) periods.

Year	Period	Month	Concentration levels in $\mu\text{g m}^{-3}$									
			SAS					MAS				
			SPM	K	Cu	Ni	Zn	SPM	K	Cu	Ni	Zn
2006	RCRB	Oct	551 ± 3	12.30 ± 1.71	0.25 ± 0.14	0.71 ± 0.61	1.88 ± 0.45	--	--	--	--	--
		Nov	405 ± 215	11.16 ± 6.57	0.16 ± 0.09	1.38 ± 0.97	2.16 ± 0.16	--	--	--	--	--
	NCRB	Dec	258 ± 50	4.79 ± 1.50	0.60 ± 0.56	1.38 ± 0.86	2.05 ± 0.99	--	--	--	--	--
2007	NCRB	Jan	158 ± 32	1.29 ± 0.85	0.05 ± 0.01	0.13 ± 0.10	0.78 ± 0.43	--	--	--	--	--
		Feb	231 ± 10	1.98 ± 0.76	0.72 ± 0.31	0.89 ± 0.29	0.53 ± 0.21	123 ± 46	1.14 ± 0.15	0.06 ± 0.01	0.66 ± 0.34	0.98 ± 0.32
		Mar	244 ± 4	2.13 ± 1.21	0.23 ± 0.10	0.74 ± 0.36	0.59 ± 0.34	147 ± 70	0.53 ± 0.31	0.03 ± 0.02	1.35 ± 1.01	1.13 ± 0.70
	WCRB	Apr	538 ± 115	37.59 ± 12.04	0.49 ± 0.19	0.65 ± 0.43	0.55 ± 0.18	302 ± 137	10.02 ± 6.62	0.21 ± 0.06	0.57 ± 0.33	1.20 ± 0.98
		May	409 ± 147	10.47 ± 2.32	0.09 ± 0.06	0.63 ± 0.63	1.04 ± 0.07	303 ± 70	9.42 ± 4.14	0.10 ± 0.07	0.10 ± 0.05	0.83 ± 0.24
	NCRB	Jun	398 ± 274	9.93 ± 1.47	0.03 ± 0.01	0.68 ± 0.68	0.99 ± 0.16	424 ± 344	13.72 ± 9.62	0.12 ± 0.02	0.59 ± 0.08	1.02 ± 0.06
		July	176 ± 56	9.84 ± 3.20	0.04 ± 0.02	0.14 ± 0.09	1.02 ± 0.09	--	--	--	--	--
		Aug	209 ± 96	15.36 ± 1.50	0.20 ± 0.10	2.07 ± 1.20	1.58 ± 1.17	137 ± 14	6.51 ± 0.33	0.02 ± 0.01	0.71 ± 0.11	1.08 ± 0.04
		Sep	--	--	--	--	--	126 ± 37	4.89 ± 1.56	0.04 ± 0.02	0.79 ± 0.12	1.12 ± 0.67
	RCRB	Oct	458 ± 96	17.38 ± 5.98	0.09 ± 0.04	1.00 ± 0.56	0.90 ± 0.33	404 ± 61	12.57 ± 5.29	0.08 ± 0.03	0.69 ± 0.35	1.15 ± 0.12
		Nov	593 ± 181	21.55 ± 11.86	0.07 ± 0.02	1.01 ± 0.42	1.05 ± 0.13	474 ± 194	18.80 ± 2.77	0.05 ± 0.01	0.46 ± 0.25	1.03 ± 0.32
	NCRB	Dec	173 ± 26	22.18 ± 5.30	0.07 ± 0.02	1.46 ± 0.76	1.07 ± 0.89	135 ± 50	21.20 ± 2.57	0.04 ± 0.00	0.02 ± 0.01	0.99 ± 0.10

Table 4: Monthly concentration of SPM and metals at SAS and MAS. Note: (--) Data not available, Bold indicates concentration during crop residue burning (WCRB, RCRB) periods.

A significant association were obtained between the levels of K and SPM. Significant spatial variation was obtained in the ambient air levels of SPM, K, Cu, Ni and Zn. Similar to the trend of SPM levels, the levels of K were higher during April-May and October-November. During crop residue burning (CRB) episodes, higher levels of SPM and K was

observed at all the sites. However, concentration levels of Cu, Ni, and Zn were not associated with the levels of SPM and K. Concentration levels of K and SPM were inclined with the residue burning activities during wheat and rice harvesting months indicating the direct influence of crop residue burnings (Figure 7).

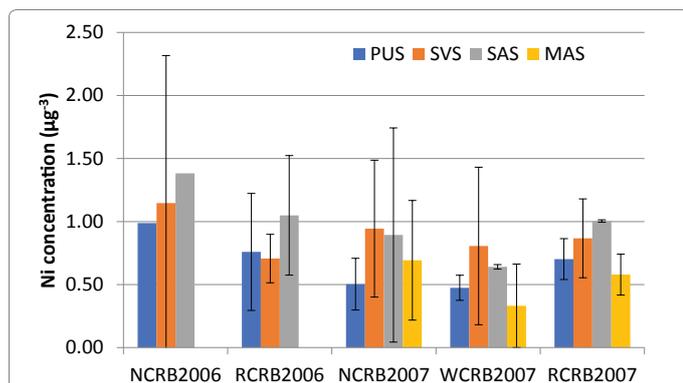


Figure 5: Variation in monthly average concentration levels of Ni during CRB and NCRB months.

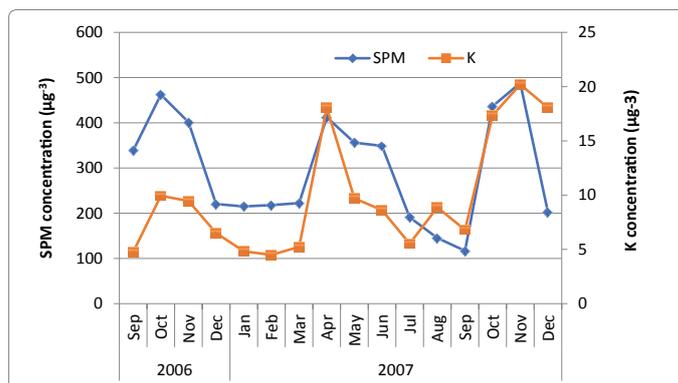


Figure 7: Association of K and SPM concentration levels during the study period.

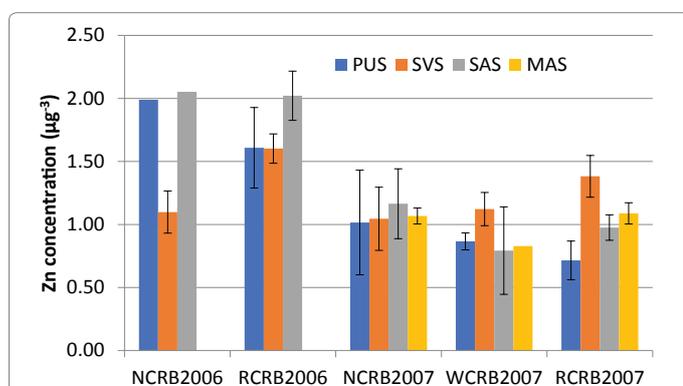


Figure 6: Variation in monthly average concentration levels of Zn during CRB and NCRB months.

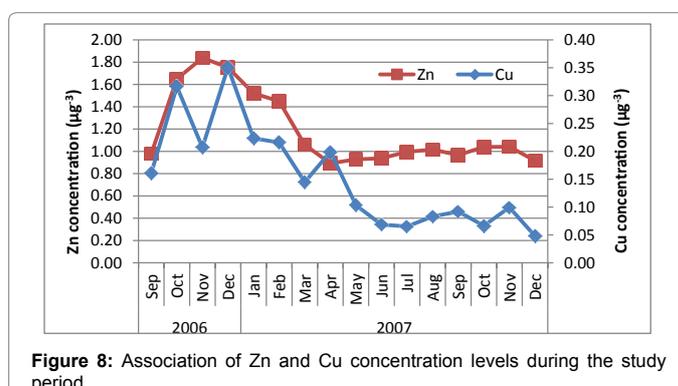


Figure 8: Association of Zn and Cu concentration levels during the study period.

Inter-relationships among K, Cu, Ni, Zn and SPM

The levels of K, Cu, Ni, Zn and SPM were analyzed statistically using excel worksheet to check any relationship among them. A positive correlation was obtained between the levels of Cu and Zn from regression analysis ($R=0.82$) indicating a similar trend of variation during different months (Figure 8). A positive association was also obtained between SPM and K ($R=0.56$), Ni and Zn ($r=0.56$), and Cu and Ni ($R=0.50$). There was no relationship in other combinations of arrays. The positive relationship indicates that there may be a similar source of Cu, Ni and Zn in the ambient air. Levels of these heavy metals were also associated with a similar range of concentration. But the concentration levels of these metals were never associated with the concentration levels of SPM and K. Results indicates that there were some unidentified sources of metal emissions in Patiala as there was no major industrial unit in the vicinity. The possible sources of Cu, Ni and Zn could be abrasion of brake linings, railway tracks and diesel driven vehicles [33,34].

The levels of Ni, Cu and Zn metals were not affected by the crop residue burning practices occurred during April-May and October-November, as there was no increase in the levels during these months. While the levels of SPM and K were associated with each other and affected by the crop residue burning practices. In this study K has been identified as a potential marker of crop residue burning activities. Various researchers have observed high K concentration levels during biomass burning episodes [35].

Conclusions

During this study, significant association was obtained in the

ambient air levels of SPM and K. Variation in SPM and K levels was clearly associated by agricultural activities during harvesting seasons of wheat and rice crops. Heavy metals like Cu, Ni and Zn were associated with the similar range of concentration but no relationship was obtained with CRB episodes. Although, increase in K levels was observed at all the sites but strong association in K levels and CRB was obtained at rural-agricultural area site (SVS) as compared to other monitoring sites. This indicated that CRB was a dominating source at agricultural site as compared to the other sources in the increment of SPM levels. Since, K metal has been identified as a marker of crop residue burning in previous studies in support of this study; crop residue burning was identified as an important source of SPM pollution in and around Patiala city integrated with the contribution of vehicular and railway emissions.

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