Potassium as a Marker in Air Particulate Matter After Crop Residue Burning Events in Patiala, India

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Abstract  Variations in the concentration levels of suspended particulate matter (SPM) and the particulate associated potassium (K) levels were studied in ambient air of Patiala during 2006-2007 at selected urban and rural locations. Samples of SPM were collected and analyzed for the K concentration using flame photometry. The monthly average of SPM levels ranged between 100±30-446±94 µgm-3 at the urban site and 111±22-491±173 µgm-3 at the rural site. An increase in SPM levels was observed during the crop residue burning (CRB) periods at the rural as well as urban area site. At the urban area site, monthly average K concentration varied between 3.3±0.58 µgm-3 to 12.74±4.82 µgm-3 while levels varied between 3.42±1.33 µgm-3 to 31.81±14.19 µgm-3 at the rural site. Peak K concentration (31.81±14.19 µgm-3) was obtained at rural area site during October 2007. The study revealed that the concentration of K and SPM was significantly higher at rural area site as compared to the urban area site during CRB months.

Keywords: Air pollution, Potassium, SPM, crop residue burning (CRB)

1. INTRODUCTION

In the major cities of India having more than one million populations, ambient air pollution levels exceed the permissible limits set by the CPCB, India and health standards set by WHO in many of them. Air pollution has become the fifth leading cause of deaths in India after high blood pressure, indoor air pollution,
tobacco smoking and poor nutrition, with more than six lacs premature deaths occurring due to air pollution associated diseases The Economic Times (2013). Urban air as well as rural air quality is degrading due to upward trends in power consumption, industrialization and vehicle use Shah et al. (2006). Crop residue burning (CRB) has also been identified as a dominating contributor of particulate and gaseous pollution in many developing and developed countries Park et al. (2005) and Mittal et al. (2009). Study conducted by Park and Kim Park et al. (2001), has shown the contribution of vehicle exhaust (26%), soil dust (13%), and field burning (4%) in an urban atmosphere. Study conducted by Begum et al in 2004 (6), has investigated 50% contribution from biomass burning in ambient air particulate matter collected at Rajshahi, Bangladesh. The five cities: Mumbai, Delhi, Kolkata, Ahmedabad, and Kanpur out of ten largest cities in India have severe air pollution problems with annual average levels of suspended particulate matter (SPM) at least three times higher than WHO standards Kandlikar et al. (2000). Particulate matter has been linked with human morbidity and mortality Kappos et al. (2004) and Dockery et al. (1994).

Since 1990, measurement of atmospheric concentration of SPM and toxic metals are being carried by NEERI in 10 major cities of India as a part of National Air Quality Monitoring programme. The profile revealed critical air quality with respect to Respirable Suspended Particulate Matter (RSPM) in industrial locations of Kanpur, Ahmedabad, Delhi and Kolkata and shared high levels of RSPM during 1997 NEERI (1998,2001). It is experienced that the toxic metals are found to be associated with fine dust, which remains in air environment for longer duration under the prevailing meteorological conditions Schroeder et al. (1987) and Bhanarkar et al. (2002). It is further transported from one place to other and contaminates the other pristine environment. It has been found that toxic metals are associated with fine particulate matter present in the ambient air of Indian urban agglomerations Negi et al. (1987) and Gajghate et al. (2005). Lead (Pb) along with other toxic elements has been observed to be present in considerable quantities in the ambient air in Mumbai, India Khandekar et al. (1984) and Chelani et al. (2001).

Burning of rice and wheat crop residues in agricultural fields can be seen easily in Indian states like Punjab, Haryana and Western Uttar Pradesh, in the areas where wheat and rice are major crops. Effect of residue burnings on the levels of particulate and trace gases in Patiala, India has been studied Singh et al (2010) and study revealed high SPM levels during stubble burning episodes.

Balanced amount of mineral fertilizers play 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 to increase the crop yield Gurmani et al. (1996) and Mehdi et al. (2008). Tracking of potassium as a marker element since the cultivation till the burning of crop residue is the most convenient & reliable method Andreae (1983) and Duan et al. (2004). Chloride (Cl-) and potassium (K+) are important ions in particulate matter emanated from open burning of crop residues Li, X., Wang et al. (2007). The present study highlights the levels of SPM and K in the ambient air of Patiala during rice and wheat seasons in 2006-2007 with special reference to CRB practices being performed in and around Patiala city from last many years. Relationship among SPM and K was also analyzed.

2. MATERIALS AND METHODS

2.1. Characteristics of study area and sampling sites

Patiala is a princely city of the state of Punjab, India with no major industry in and around its vicinity. It has head quarters of 15 state government offices including that of Punjab Pollution Control Board (PPCB), and has a railway and a bus terminus. It is located in the southeastern part of the Punjab state of Northern India (29°49’ and 30°47’ North Latitude, 75°58’ and 76°54’ East Longitude). The area around Patiala city is predominantly agricultural (rural) and wheat and rice (paddy) crops are the two major crops of the district with a combined cropping area of more than 86%. Farmers usually burn crop residue after crop harvesting during April–May (wheat crop harvesting period) and October–November (rice crop harvesting period). The climate here is typical of the Punjab plain, i.e., very hot in summer (max. temp. 43±2°C) and very cold in winter (min. temp. 2±2°C). On an average there are 61 rainy days with annual average rainfall of 650±30 mm. The variation in rainfall is appreciable. May is the hottest month and January is the coldest month TERI (2003).

Wind direction of Patiala is North-West (NW) for most of the time period. Two sampling sites Punjabi University Site, PUS (30°21’28.10’’N, 76°27’02.57’’E) and Sidhuwal Village Site, SVS(30°22’42.14’’N, 76°20’31.52’’E) representing semi-urban and rural areas respectively were selected. These sampling sites were located in downwind direction with a distance of 10 km to each other.

2.2. Monitoring and analysis of SPM

To get entire coverage of ambient SPM and metal concentrations emanating from CRB activities and other activities, two High Volume Samplers (HVS, Envirotech, India), were operated actively during the year 2006-2007 at both
rural and urban sites in Patiala Pulikesi et al. (2006). SPM samples were collected twice in a week during harvesting period and weekly during rest of the period on pre-weighed glass micro fiber sheets (GMF/A, 20 ×25 cm² size, Whatmann) with an average air flow rate of 1.5 m³ min⁻¹ for 24 hours Marrero et al. (2005). In order to determine the mass of the collected particles, sampled sheets were reweighed after sampling and subsequent conditioning to remove any moisture. The concentrations of particulate matter in ambient air were then calculated by dividing mass by the total volume of air sampled during sampling period IS: 5182 (1974) and Katz, M (1977).

2.3 Characterization of SPM for K metal

The collected SPM samples were further selected (55 samples from urban area site and 75 samples from rural area site) and prepared for the determination of K concentration in the ambient air. The one fourth part (¼ portion) on each single sample was digested at 70°C temperature in a mixture of concentrated nitric acid (HNO₃) and concentrated hydrochloric acid (HCl) (3:1 ratio) for 90 minutes using hot plate digestion system. The content was filtered through Whatman filter paper No. 42 and the final volume of the filtrate was made up to 100 mL by adding deionized water. This filtrate was used to determine the K metal concentration by Flame Photometer Zhuang et al. (1992) and Sun, et al. (2004). A blank fiber filter sheet was also digested and analyzed by following the similar procedure to establish a baseline concentration of K (0.382 µgm⁻³) in fiber sheets. The baseline concentration was subtracted from the concentration obtained in the true samples.

3. RESULTS AND DISCUSSION

The monitoring of SPM levels (the most important criteria pollutant) was carried out at the selected sites, representing rural and urban sites in Patiala. Sampling sites were selected in the downwind direction to the burning fields to get full exposure of ambient SPM emanating from crop residue burning activities and other activities. At Punjabi University Site (Urban Area), average monthly concentration of SPM varied between 100 µgm⁻³ to 446 µgm⁻³ whereas at Sidhuwal Village Site (Rural Area), the concentration varied between 111 µgm⁻³ to 491 µgm⁻³ during the study period (Figures 1 and 3). A high level concentration of SPM was observed at Sidhuwal Village Site (Rural Site) during the study period as compared to the Punjabi University Site (Urban Site) especially during the months of crop residue burnings.

The high SPM levels were obtained in the samples collected in the month of April, May, October and November at both the sites during this period. Though
high levels were observed during these four months but comparatively higher levels were obtained during October-November at both the monitoring sites (446 µgm⁻³ in October and 429 µgm⁻³ in November during 2007 at PUS (Table 1) due to the reason that the crop residue left in the fields during rice harvesting months is much larger than the residue left after wheat harvesting. The wheat crop residue is not generally used as a feed stock for cattles whereas large amount of rice crop residue is used as cattle feed and stocked by the farmers.
At semi-urban area site (PUS), the SPM levels varied between 345 µgm\(^{-3}\) to 446 µgm\(^{-3}\) in October-November (2006-2007) and the peak concentration was obtained in October 2007 (Figure 1, Table 1). The high SPM levels were obtained at semi-urban site (PUS) due to the mixed influence of crop residue burning activities (CRB), domestic emissions and vehicular emissions. The levels of SPM were significantly high during CRB months at both the locations and exceeded the standards set by the regulatory bodies of the government. The monthly concentrations of SPM and K are presented in the Table 1 whereas trends of variation are presented in Figures 1-4.

Monthly average Potassium (K) concentration varied between 3.3 µgm\(^{-3}\) to 12.74 µgm\(^{-3}\) and 4.7 µgm\(^{-3}\) to 31.8 µgm\(^{-3}\) at urban and rural area sites, respectively. Peak K concentration (31.8 µgm\(^{-3}\)) was obtained at rural area site during October 2007 indicating the dominating effect of crop residue burning at this site, however at semi-urban area site, highest K concentration was

<table>
<thead>
<tr>
<th>Year</th>
<th>Month</th>
<th>Semi-Urban Site (PUS)</th>
<th>Rural Area Site (SVS)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>K</td>
<td>SPM</td>
<td>K</td>
</tr>
<tr>
<td>2006</td>
<td>Sep</td>
<td>--</td>
<td>339±4</td>
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<tr>
<td></td>
<td>Oct</td>
<td>345±37</td>
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<td>Nov</td>
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<td>Dec</td>
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<td></td>
<td>Dec</td>
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<td>6.50±2.12</td>
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</tbody>
</table>

Table-1: Potassium and SPM concentration in different sampling months at Semi-urban and Rural Area Site during 2006-2007.
Potassium as a marker in air particulate matter after crop residue burning events in Patiala, India.

**Figure 3:** Variation in monthly SPM concentration at rural site (SVS)

**Figure 4:** Variation in monthly K concentration at rural site (SVS)

obtained in the month of October 2007 again supporting the effect of crop residue burning (Figures 2, 4). Use of NPK fertilizers (composed of Nitrogen, Phosphorous and Potassium) by the growers for the better production of wheat and rice crops may be the source of K in the ambient air. The study revealed that the Potassium can be analyzed as the marker element in the analysis of ambient air particulate matter to see the effect of crop residue burning.

The levels of K in the atmosphere originate from the combustion of crop residue at high temperature and may include earth-crust like some other sources Chow, et al. (2007) Begum, et al. (2007). The monthly concentrations of K and corresponding SPM with their standard deviations are presented in Table 1
and the trends of monthly variation in ambient potassium concentration are presented in figures (Figure 2, 4).

During non-crop residue burning months (NCRB period) of the study period, the peak K concentration (19.8±12.9 µgm⁻³) was obtained in December 2007 at the rural area site whereas peak concentration (31.8±14.19 µgm⁻³) was obtained in the month of October 2007 at the same site. (Figure 4). During NCRB, the average K concentration at semi-urban area site was 5.71±1.71 µgm⁻³, while at rural area site the concentration obtained was 8.24±5.30 µgm⁻³ clearly indicating the impact of rural background. Through the CRB period,

**Figure 5:** The difference in average potassium (K) concentration during CRB and NCRB periods at semi-urban (PUS) and rural site (SVS)

**Figure 6:** Average levels of SPM during CRB and NCRB periods at semi-urban (PUS) and rural site (SVS)
the average K concentration was obtained at a level of 8.71±2.65 µgm⁻³ and 17.58±9.62 µgm⁻³ at semi-urban and rural site respectively indicating higher concentration during crop residue burning months (Figure 5). Similar results are obtained when the episodic average of SPM concentration is compared at both the sites i.e. higher SPM concentration was obtained during CRB episodes (Figure 6). The higher concentration at rural area site further revealed that the potassium levels are linked with the crop residue burning events performed by the farmers after harvesting.

At semi-urban area site, during non-crop residue burning months of 2006-2007, the highest K concentration (9.6±8.1 µgm⁻³) was obtained in March 2007 whereas during crop residue burning months, highest K concentration (11.1±6.8 µgm⁻³) was obtained in the month of October 2006. Average K concentration during non-burning and burning months was 6.4 µgm⁻³ and 8.2 µgm⁻³ respectively at this site, indicating higher concentration during crop residue burning months (Figure 6).

4. CONCLUSION
Crop residue burning was identified as an important source of SPM pollution in and around Patiala city integrated with the contribution of vehicular and domestic emissions. The concentration of SPM and K varied independently at two selected sites during the different sampling months but high concentration levels of both the parameters were obtained during crop residue burning periods at both the sites. At rural area site, much higher levels of K were obtained as compared to the semi-urban area site especially near crop residue burning months indicating the contribution from crop residue burning episodes. The K was found as a marker element that can be considered for the source apportionment of crop residue burning. Crop residue burning was dominating source at rural site in increasing the SPM load whereas automobile exhaust was dominating source for SPM at semi-urban area site. In Patiala, ambient air quality with respect to the levels of SPM was found deteriorated as high levels were obtained in most of the samples even in non-crop residue burning months. However, crop residue burning, increased vehicular traffic and swelling of urban population in and around the city will lead to severe air pollution problem in near future. Consequently it is supported that air quality management especially for crop residue burning should be formulated. Raising public awareness about dangers of SPM in ambient air will help in the improvement of urban air quality. It is also advocated to grow plantation along the roadsides to capture the pollution from mobile sources.
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Potassium as a marker in air particulate matter after crop residue burning events in Patiala, India


