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RESEARCH ARTICLE

Particle Bound Metals at Major Intersections in an Urban Location and Source Identification Through Use of Metal Markers

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Abstract Air quality monitoring for Kanpur in North India, an industrial city ranked among the top ten most polluted cities worldwide, was conducted in summer 2011. Airborne particulate matter (PM) sample from six locations were analyzed for metals. Source identification conducted using metals as source markers reveals probable sources of airborne particles being vehicular emissions, industrial, and railway activity. Findings were substantiated by investigating morphological characteristics and elemental composition of PM using SEM-EDX analysis at three major sites. In addition to confirmation of results by metal marker method, SEM-EDX analysis revealed presence of sulphur (S) which highlights influence of Panki Thermal Power Plant on air quality. The study shows that high levels of metals observed in airborne particles at major intersections may pose a significant cancer risk by exposure to toxics such as Cr, Pb and Ni.

Keywords Air quality monitoring · Traffic intersection · Railway lines · Metal marker · Particulate matter · Source identification · SEM-EDX

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1 Introduction

Several epidemiological studies [1–3] show the impact of airborne particles on urban atmosphere as well as on human health [4, 5]. Particles act as carrier for toxic substances [6, 7], ranging from metals to organic compounds. The contribution of these chemical species to PM increases its toxicity [8, 9]. Fine particles, which carry a higher proportion of these compounds generally, easily get deposited in alveolar region of the lungs [10–12] and cause several respiratory and cardiovascular diseases [7, 13, 14]. Not surprisingly, PM in outdoor air has recently been certified as carcinogenic to humans by World Health Organization.

Metals are important components of PM and act as markers to reveal the emission source [15, 16]. An understanding of their emission from various sources to the atmosphere and their contribution to PM toxicity has been noted as a requirement for assessment of their impact on environment and human health by several studies [7, 17]. Rapid growth in the number of vehicles, leading to frequent traffic jams, and industrial activities are the main reason for air pollution in Kanpur, the second most polluted city in India [18]. A study conducted by Central Pollution Control Board (CPCB) and Indian Institute of Technology Kanpur (IIT Kanpur) [19] in 2007 has shown that 22 % of the particles (PM) are from vehicles, and 33 % are from industrial emission. This paper is a follow up to an earlier paper examining PM distribution in Kanpur [20]. The study reveals alarming levels of airborne particles in the city. In the present work, we investigate the probable sources of PM in ambient environment by using metals as a source marker. In addition, the Scanning Electron Microscope (SEM) with Energy Dispersive X-ray (EDX) technique is

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used to corroborate the findings. The main objectives of the study were:

(1) Determination of particle bound metal content at major railroad and road intersections in Kanpur city
(2) Use metal marker technique, complemented by SEM-EDX analysis, to identify probable sources of airborne particles.

Investigation and evaluation of health risk for the people exposed in polluted area is essential, especially because these toxic metals are carcinogenic in nature. Research findings will be useful to assess health risk for public health officials and policy makers working towards limiting public exposure.

2 Site Description

Air samples were collected in June 2011 at six locations in Kanpur city (Fig. 1), which include major traffic intersections, railway intersections and construction sites. Site abbreviations (used henceforth) and related details are given in Table 1.

The study region is Kanpur (26°27′N 80°20′E), one of the largest and highly polluted cities [21] in India. It has an area of over 829 square km with a population of approximately 3 million. Due to high traffic, samples collected at all six sites have a high contribution from vehicular emission. In this study, site Parade Chowk (PC) is a road intersection, and connects the major commercial area to the residential locations. Traffic at PC is free flowing, and less traffic jams occur as compare to other sites. In addition, sample from PC experienced influence of construction activity which was underway at the time of sampling in June 2011 [20]. Second site Naveen Market (NM) located near PC (~50 m), completely crowded market area, and is influenced mainly by light vehicular activity. On the other hand, third site Ramadevi (RD) is near highway connecting three major cities viz., Kanpur, Lucknow and Allahabad, and is a very busy intersection that is affected by heavy traffic. Other sites Kalyanpur (KP), Gumti no. 05 (G5) and Rawatpur (RP) are railroad intersections, located near the

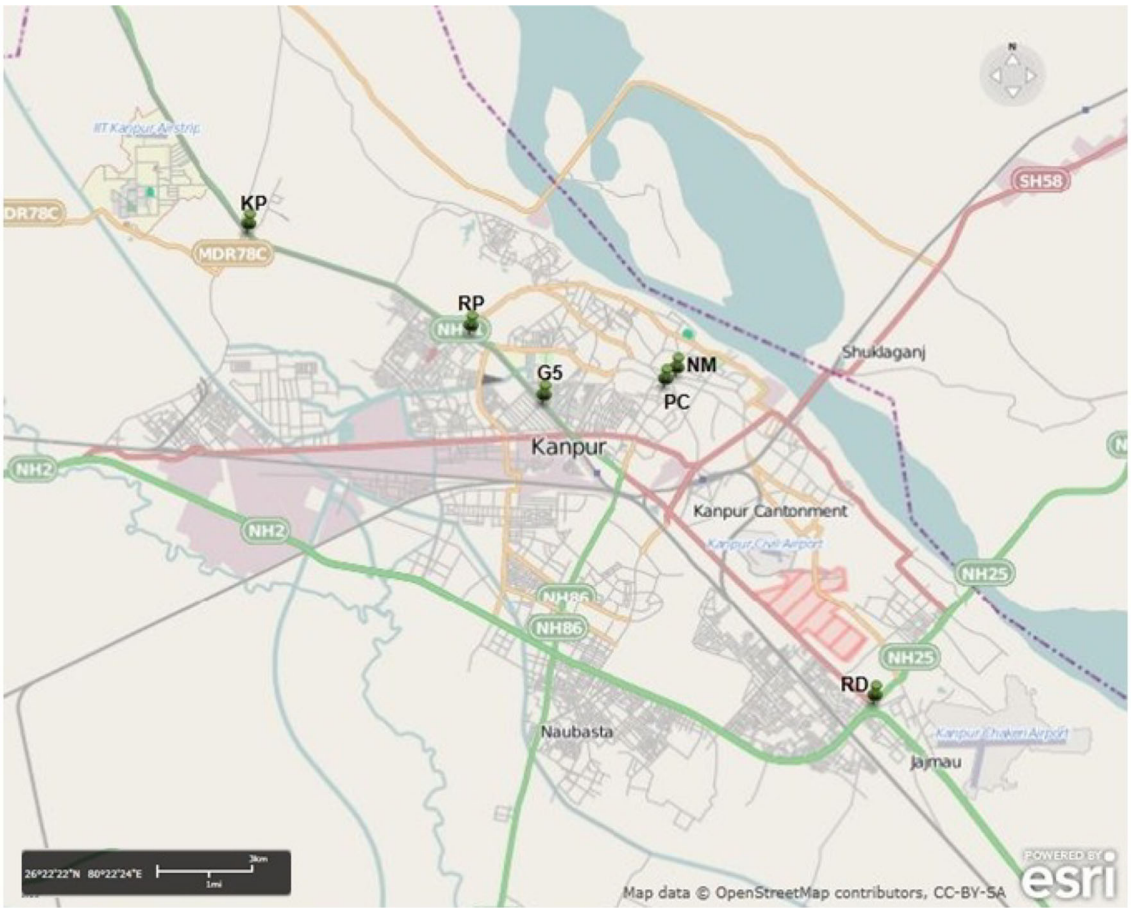

Fig. 1 Map of sampling sites

Table 1 Description of sampling locations along with K/Na Ratio at each sampled

Location	Abbreviation	Site	Temperature range during sampling (°C)	K/Na
Naveen market	NM	Near a shop 50 m from construction sites at traffic intersection	36.4–41.9	0.86
Ramadevi	RD	Near the traffic intersection ('Chouraha')	38.2–40.2	0.53
Parade Chowk	PC	Parade chowk traffic intersection	37.2–41.9	0.74
Kalyanpur	KP	Railroad intersection	34.2–36.0	3.10
Rawatpur	RP	Railroad intersection	34.2–36.0	2.20
Gumti no. 05	G5	Railroad intersection	31.7–36.1	1.25

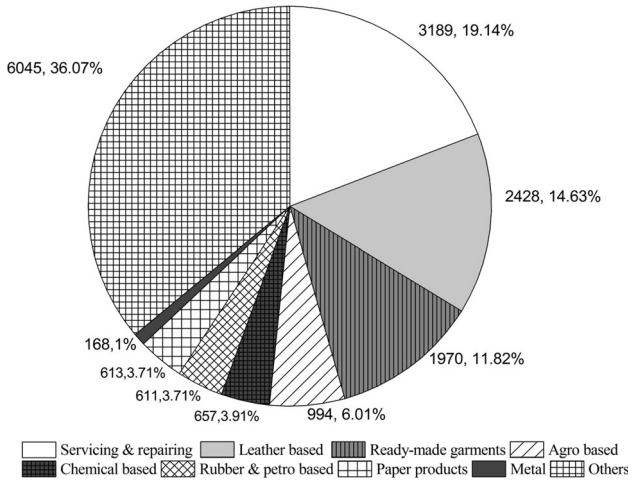

Fig. 2 Contribution of different industry type to total industries registered in Kanpur

railway line. Railway traffic at these sites is high, 4–5 trains pass the crossing every hour. Long waiting times of vehicles (average waiting time: 10-15 min) at these sites leads to huge traffic jams several times in a single day. Additional details on sampling sites are given in Kumar et al. [20].

Industries are a big source of pollutants recorded in Kanpur. Emission inventory data for the city in 2007 revealed that industrial emissions account for unto 26 % of PM_{10} and 37 % of NOx in ambient air [19]. As per data provided by the district industrial office, total no of industries registered in Kanpur till 2011 are 16,675. Contribution of industry type to total registered industries in the city is presented in Fig. 2. Major portion is covered by servicing and repairing industries, which contribute 19.1 % to total, followed by leather based industries, ready-made garments industries, agro based industries, chemical industries, rubber and petro based industries, paper products, and metal industries, respectively. Contributions of other industries are ~36 %, which mainly includes wood based industries, jute products, cotton textiles, soda water etc. Leather based (tanneries) and other industries are located in Jajmau area, which is near to our sampling site RD.

3 Sampling Procedure

3.1 Sample Collection

All samples in city were collected in a day for at least 6 h (at each site) in summer 2011. Sampling was conducted during peak daytime traffic hours (0900–1200 and 1600–1900 h) when the impact of vehicular pollution and the possibility of human exposure are maximum. Optical Particle Counter (OPC; Grimm Laser Aerosol Spectrometer model 1.108, Grimm Aerosol Technik GmbH, Ainring, Germany) was used for sample collection. Flow rate of OPC was 1.2 lpm. An integrated gravimetric Teflon filter (47 mm diameter, pore size: 1.2 μm) used inside the OPC is utilized for chemical analysis (see Kumar et al. [20] for details).

4 Methodology

4.1 Sample Analysis

4.1.1 Gravimetric Analysis

All filters were pre- conditioned in a vacuum desiccator for 24 h (both before and after sampling) to de-moisturize the filter at room temperature with a relative humidity of 40–50 %. Filters were weighed thrice before and after sampling by a microbalance (Mettler AB135S; sensitivity of 1 mg).

4.1.2 Chemical Analysis

Post gravimetric analysis, sampled filter paper (from OPC) was cut into two parts, one part each for metal and physical analysis on SEM-EDX. In addition, field and laboratory

blanks were also collected to check for any possible contamination.

4.1.3 Metal Analysis

Hot-plate digestion method was used for extraction of metals from filter paper. One half of filter paper was cut into several small pieces and placed into a 100 ml digestion flask. Then 15 ml of concentrated HNO_3 (65 %, GR Merck Supra pure) was poured into the digestion flask and placed over a hot plate (180 °C) for 2 h. After the completion of digestion, the sample was allowed to cool to room temperature. Digested solution was filtered through 0.22 μm Whatman filter paper to remove any solid residue and then transferred to 100 ml volumetric flask. Volume of volumetric flask was made to 100 ml with MILI-Q water. Similar procedure was followed for blank preparation. Samples were refrigerated at 4 °C for further analysis.

The extracted sample was injected into an Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP-OES, ICAP 6300 Thermo Inc.) instrument for analyzing various metal elements viz., Ba, Cd, Cr, Cu, Fe, K, Mg, Na, Mn, Ni, Pb and Zn.

4.1.4 SEM EDX Analysis

SEM EDX is an important tool, which is used to identify the morphology and elemental composition of PM. It helps to identify the origin of particle as anthropogenic or natural. SEM-EDX analysis was carried out with the help of a computer controlled field emission SEM (Carl Zeiss NTS GmbH, Oberkochen (Germany) Model: SUPRA 40VP), coupled with an Energy Dispersive X-ray Spectrometer. Samples were prepared by randomly cutting 1 mm^2 size out of the main filter paper. A very thin film of gold was deposited on the surface of the samples to avoid the charging effect using vacuum coating unit. These samples were mounted on electron microprobe stubs.

In the current study, for SEM/EDX analysis, an accelerating voltage of 10 kV, acquisition time of 30 s, and working distance of 8.5 mm were used. Note that the elements with atomic number less than 11 and fine particulates ($dp < 1$ μm) are not considered during visual examination [22].

Levels of metals detected in particles have been utilized for source identification.

5 Results and Discussion

Level of metals in PM, and their probable sources, was examined at the six sampling sites described earlier. Results of source identification based on metal as a source marker is supported by morphological characteristics of particles examined using SEM EDX analysis at three major intersections.

5.1 Summary of Particle Source Identification Using Metal as Source Markers

Information presented in Table 2, sources of metals present in ambient environment, and lists sources proposed by earlier studies. It can be seen clearly that studies in India have focused mainly in metro areas and very little information from smaller towns (Agra, Surat, Mithipur and Jorhat) is available. Discussion below has been organized on the basis of source activity (mainly anthropogenic).

5.1.1 Vehicular Activity

Nickel (Ni) is among the most common metal identified from vehicle exhaust by most studies. Main source of Ni is automobile exhaust fitted with catalytic convertor where Ni is used as an additive in fuel [23]. As reported by a study conducted in Chennai [4], another source of Ni is tire dust that contributes significantly in the form of atmospheric dust. Ba is mainly associated with brake wear, and the main roadside source considered is non vehicular exhaust [9, 23–25].

Lead (Pb) had been added traditionally to petrol as anti-knock agent, and Pb containing fuel was recorded as the major source of emission of this toxic metal in the atmosphere. Since 2000 the use of Pb as an anti knocking agent has been banned by the government of India across the country, which led to a decrease in the Pb level in ambient air [26]. However, at few places, significant level of Pb has been found, and is confirmed by studies that Pb is still persistent in atmosphere in the form of road dust particle from earlier vehicular exhaust emissions [27]. This might be due to its longer residence time [26, 28].

Non vehicular exhaust such as brake wear from vehicles is an important source of atmospheric (particulate) Cu [29]. Brake wear of road vehicles is due to forced deceleration, during which brake linings are subjected to produce large frictional heat. This wear generates brake lining particles which are partly released to the environment. Non-vehicular exhaust such as tire wear (used in rubber production), galvanized materials and brake linings [30–32] has been suggested as the most common source of Zn in the ambient environment.

Brake linings and tire wear is considered as main source of Mn [33, 34] present in environment. The other important source of Mn in ambient air is the influence of road dust matrix [4]. The influence of vehicular activity is reflected by the fact that sources of Cr include road dust contaminated by emissions of Cr based catalytic converter used in

Table 2 Use of metals for source identification in Indian and International studies

Source signature	Probable sources	City	References
Na, K	Marine	Mumbai	[49]
Na, K	Anthropogenic	Agra	[48]
Na, K		Japan	[50]
Ca, Co	Construction	Delhi	[59]
Fe, Pb, Ni		Agra	[34]
Co, Ni, Cu, Zn, Cd, Te	Industrial	Jorhat	[36]
Zn, Cu, Br,V, Mn		Bombay	[32]
Ca, Mg, Fe, Al, Mn	Re suspension of dust	Delhi	[7]
Pb, Cr, Co		Mithapur	[27]
Ni, Cr, Zn, Mn, Cu	Vehicular	Bombay	[32]
Ni, Cd, Ba, Na		Delhi	[24]
Ni, Cr, Mn, Cu, Zn, Pb		Delhi	[7]
Ni, Mn		Kolkata	[28]
Cu, Sb, Zn, Mo		Barcelona (Spain)	[30]
Ni, Mn		Urbana, Illinois (USA)	[23]
Cr, Pb, Ni, Mn, Fe		Seville (Spain)	[15]
Fe,Zn		Taiwan	[42]
Ca, Mg, Fe, Al, Mn		Niigata (Japan)	[33]
Fe, Mg, Na, Cr, Cu, Mn	Railway emission	Mexico	[44]
Fe Mg		Switzerland	[40]

vehicles. Hence, high loading of Cr also reflects the bulk matrix of road dust [4].

5.1.2 Industrial Activity

The major source of Cd in the environment has been reported to be industrial activities which include mainly nonferrous metal mining and refining, application of phosphate fertilizers, waste incineration and disposal, coating and plating, smelting operations [35]. Study by Shevchenko et al. [35] also suggests that Cd can travel long distance in the atmosphere and then deposit (wet or dry) onto surface soils and water [36]. Sometimes these soil dust particles are carried over by the action of wind from a source, which can result in elevated Cd levels even in remote locations.

Presence of Chromium (Cr) and Copper (Cu) in the atmosphere is also considered to be a result of industrial activity [37]. Source of Cr mainly includes metal industries, such as chrome plating and steel production [38]. Other important anthropogenic stationary point source of Cr emission to the atmosphere is residential fuel combustion, via the combustion of natural gas, oil, and coal [37, 38]. Sources of Cu in air are both natural and anthropogenic. Since copper is a component of the earth's crust, the earth's crust is the primary natural source of copper. Anthropogenic sources mainly include industrial applications such as nonferrous metal production, wood production, iron and steel production, waste incineration, coal combustion, nonferrous metal mining, and phosphate fertilizer manufacture [39].

5.1.3 Railway Activity

Iron (Fe) dust is an important contributor of railway emissions to ambient atmosphere [40]. Other sources of Fe include emissions from the brake lining material [41], automobile rust [23] and motor car exhaust [42].

A study focused on examining emissions to ambient air from cargo and passenger trains in Zürich (Switzerland) found that railway line also contributes significant amount of Cu, Cr, Mn, Mg, Na and Ni to the atmosphere [43]. Based on a study carried out in underground subway stations in Mexico City, Mugica-Alvarez et al. [44] have reported an increase in content of these metals, possibly due to enrichment of the particles stock within the station. It has been associated with un-lubricated sliding contact and arc ablation wear under a large electric potential difference, applied through the rubbing components engaged in power transmission [45, 46]. However, compared to iron, these elements are emitted in very low quantities. Crustal elements such as Mg and Na are mainly associated with coarser particles [47]. Through their study to examine contribution of railway traffic to local PM_{10} concentrations,

Gehrig et al. [40] reported presence of these elements at a site near railway line in Switzerland. The influence of railway line is a considerable reason for generation of coarser particle at these sites apart from resuspension of dust. Presence of coarser particles at these sites might also be attributed to erosion, abrasion, and resuspension of the gravel below the tracks [40]. Other probable source of crustal element Mg in the ambient atmosphere is resuspension of soil dust.

5.1.4 Marine/Anthropogenic Activity

Presence of K and Na is considered as a source signature of marine activity. A study from Agra [48] reported that when K/Na is greater than sea water ratio (0.037), implies no influence of marine source, and signifies the dominance of some other sources. Source apportionment efforts for Na in atmospheric PM, and PM in Mumbai [49, 50] reveal that K/Na ratio can act as a tool which distinguishes the possible source of Na and K, as either anthropogenic or marine activity. K/Na ratio in the range of 0.9–4.4 suggests an anthropogenic source [50].

5.2 Levels and Prospective Sources of Metals Observed on Airborne Particles in this Study

Figure 3a, b present levels of metals observed on PM in this study. A large variability was observed in the concentration of metals detected in ambient air. Most notably, concentration of the group of metals in Fig. 3a (Fe, K, Na, Mg, and Zn) (0–50 μg m^{-3}) is nearly five times higher than the metals presented in Fig. 3b (Mg, Ni, Cr, Cu, Mn, Pb, and Ba): range (0–10 μg m^{-3}). It is important to note that although levels of Ni, Cr, and Pb (Fig. 3b), which are the most toxic among all the metals studied in this work [51, 52] are low, they were detected at all sites. It must be noted here that since the samples were collected at the major traffic intersections at the time of peak traffic, the influence of vehicular activity, both exhaust and non-exhaust sources, are expected to be very significant. This accounts for the high levels of metals observed in the current study, which is much higher than the levels reported in previous studies.

Concentration of Zn (Fig. 3a) at two sites RD and KP (36.94, and 34.58 μg m^{-3} respectively) were found to be much higher than other sites. Zn levels at other sites G5, RP, PC and NM are relatively high, in the range: 17–22 μg m^{-3}. RD and KP are the busiest traffic intersections in the city and have high influence of heavy vehicles. As mentioned earlier, non-vehicular exhaust could be a possible reason for the presence of high Zn levels at these sites. Earlier studies focusing on chemical characterization and source apportionment of PM [49, 53], have stated that proximity to industrial area can also contribute to Zn levels in PM. Zn is known to occur in significant amount in effluents from leather industry [54] and has been detected in surrounding environmental media. In addition, new products like nano ZnO are being developed and used on leather as a retaining and antibacterial agents [55]. This combined with the fact that Kanpur is a major hub of Indian leather industry, and most of it is located in Jajmau, close to RD, supports the possibility that industrial influence of high levels of Zn is noted at RD. This in turn suggests that both industrial and vehicular emissions contribute significantly towards the presence of Zn at RD, while rests of the sites are affected only by vehicular activity.

Cadmium (Cd) occurred below detection limits at all sites, except at RD (0.56 μg m^{-3}). Primary source of Cd is reported to be industrial emissions (Table 2). To investigate possible industrial sources of Cd, industrial data were collected for Kanpur and nearby city (Source: Industrial District Office, Kanpur and Unnao). In summary, data contains information about input material and chemicals used in the manufacturing processes of final products. Examination revealed that no proper source of Cd lies in the vicinity of site RD. However, Cd has been reported as a heavy metal that occurs in significant amount, along with Zn and Cr in leather industry effluent [56]. Similar to Zn, proximity of RD to local leather industry could be a possible source. The fact that Cd was not detected at any other location supports this possibility. As suggested by previous studies Cd can travel long distance in the atmosphere [35], another possible source of traces of Cd at RD in our study could be long range transport of dust particles. This needs further examination.

Concentrations of Ni recorded at rail road intersections: KP, G5 and RP (>1.53 μg m^{-3} at each site) were approximately three times higher than other sites. Levels of Ni at other sites PC, NM are 0.53, 0.45 μg m^{-3}, respectively, and lowest value is recorded at RD (0.21 μg m^{-3}). Observation of highest levels of Ni at these railroad intersections strongly supports results of the study carried at underground stations in Mexico City [44] that railway emission are a probable source of Ni in ambient air. This can be attributed to dominance of vehicular and non-vehicular exhaust at these sites. This has also been proposed by earlier studies [4, 23] as a most common source of Ni in ambient air.

All railroad intersections showed level of Ba > 1 μg m^{-3}. Highest concentration is observed at G5 (1.79 μg m^{-3}), while level at other sites KP (1.05 μg m^{-3}), RP (1.47 μg m^{-3}) and RD (1.45 μg m^{-3}) is comparably low. All these sites are busy intersections which experience huge traffic jams several times in a single day. Most common reason of getting high Ba level at these

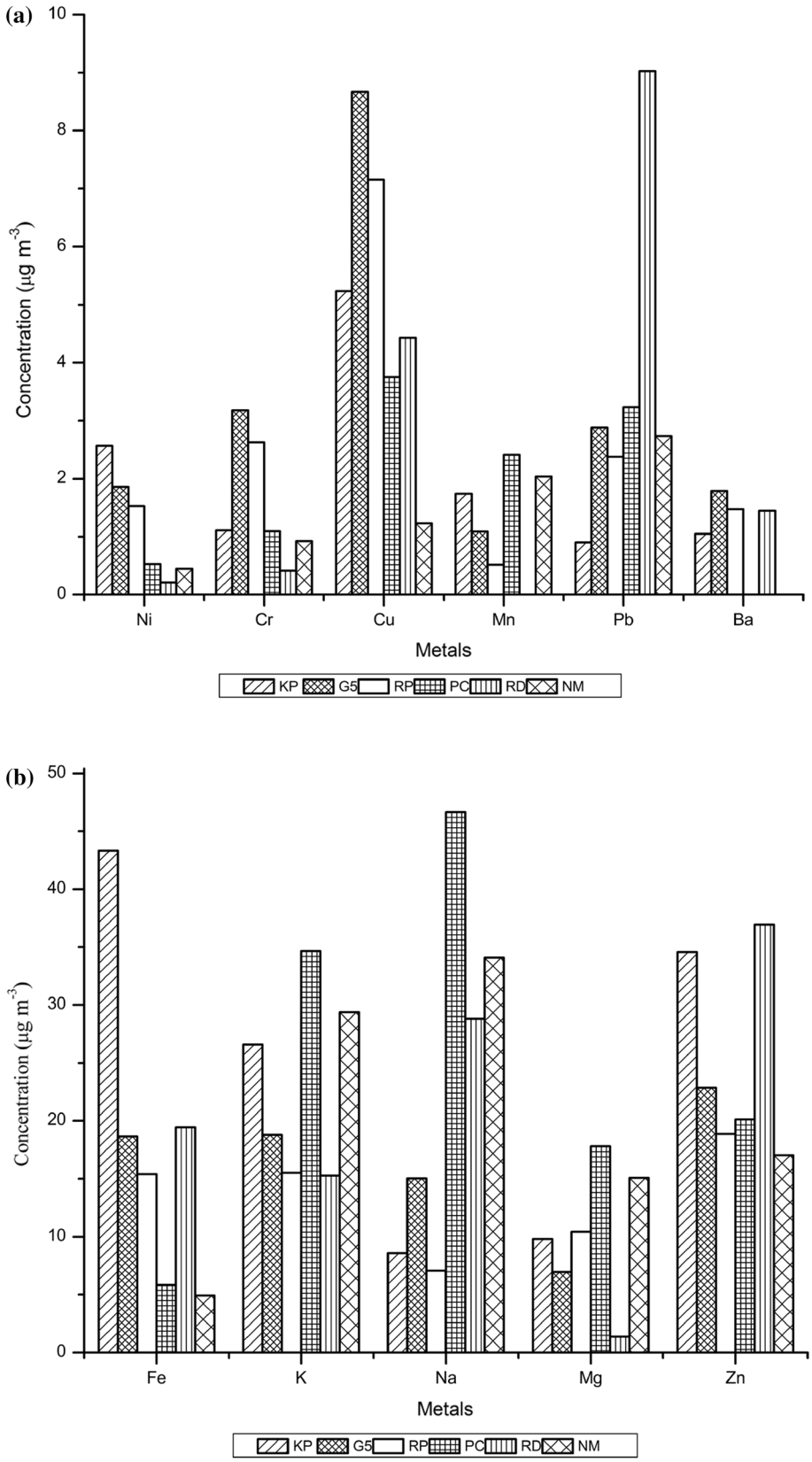

Fig. 3 **a**, **b** Concentration of metals detected at sampling sites

sites could be non vehicular exhaust as mentioned above such as break wear. Note that the levels at traffic intersections, PC and NM, with better traffic conditions and influence of light duty vehicles [57], are below detectable limit.

Metal with known toxicity, Pb, occurred in a significant amount at all the sites (Fig. 3b). Though the use of Pb as a fuel additive has been discontinued since 2000, levels at all sites were still higher than the CPCB permissible level (1 μg m^{-3}). Highest value is recorded at RD (9.03 μg m^{-3}) and lowest value at KP (0.90 μg m^{-3}). Rest sites have shown the Pb level in the range 2–4 μg m^{-3}. Our results suggest that the city environment is influenced by road dust which contains persistent Pb, remnant from earlier vehicular emissions [26].

Levels of Mn followed the trend road + construction > rail-road intersection > traffic intersection. Mn occurred in highest concentration (>2.00 μg m^{-3}) at sites influenced by major construction activity during time of sample collection, viz., PC and NM. It should be noted here that neither of these sites has influence of railway lines, which is another possible source of Mn. Non-vehicular exhaust is also considered as one of the source of Mn in ambient air as mentioned earlier. Thus, the atmosphere at these sites could include mixing of dust from construction activity with pollution from non-vehicular emission. Level of Mn observed at road railway intersections KP, G5 and RP (range: 1.74–0.51 μg m^{-3}) suggests that in addition to non-vehicular exhaust, railway activity is also contributing significantly to Mn levels. It is important to note that Mn level at site RD is below detectable limit. RD does not have influence of either construction nor of railway activity, which clearly suggest that rather than other sources, railway and construction activity are the prominent sources of Mn in ambient air of Kanpur.

5.2.1 High Fe Levels at Railway Sites

Fe concentration was highest at the railway intersection sites (Fig. 3a) viz., KP (43.33 μg m^{-3}), G5 (18.66 μg m^{-3}), and RP (15.41 μg m^{-3}) which supports earlier hypothesis that railway emissions contribute to levels observed in ambient air (Table 2). It is interesting to note that RD which is not affected by any railway activity shows the second highest concentration (Fe: 19.44 μg m^{-3}). This strongly suggests that in addition to railway activity, vehicular activity (heavy vehicles and traffic jams) also contributes significantly to Fe levels in ambient atmosphere. Low level of Fe is observed at sites PC (5.83 μg m^{-3}) and NM (4.94 μg m^{-3}). Traffic at these sites is mostly free flowing. Less traffic jams as compare to other sites is probably a major reason for low Fe level at these sites.

Cr level is high at all the railway intersection sites viz., KP (1.11 μg m^{-3}), RP (2.63 μg m^{-3}) and G5 (3.18 μg m^{-3}) than the other sites, which strongly suggests the influence of railway activity to Cr levels in ambient atmosphere. This fact has also been reported by earlier studies as mentioned in previous section. Significant amount of Cr level was also observed at sites PC (1.09 μg m^{-3}) and NM (0.92 μg m^{-3}). These sites have no influence of railway activity which suggests that high loading of Cr is due to bulk matrix of road dust [4]. As mentioned earlier due to construction activity these sites have experienced huge amount of road dust at the time of sampling. Our results suggest that at PC and NM, level of Cr is due to combined effect of vehicular and construction activity. Lowest level is recorded at RD (0.42 μg m^{-3}). Collected industrial data are also used to check their emission from industries; surprisingly we have observed the significant source of Cr present near the sampling site. But in our study the low level of Cr at this site suggests that proper disposal maintenance of Cr has led to low level in ambient atmosphere.

Concentration of Cu at sites G5 and RP (8.67 μg m^{-3}, and 7.16 μg m^{-3} respectively) were found to be higher than other sites. Cu also occurred in significant amount at other sites viz., KP (5.23 μg m^{-3}), RD (4.43 μg m^{-3}), PC (3.75 μg m^{-3}) and NM (1.25 μg m^{-3}). Sites G5, RP and KP are railway intersections, which clearly suggest the contribution of railway activity to ambient atmosphere. Other most probable source of Cu is break wear as mentioned earlier. Due to frequent railway activity, these sites have also experienced huge traffic congestions at several times which led to release of break wear particles. RD has no influence of railway line and shows lower levels of Cu. This again suggests that railway and vehicular activity both are adding significant level of Cu in ambient atmosphere.

Highest amount of Mg is observed at sites PC (17.82 μg m^{-3}) and NM (15.10 μg m^{-3}). It is important to note that traffic at these sites is always in flow and traffic jams are not common. Besides that, resuspension of soil dust is found to be high at these sites than other sites due to the construction underway at the time of sampling. Resuspension of soil dust also considered as most probable source of Mg in atmosphere. Mg (Fig. 3a) is also present in significant amount at sites KP (9.79 μg m^{-3}), RP (10.42 μg m^{-3}) and G5 (6.96 μg m^{-3}). An earlier study by IIT Kanpur [20] reports the dominance of coarser particles at these sites. High levels of crustal elements reported here support the findings made in earlier work [20] that railway line probably act as a major cause behind higher coarser particles. Presence of crustal elements at railway sites has been also identified by some previous studies [40].

As mentioned in the previous section, K/Na ratio can be used to identify the influence of marine activity. K/Na

ratios for all sites are given in Table 1. In current study, it is observed that K/Na ratio at railway intersection sites KP, G5 and RP fall in the range 0.9–4.4, which confirms the contribution of anthropogenic sources to K and Na levels in the atmosphere [50]. Similarly, at traffic intersection sites PC, RD and NM, the ratios fall in the range $0.037 < K/Na < 0.9$. Source of Na and K at all the sites is most likely anthropogenic, not marine (since $K/Na > 0.037$) [17]. In current study, levels of Na at sites KP (8.59 μg m^{-3}), G5 (15.03 μg m^{-3}) and RP (7.07 μg m^{-3}) are quite significant. Source of Na at these sites could be result of railway emission, an anthropogenic activity, which has also been noticed by a previous study [40] which examined contribution of railway traffic to local PM_{10} concentrations.

5.3 Source Identification Through SEM EDX Analysis

Morphological characteristics and elemental composition of the individual particles were determined with the help of SEM EDX analysis. SEM images for sites near the railway line (KP) and major road intersection (PC, RD) are presented in Fig. 4 and are discussed below. It may be mentioned here that each figure contains EDX for an individual particle present on the filter paper. Results for KP are presented in Fig. 4a, b, For PC in Fig. 4c, d and for RD in Fig. 4e. Results for the three sites have been further broken up into two sections, morphology and metal content.

5.3.1 Major Railway-Road Intersection (Location: KP)

KP—Morphology: Micrograph 4(a) and 4(b) show that particles of different shapes are randomly distributed upon the filter paper. Particle in micrograph 4(a) are triangular, rectangular and oblong in shape with sharp edges; that in micrograph 4(b) appears to be cylindrical in shape.

KP—Metal content: EDX results for particle in Micrograph 4(a) reveal that presence of Na, Mg, S, K, Ca, Fe, Ni, Co, and Pb in these particles. Occurrence of Au in EDX result is only due to the fact that Au was used in coating to avoid charging of electrons. It should be noted that all these particles belong to the same filter. EDX results of other particles present in micrograph 4(a) and 4(b), which are not shown in this paper, also confirm the presence of these metals. Rectangular and triangular shaped particle (Fig. 4a) shows high carbon percentage along with Na, K, O, and Fe. The occurrence of C is maximum at site KP which shows the presence of heavy vehicular traffic site [1]. Significant oxygen content shows that the selected particle contains metal oxides [58].

EDX result of particles confirms the presence of elements, namely Fe, Na and Mg, whose occurrence is attributed to emission from railway activity at KP site. Presence of other metals could be due to vehicular emission and resuspension of dust. Soil and crustal dust could be the reasons for the presence of Cl [59]. It is important to note that EDX analysis reveals the occurrence of S, for which the previous method—ICP-OES cannot not be used. Occurrence of S in particles from KP can be attributed to emissions from Panki Thermal Power Plant (coal based fire) located near the KP site (approximately 5 km away from KP) [60]. KP is located downwind from Panki, and presence of S at KP confirms that the power plant is affecting the air quality in the downwind locations.

5.3.2 Major Traffic Intersection (Location: PC/RD)

PC/RD—Morphology: Irregular shaped particles are quantitatively high in samples at these sites. SEM images for the particles from PC are presented in Fig. 4c, d, and for RD image is presented in Fig. 4e respectively. Particles shown in micrographs occur in aggregate form and are irregular in shape. All the particles shown here are porous in nature, this suggests that the origin of these particles is mainly combustion sources (fuel oil combustion) [61]. Micrograph 4(e) shows particles of varying shapes such as cylindrical, spherical and triangular.

PC/RD Metal content: EDX results for micrographs 4 (d), and 4(e) indicate that most of the particles contain C, O, Na, Cl, Zn, Al, Ni, Mg, Si, Ca, and Pb. Presence of F in spectrum may be because it is the content of filter paper. Presence of C shows the dominance of vehicular source [59, 62]. Sources of other metals could be emission through the combustion of fossil fuels, vehicular activity, and resuspension of dust.

Railroad versus Traffic (road) intersection: From the SEM- EDX analysis it is clear that particles present at KP are crystalline, having sharp edges with high carbon percentage. The presence of elements such as Na, Mg, and Fe in abundance, confirmed that the site KP is most probably influenced by the railway activity, as suggested by previous studies. SEM-EDX result of particles present at RD and PC shows that particles are porous in nature, and dominance of metals Na, Cl, Zn, Al, Ni, Mg, Ca and Pb suggest that these sites are highly influenced by vehicular emission.

Sources of PM suggested by SEM-EDX analysis are the same as mentioned earlier by using metal as source marker. Besides this, SEM-EDX analysis has also provided important information regarding the origin of particle. SEM-EDX analysis also confirms the presence of S in particles originated from KP, even though Panki Thermal Power Plant is located downwind near the KP site. Influence of Panki Thermal Power Plant at site KP, which had not been recognized by the bulk composition analysis, suggests that examination of individual particle is essential for source identification.

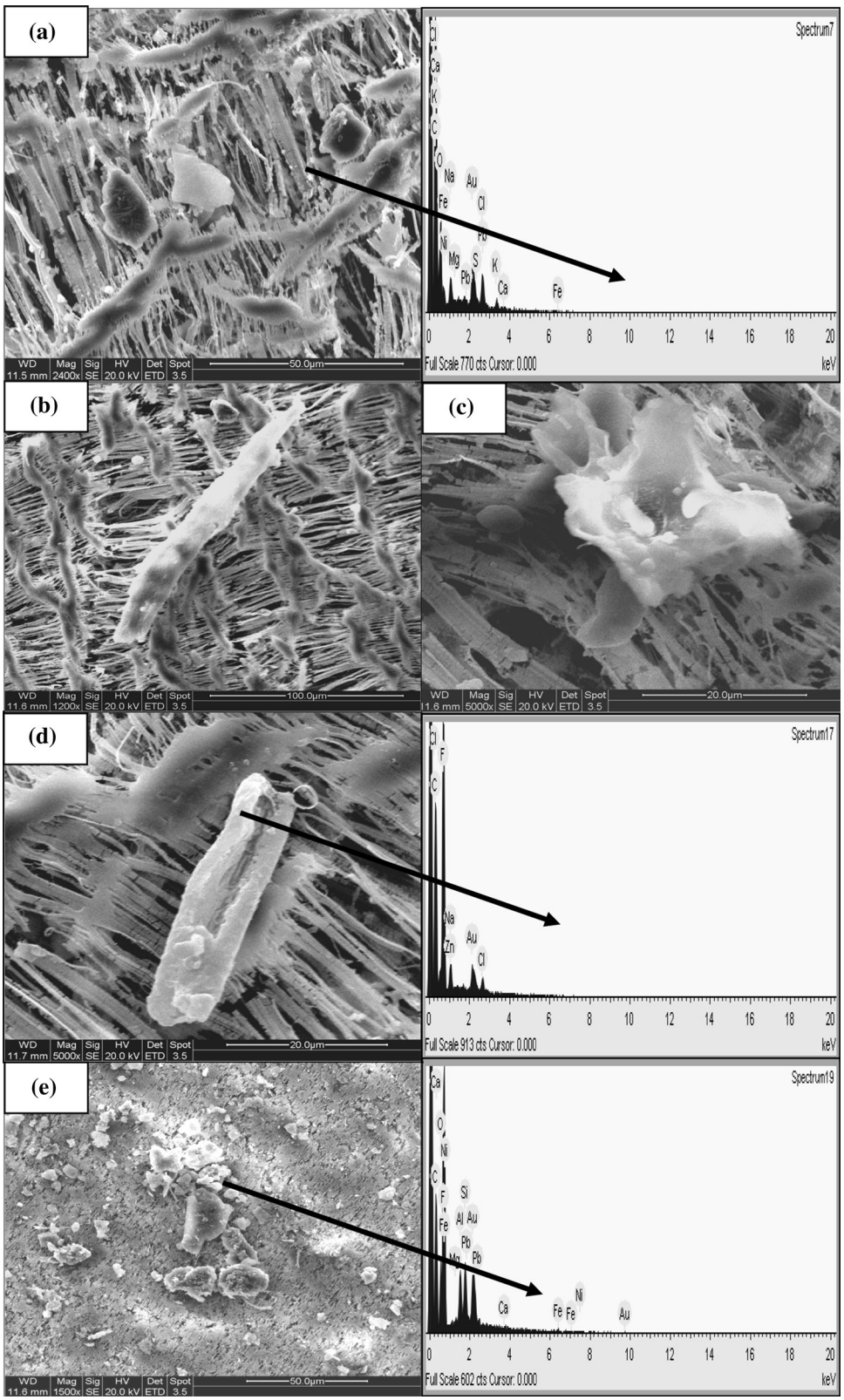

Fig. 4 SEM images for sites near railway line (KP) and major traffic intersections (PC, RD). **a**, **b** KP, **c**, **d** PC, **e** RD

6 Conclusions

Metals occur in a significant amount in the ambient air at peak traffic times at major intersections of Kanpur city. Among the toxic metals (Ni, Cr and Pb) examined, Pb, which has been banned as an anti-knocking agent in fuel for more than a decade (post 2000), still occurred at, are above permissible limits at all locations except KP, a major railroad intersection. High levels of the toxic metals examined (Ni, Cr and Pb), suggest potential carcinogenic risk to population exposed. Effort should be made to reduce metal levels and exposure duration at these locations. Influence of Panki Thermal Power Plant on air quality at KP is confirmed by the presence of sulphur (S) in particles from site through SEM EDX analysis. This observation highlights the fact that consideration of individual particle composition is useful and should be considered along with bulk composition in establishing a relationship between metal detection and their sources. This may lead to a more comprehensive assessment of sources and help manage their impact on human health.

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