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Full Length Research Paper

Compandium of sampling methods for the determination of compound phases and trace metals in suspended particulate matter

Naveed Ahmad[1], Muhammad Attique Khan Shahid[2]*, Khadim Hussain[3] and Nasir Ahmad[4]

[1]Department of Physics, University of Education, Lahore, Punjab, Pakistan.
[2]Department of Physics, UDC, GCU, Faisalabad, Punjab, Pakistan.
[3]Centre for High Energy Physics, University of the Punjab, Lahore, Punjab, Pakistan.
[4]Institute of Geology, University of the Punjab, Lahore, Punjab, Pakistan.

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Air quality of Lahore, a heavily populated city of the Punjab, was determined collecting samples of different types. The study was carried out on samples collected during December 2001 to January 2002. Indoor suspended particles using AC filters were also collected along with dust from room carpets. Eight-hourly average loading of outdoor suspended particulate matter (SPM) was found to be in the range of 670 to 1523 µg/m^3. Twenty-four hourly bulk deposition of free fall dust was found to be varying from 16 to 60 gm/m^2/month. Minerals, such as Quartz, Illite, Cholrite, Calcite, Albite, etc., were detected in all samples (SPM, free-fall dust, indoor suspended particles samples and carpet dust) using the Powder method. Elemental loadings of all samples were determined employing the atomic absorption spectroscopy. Cu, Ni, Cd, Zn and Pb were detected in all the samples. Since there are no ambient air quality standards enacted in Pakistan, a comparison with ambient air quality standards (WHO, USA, and Europe) showed that loading of airborne particulate matter were several times higher than the maximum permissible limits accepted there as standard. In this study, the Pb concentration was found to range from 1 to 9.8 µg/m^3; Cu, Ni, Zn and Cd were within the permissible levels.

Key words: SPM, air pollution, free fall dust, trace elements, XRD, atomic absorption spectroscopy.

INTRODUCTION

The history of studies of air pollution in Pakistan is not very old. About three decades ago, a global air monitoring program for the study of suspended particulates was launched by the World Health Organization as a part of Global Environment Monitoring System (GEMS). Some 50 countries participated in the program except Pakistan and data were collected from 175 sites of the participating countries. The GEMS results were later reported by WHO (1984); the results showed that the SPM concentrations for a Lahore commercial city centre were 332 µg/m^3 in 1978 and for a Lahore residential site were respectively 749 and 690 µg/m^3 in 1979 and 1980. Bennett et al. (1985) and Koning et al. (1986) reported from the GEMS results that Tehran, Mumbai, and Calcutta were emerging as highly polluted cities in the southern Asia. In order to know the air pollution situation prevailing in Lahore at that time, Hussain et al. (1990) collected suspended particulates from different urban and suburban sites of Lahore and studied those by X-ray Powder Diffraction and Wet Chemical Analysis. Owing to nonavailability of any air volume sampler, mass concentration of SPM could not be found. Some samples were studied by Scanning Electron Microscopy for knowing the suspended particulate size. The X-ray Diffraction results showed the presence of soil minerals namely, albite, calcite and quartz in the samples not in apportionment to the soils of the area. The approximate size of suspended particles

*Corresponding author. E-mail: profkhan786@yahoo.com.

as determined from SEM micrographs was found to be in the range of 1 to 10 µm. Particles of such size were indicated in the study to remain suspended in the air for long periods of time if not scavenged on account of microphysical processes of the atmosphere. In a later study on Lahore conducted in 1994 to assess any climate change in the area, the role of suspended particulates appeared to be evident because about 0.5°C rise in the average temperature of the city was observed from the analysis of 1950-1992 temperature data (Munir et al., 1995). A group of Pakistani, Portuguese and British scientists studied SPM collected from Lahore (Pakistan), Coimbra (Portugal) and Birmingham (Britain) for knowing their mass concentration, phase and elemental analysis (Smith et al., 1995, 1996; Smith and Harrison 1996 and Harrison et al., 1997). The co-workers reported mass concentrations of SPM and 24 elements in the samples of Lahore (Pakistan), Birmingham (UK) and Coimbra (Portugal). The SPM concentrations in these cities were respectively 607, 47.0 and 52.1 µg/m^3. As we quantified the elements Cu, Cd, Zn, Pb and Ni in the samples we collected, we mention here the mass concentrations of these metals only. Cu was respectively 0.420 and 0.0402 µg/m^3 for Lahore, Birmingham and Coimbra; Cd was respectively 0.00924 and 0.00176 µg/m^3 for Lahore, Birmingham and Coimbra; Zn was respectively 277.0, 0.353 and 0.070 µg/m^3 for Lahore, Birmingham and Coimbra; Pb was respectively 3.920, 0.0091 and 0.0031 µg/m^3 for Lahore, Birmingham and Coimbra, and Ni was respectively 0.0797, 0.0048 and 0.0061 µg/m^3 for Lahore, Birmingham and Coimbra. In another study carried out on Lahore SPM in April 5-10, 2000, SPM concentration (hourly average) as high as 895 µg/m^3 was reported by Pak-EPA/JICA (2001).

In recent years, airborne particulates collected from Lahore during January 2007 to January 2008 were studied by a group of Pakistani and American scientists with the major objectives of samples' chemical characterization and source apportionment, and determination of coarse (PM_{10}: 2.5-10 µm) and fine ($PM_{2.5}$: <2.5 µm) particulates concentrations and toxic metal loadings (Fang et al., 2000; Zhang et al., 2008; Schneidemesser et al., 2010). Their first paper (Zhang et al., 2008) showed that dust was the major contributor to the PM_{10} suspended particulates with minor contributions from man-made sources. The PM_{10} concentration was found to be high with the average value of 459 µg/m^3. In another publication (Schneidemesser et al., 2010), extremely high concentrations of Pb (4.4 µg/m^3), Zn (12 µg/m^3) and Cd (0.077 µg/m^3) were reported. These metals were found to be respectively 84, 98 and 90% in fine particles ($PM_{2.5}$ and smaller). Annual average $PM_{2.5}$ and PM_{10} concentrations were reported to be 194±94 µg/m^3 and 194±94 µg/m^3, respectively, with daily 24-hour maximum concentrations of 410 µg/m^3 and 650 µg/m^3 for $PM_{2.5}$ and PM_{10} respectively (Stone et al., 2010). Coarse aerosol (PM_{10-25}) was dominated by crustal sources like dust (74 ± 16%), whereas fine particles were dominated by carbonaceous aerosol (organic matter and elemental carbon, 61 ± 17%). To determine likely categories for source apportionment, seven factors including a number of industrial sources, re-suspended soil, mobile sources, and regional secondary aerosol were identified explaining 91% of the variance of the measured components (Schneidemesser et al., 2010).

Other important recent references which reported SPM concentrations for Lahore and other Pakistani major cities are Waheed et al. (2005, 2006), Ghauri et al. (2007), Lodhi et al. (2009), Ali and Ather (2010) and Alam et al. (2010). In the study by Waheed et al. (2005, 2006), the SPM levels in Lahore were 1128-1870 µg/m^3. In the study of Ghauri et al. (2007), mean PM_{10} conentrations (24 h - average) were 200 µg/m^3 for Lahore, 193 µg/m^3 for Karachi, 185 µg/m^3 for Rawalpindi and 219 µg/m^3 for Peshawar. Lodhi et al. (2009) reported $PM_{2.5}$ concentrations for Lahore as, 191 µg/m^3 and 143 µg/m^3 respectively in the winter and spring. Ali and Ather (2010), using a high-volume sampler obtained PM_{10} concentrations from a three-day average during the months of April and May and those to be 660 µg/m^3. Raja et al. (2010) worked on Lahore SPM between November 2005 and January 2006 and focused their study for determining percent fine particles ($PM_{2.5}$) concentrations larger than 200 µg/m^3, between 200 µg/m^3 and 100 µg/m^3, and below 100 µg/m^3. They report that for these three ranges, the fine particle concentrations were 36%, 52% and 12% respectively. In a more recent study by Alam et al. (2011), using an optical particle counter found 24-hour average PM10 concentrations for Lahore, Karachi, Rawalpindi and Peshawar respectively as 198, 461, 448 and 540. The corresponding 24-hour average $PM_{2.5}$ concentrations for these cities were 91, 185, 140 and 160 µg/m^3 respectively.

It should be mentioned that the results of the studies on Lahore with particular reference to SPM mass concentration and their phase and elemental analyses are sporadic; the studies were carried out on eight occasions between 1978 and 2010. Some occasional data have also been reported in literature for other major cities of Pakistan, namely Karachi, Quetta, Faisalabad, Gujranwala, Rawalpindi, Islamabad, and Peshawar, but we have mentioned it here. However, SPM mass and elemental concentrations reported in the literature carried out in some major Asian, European and American cities are also reproduced in Table 1 for comparison with Lahore data mentioned above and that we have included in this paper.

The results on Lahore given in this paper were obtained during December 2001 to January 2002 and are compared with the previously reported results, in which some studies were carried out after January 2002. The crux of the comparison is actually to bring on record the pollution situation which prevailed during December 2001 to January 2002 in Lahore. At that time, the authors did not publish

Table 1. Mass concentrations (μg/m^3) of suspended particulates in world's major cities.

Area/City/Country	Fine (PM2.5)	Coarse (PM10)	Reference
Helsinki (Finland)	11.8	12.8	Pakkanen et al. (2001)
Nanjing (China)	481.4	774.5	Wang et al. (2002)
Hon Kong	Daily Ave.: 42.37 – 57.38	Daily Ave.: 73.1 – 83.52	Ho et al. (2003)
Four Locations in Southern Tainan (Taiwan)	**Highest 116.89** 31.0±7.8 40.1±10.8 44.3±9.1	**Highest 125.89** 49.6± 12 62.1±14.5 72.5±16.5	Tsai and Chen (2006)
London and Birmingham (UK)	**43.7±17.1** Mean PM2.5: 8.0	**74.5±14.6** Mean Roadside PM10: 34.7 Mean Urban PM10: 23.2 Ave. PM10:	Harrison et al. (2004)
EU Regions		**11.5** 28 to 42 at urban background	Querol et al. (2004)
Athens, Koebel and New Albany (USA)	**37 to 53 at** Outdoor 13.66± 8.91 13.89±9.29 12.72± 8.86 Indoor 17.20±13.56 14.98 ±12.30	**Kerbsidesites**	Crist et al (2008)
Oslo (Norway)	Mean: 25.4±16.5 Higher conc. in summer: PM2.5, 27.9±8.7 (2004) and 27.8±9.7 (2005). Lower concentration in winter PM2.5 21.0±13.0 (2004/2005) and 21.4±21.9 (2005/2006)	**16.52 ±13.53** Mean: 35.0±17.7 Higher conc. in summer: PM10, 38.7±10.8 (2003); Lower concentration in winter PM10 28.7±22.5 (2003/2004);	Lazaridis et al. (2008)
Leicester (UK)	10.9 ±5.7	22.1 ±9.8	Gulliver and Briggs (2007)
A traffic sampling site (Central Taiwan)	Daytime daily ave.: 39.17 Nighttime daily ave.: 37.15	Daytime daily ave.: 34.35 Nighttime daily ave.: 33.72	Fang et al. (2006)

the results as little was known about the pollution scenario of Lahore. Measurement of suspended particulate matter (SPM) in air, is often difficult; partly because of the variety of the compound phases and trace metals of potential concern, and partly due to the variety of available experimental techniques for sample collection and lack of standardized and documented methods. The compendium is one of the three compendia of methods which produce documented and technically reviewed methodology for determining concentrations of selected pollutants of special interest in the ambient air of Lahore, Pakistan. The methods contained in this compendium provide cost-effective sampling procedures for suspended particulate matter. These methods are provided only for consideration of researchers to use in applications for which they may be deemed appropriate. Especially, these methods are not intended to be associated with any specific regulatory monitoring purpose and are offered with no specific endorsement for fitness and recommendation for any particular application; other than for an attempt at standardization. This manuscript has been submitted for publication to provide easiest approach for sample collection and information transformation to facilitate the scientific community and young researchers involved in atmospheric and Environmental Physics related studies, especially, in under-developed and developing countries like Pakistan.

SAMPLING AND METHODOLOGY

Sampling of outdoor, indoor suspended particulate matter and free fall dust

Samples of three different categories were collected from various locations of the metropolitan city of Lahore. Those are outdoor suspended particulates (SPM), indoor suspended particulate matter (SPM) and freely falling dust (FFD). A portable high volume sampler was used to collect outdoor SPM samples at thirteen different sites and indoor SPM at five locations. Whatman 41 cellulose and Millipore glass filters were used to capture the particulates. Air was drawn through the sampler by an inbuilt sucking pump for the durations of an average period of 8 h and 24 h. Flow rate was initially set at 38 l/min which gradually decreased due to clogging of filters but was kept close to it. The range of the sampling rate however remained in the range of 28-38 l/min. At all sites/locations, sampling was accomplished keeping sampler at the same height. The sampling was carried out during the months of December 2001 and January 2002. The filters were dried in oven at about 105°C before sampling and then analyzed to compute metallic loadings in $\mu g/m^3$. During the sampling of particulate matter, meteorological parameters like temperature, relative humidity, atmospheric pressure, wind speed and wind direction were also recorded.

Indoor SPM was collected on air conditioners filters installed in the houses. Dusts from the floor carpets and house courtyards were also collected from some houses in the sampling locations. Prior to collection of particulates from indoor air, air conditioner filters were cleaned and washed. The particulate matter deposited on the filters during the summer of 2002 were collected and strained for removal of fibrous material. Likewise, vacuum cleaners were also cleaned and washed before using them to suck carpet and courtyard dust.

In order to determine the deposition flux for free fall dust, falling dust was also collected using open plastic buckets wetted with de-ionized water to facilitate the capturing of gravitationally settling particles.

Method of analysis

Trace metal/Element analysis using AAS technique

Trace element contents of the samples of all categories were determined using Atomic Absorption Spectroscopy (AAS). A Shimadzu Atomic Absorption/Flame Spectrophotometer (Model No.AA-630-12) was employed for the analysis.

Phase analysis of samples using XRD technique

Identification of phases in all categories of samples was determined by the X-ray Diffraction (XRD) technique. The samples were then kept in dry bottles before their XRD analyses were carried out. A Siemens Powder X-ray Diffractometer (Model D 5000) was employed in the present study. Each sample was pressed gently to make pellets and then loaded in the diffractometer goniometer. Qualitative phase analysis was carried out at the Center for Excellence in Solid State Physics, University of the Punjab, Lahore, employing the Hanawalt method and using the Powder Diffraction File of the International Commission of Diffraction Data.

RESULTS

Mass concentration of suspended particulate matter

Daily average concentration (eight-hourly mean) of all SPM samples collected from different locations in the metropolitan city of Lahore was determined from the sampling flow rate and the sampling time. The results are given in Table 2 and plotted in Figure 1. The mean concentration of SPM varied from 670 $\mu g/m^3$ to 1523 $\mu g/m^3$ with an overall average value of 1091±260 $\mu g/m^3$. The lowest concentration of 670 $\mu g/m^3$ was found for Mozang Chungi whereas the highest concentration of 1523 $\mu g/m^3$ was found for City Railway Station. These concentrations are one to three times higher than Pak-EPA (twenty-four hourly) standard value for SPM which is 500 $\mu g/m^3$ (Pak-EPA, 2012). However SPM concentrations reported previously for Lahore were between 332 and 749 $\mu g/m^3$ (WHO, 1984), 607 $\mu g/m^3$,

Table 2. Concentration of total suspended particles at different locations.

Location	Daily Average Concentration* (µg/m^3) with SDEV
Walton	860
Shadman	1350
Town Ship	745
Misri Shah	1192
Charring Cross	1192
City Railway Station	1523
Bhatti Chowk	854
Mozang Chungi	670
Niazi Chowk	1308
Shehzan Factory (Bund Road)	1104
Chauburji Chowk	1210
Mean with Standard Deviation	1091±260

*Daily mean value for one month.

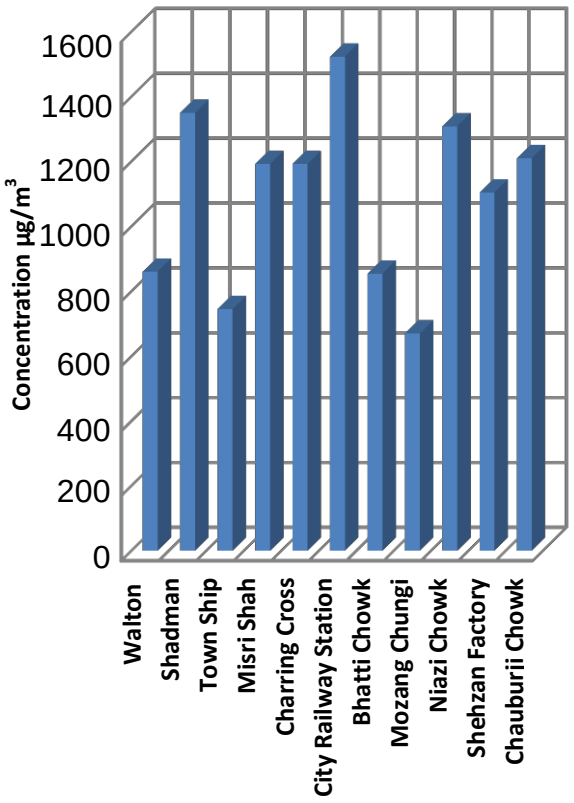


Figure 1. Concentration of SPM (Daily averages for a month).

590 µg/m^3 and 838 µg/m^3 respectively for Lahore city centre, industrial and rural locations (Smith et al., 1995, 1996; Harrison et al., 1997), 895 µg/m^3 (Pak- EPA/JICA, 2001), and 1128-1870 µg/m^3 (Waheed et al., 2006). The later data reported for Lahore specified PM_{10} and $PM_{2.5}$ show SPM concentrations as 851 µg/m^3 (PM_{10}: 660 µg/m^3; $PM_{2.5}$: 191 µg/m^3) (Lodhi et al., 2009) and 289 µg/m^3 (PM_{10}: 198 µg/m^3; $PM_{2.5}$: 91 µg/m^3) (Alam et al., 2011). The present concentrations are also much higher than these data. All SPM values reported in the literature cited above and the present result are higher than the Pak-EPA current SPM Pak-EPA Standards. The present SPM mass concentrations are also compared with the major world cities concentrations of PM_{10} and $PM_{2.5}$ (Table 1). The present concentrations are much higher than the word data except for Beijing (China); these later concentrations are comparable to the present data.

All SPM samples were analyzed by the X-ray Powder Diffraction (XRPD) Technique to determine the constituent phases and by Atomic km^2/month. The average contents of dust are six times higher than the permissible limits (5 tons/km^2/ month) (Ahmad et al., 2006).

Elemental analysis of outdoor suspended particulate matter (High volume air sampler and open bucket method)

Elemental concentrations of the outdoor particulate matter are given in Table 4. The Pb content matter Absorption Spectroscopy (AAS) was used to determine the metallic traces. The XPRD results show that in all the samples the phases present in variable amounts are the soil-derived minerals, namely: Quartz, Illite, Calcite, Cholrite, Albite, Talc and Gypsum. Kaolinite was not however indicated in any SPM sample. These results are in agreement with many similar studies reported previously.

Free fall dust flux using open bucket method

Freely falling dust was collected using open plastic buckets wetted with de-ionized water to facilitate capturing of the falling particles. The deposition rate of freely falling dust for all the sampling sites are given in

Table 3. Deposition flux of free fall dust at different locations.

Location	Free fall dust	
	Tons/km^2/month	Tons/km^2/year
Walton	23.9	286.9
Shadman	32.0	384.0
Town Ship	30.0	360.0
Misri Shah	45.0	540.0
Mozang Chungi	20.0	240.0
Shehzan Factory	42.0	504.0
Chuburji Chowk	22.0	264.0
Mean with Standard Deviation	30.7±9.7	368.4±117.0

Table 4. Elemental concentration in suspended particles from different locations.

Location	Concentration (µg/m^3)				
	Cu	Zn	Cd	Pb	Ni
Walton	0.1	0.2	ND	0.7	ND
Shadman	0.07	0.4	ND	2.5	ND
Town Ship	0.2	1.0	0.02	3.0	ND
Misri Shah	0.4	1.4	0.02	6.1	ND
Chairing Cross	0.1	1.1	ND	4.5	ND
Ichhra	ND	1.0	ND	1.3	ND
Bhatti Chowk	0.1	0.9	0.07	5.0	ND
Mozang Chungi	0.06	0.3	ND	3.8	ND
Shehzan Factory (Bund Road)	0.4	1.0	ND	3.7	ND
Chuburji Chowk	0.3	0.8	ND	4.0	ND
Rang Mahal	0.1	0.9	0.02	5.5	ND
Mean with SD	0.19±0.14	0.79±0.40		3.7±1.5	

ND: Not Detected.

Table 3. Phase analysis carried out by the XRPD technique indicated the same minerals as detected in the SPM samples. Table 3 shows that the rate of deposition of free fall dust at different sites varied from 20 tons/km^2/month to 45 tons/km^2/month with the average value of 30.7 tons/km^2/month as given in Table 4. The Pb content appears to fall in the range of 0.7 to 6.1 µg/m^3 and much higher than the Pak-EPA 2012 standards for Pb in the ambient air (annual average: 1 µg/m^3 and 24-h average: 1.5 µg/m^3. Concentrations of Cu and Zn were respectively found as 0.19±0.14 and 0.79±0.40 µg/m^3. As permissible values of these elements were not available in literature, we have nothing to compare with the present data. Elemental loadings of free fall dust are recorded in Table 5 which shows high values of Pb in the samples ranging from 81 to 724 µg/m^3. High lead content of both SPM and free fall dust is evidently due to voluminous traffic size and use of high lead content fuel. The high content of lead in petrol is a serious issue, as the end product of it is the release of lead into the environment. In Pakistan presently, the lead content in regular super premier and HOBC petrol is reported to be 0.63 and 0.84 g/L, respectively (Baluchistan Conservation Strategy, 2000; Lovei, 2000).

Elemental analysis of indoor suspended particulate matter (Using AC filters and vacuum cleaners)

As mentioned in the methodology, indoor suspended particles were collected using air conditioner filters. Dust was also collected from carpets using pre-cleaned vacuum cleaner. The elemental analyses of both types of samples collected from all sites are given in Tables 6 and 7 respectively. These loadings are also plotted in Figures 5 and 6 respectively. Here again in both types of these samples, the Pb loadings are the highest; in the range of 14 to 979 mg/kg for AC filters and 79 to 390 gm/kg for carpet dust. Pb concentrations in all types of samples are also plotted in Figure 7 for mutual comparison. We find that Pb concentrations are much higher in free fall dust, AC dust and carpet dust than in the SPM samples.

Table 5. Element Loadings of Free Fall Dust

Locations	Concentration of elements in free fall dust (µg/m^3)				
	Cu	Zn	Cd	Pb	Ni
Walton	**21**	**26**	**0.4**	**81**	**10**
Shadman	**24**	**23**	**0.8**	**280**	**40**
Township	**76**	**24**	**0.8**	**764**	**30**
Mozang Chungi	**22**	**30**	**0.5**	**124**	**19**
Shehzan Factory	**80**	**30**	**0.7**	**724**	**35**
Chauburji Chowk	**230**	**50**	**1.2**	**590**	**30**
Mean with SD	**75.5±80.5**	**30.5±10.0**	**0.73±0.30**	**427.2±303.8**	**27.3±11.0**

Table 6. Elemental loadings of A.C. filters.

Location	Concentration of elements in A.C. Filter Dust (mg/kg)				
	Cu	Zn	Cd	Pb	Ni
Walton	24	23	0.4	14	14
Shadman	63	23	0.4	130	9
Township	17	23	1.0	240	19
Misri Shah	12	25	1.5	520	21
Charring Cross	15	24	2.0	979	29
Mean with SD	26.2±21.0	23.6±0.9	1.06±0.69	376.6±385.5	18.4±7.5

Table 7. Elemental loadings of carpet dust.

Location	Concentration of elements in Carpet Dust (mg/kg)				
	Cu	Zn	Cd	Pb	Ni
Walton	13	13	0.4	75	15
Shadman	16	21	0.3	190	15
Township	11	18	0.3	70	28
Misri Shah	23	22	0.5	142	18
Chairing Cross	28	26	0.3	390	30
Mean with SD	18.2±7.1	20.0±4.8	0.36±0.09	173.4±130.9	21.2±7.3

DISCUSSION

The average concentration of SPM at various sites in Lahore was 1092±272 µg/m^3 which is much higher than the Pak-EPA standard values made public in January 2012. The average deposition flux of free fall dust was 30.7±97 tons/km^2/month, which is also much higher than the permissible value of 5 tons/km^2/month. Higher SPM and Free Fall Concentrations (Figures 2 and 3) can be attributed to all types of vehicular traffic plying on roads with 'kacha' road sides. As the number of vehicles has increased many fold in recent years, all vehicles in general and those with poor conditions in particular release suit particles and are thus another big source of airborne particulate matter (Valipour et al., 2013; Valipour, 2012a, b).

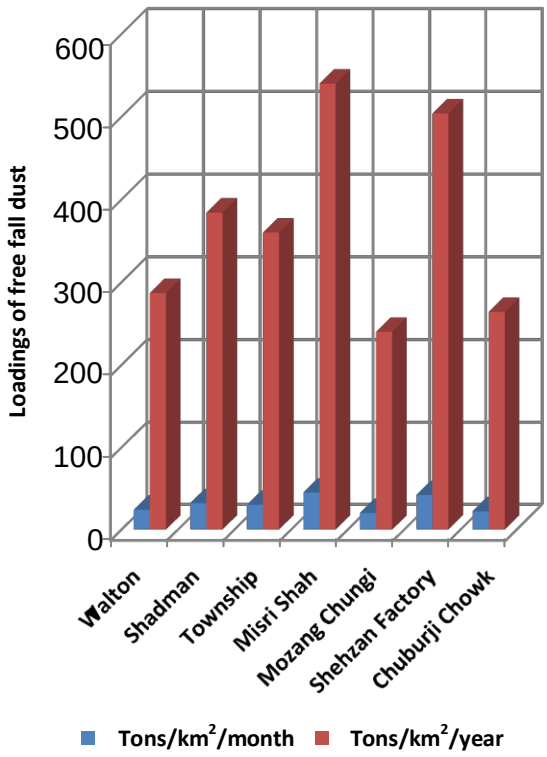


Figure 2. Deposition flux of free fall dust.

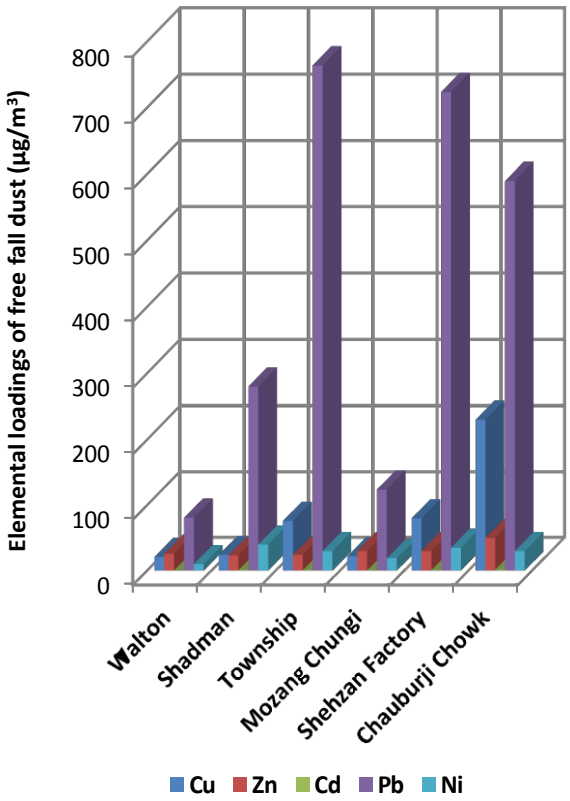


Figure 4. Elemental loadings of free fall dust.

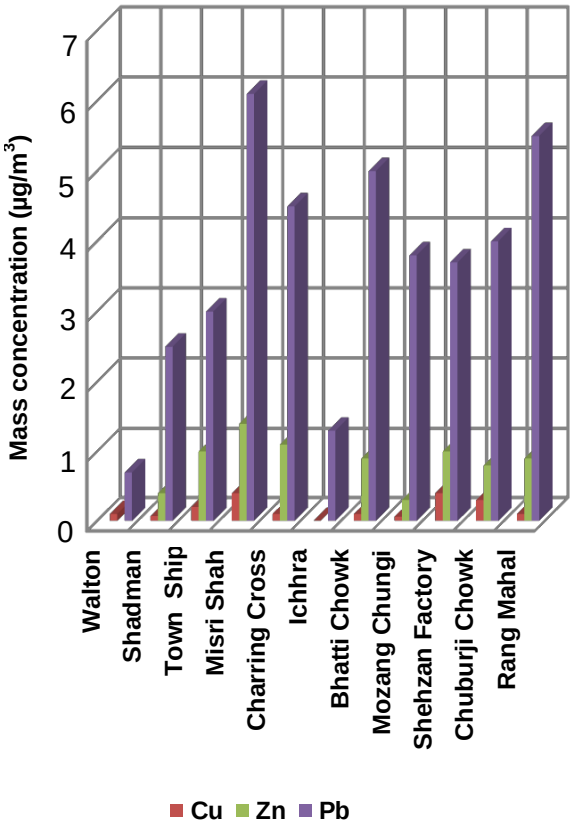


Figure 3. Elemental concentrations in SPM samples.

The elements detected in SPM (Figure 5) show that the Pb concentrations are several times higher than other elements, namely Cu and Zn and also higher than allowable Pb concentrations (Pak-EPA, 2012). The major source of Pb is the heavy vehicular traffic plying about 18 h a day on city roads which use petrol and diesel as fuels. There are several sources of Cu, Cd and Zn including brake lining, burning of fossil fuels in motor vehicles and industrial/urban areas, flyash of power plants, rubber tyres and asphalt (ECE, 2007; Sorme et al., 2001; Davison et al., 1974 and Richard et al. 1974).

Concentrations of Pb, Cu and Zn are also plotted separately against SPM concentrations in Figures 8, 9 and 10 respectively. The Pb concentrations appear to show almost a positive correlation with the SPM concentrations for all samples. There is no correlation between Cu and SPM concentrations and Zn and SPM concentrations for all samples. It appears therefore that the suspended particulates derive their Pb loadings from some potential source like leaded petrol, the consumption of which has increased manifold during recent years because of larger number of vehicles plying on the Lahore city roads. The sources of Cu and Zn do not appear to be permanent; they vary from place to place in the city (Valipour, 2012, Valipour et al., 2012).

It is evident from Figure 4 showing elemental loadings of free fall dust that the Pb concentration is higher than the other elements. Like SPM samples, Pb and Ni

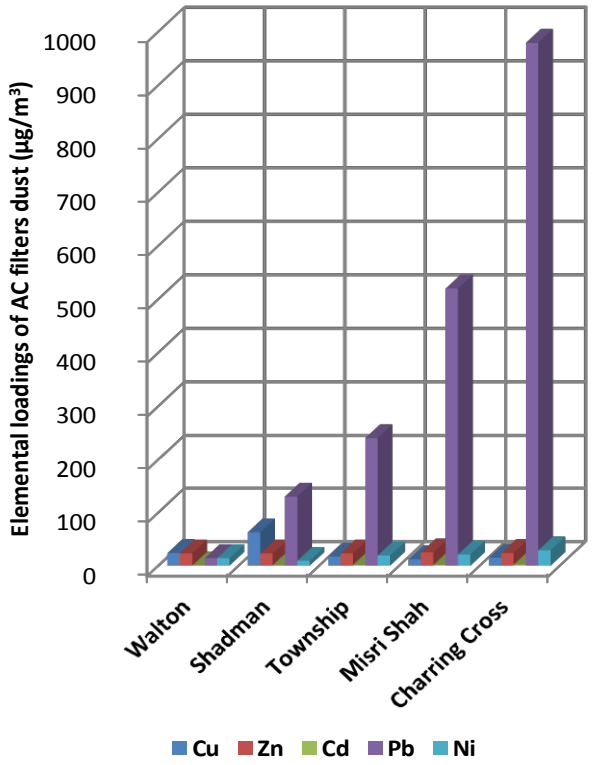


Figure 5. Elemental loadings of A.C. filters dust.

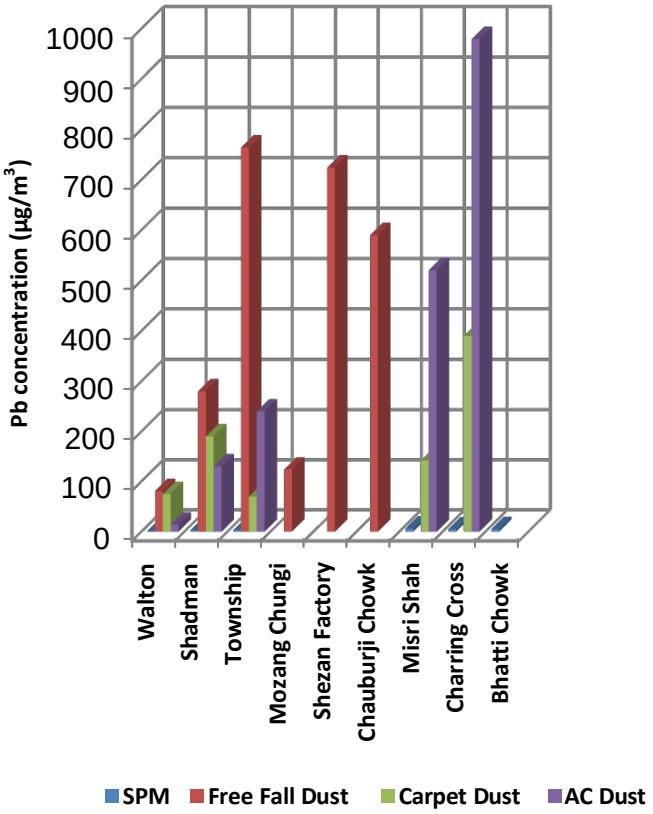


Figure 7. Pb concentrations in all types of samples.

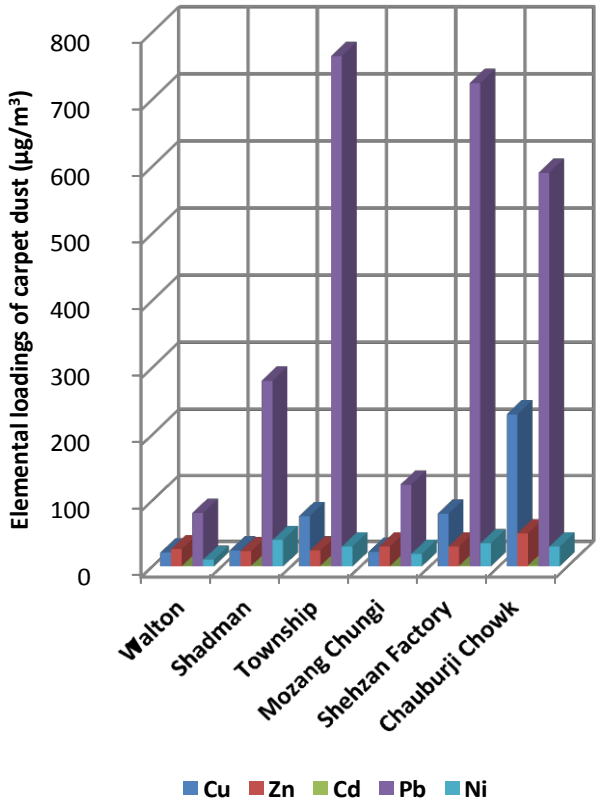


Figure 6. Elemental loadings of carpet dust.

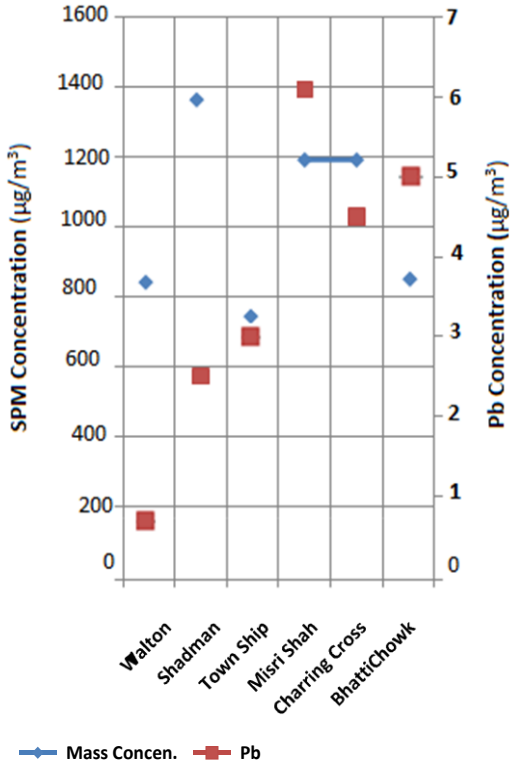


Figure 8. Pb concentrations in SPM samples

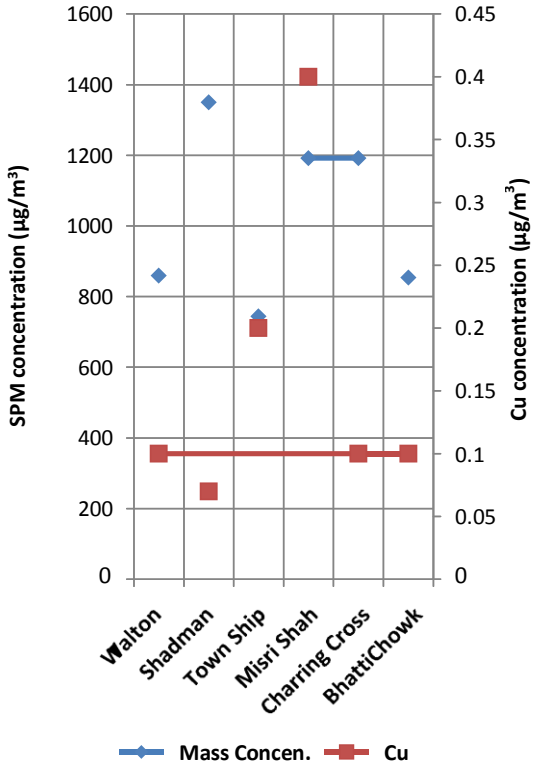


Figure 9. Cu concentrations in SPM samples.

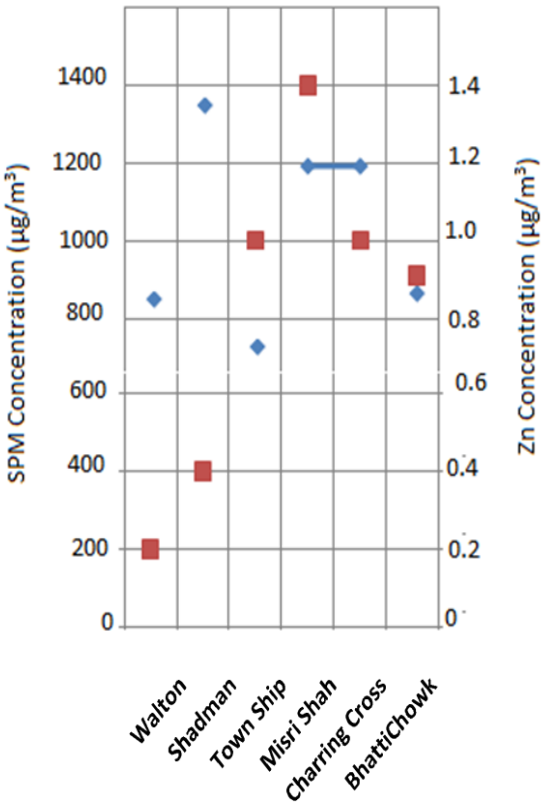
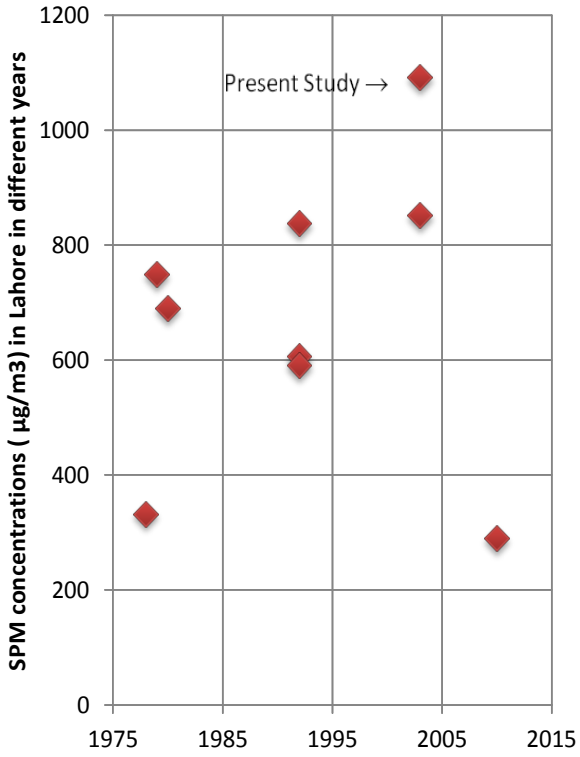


Figure 10. Zn concentrations in SPM samples



(Courtesy: WHO, 1984: *1978, 1979, 1980*; Smith et al 1995, 1996 and Harrison et al 1997: *1992*); Lodhi et al 2009: *2003;* Alam et al 2011: *2010*)

Figure 11. Comparison of present SPM concentration with data published before and after the Year 2003

loadings of the free fall dust appear to exhibit a positive correlation with the dust concentration. Elemental analysis of AC dust samples and carpet dust samples also show Pb as highest of all the elements detected in these samples (Figures 5 and 6).

Comparison of the present SPM mass concentrations with similar data reported earlier and after 2003 (Figure 11) indicates higher SPM concentrations in the present study. Because of scarcity of the data points, it is not possible to comment on the variability of the SPM concentrations over the years.

The present study shows that the SPM average (24-h) concentration in Lahore is 1091±260 µg/m^3 and the average (24-h) concentration of Pb is 3.7±1.5 µg/m^3. The present particulate matter concentration values are much higher than those given in Table 1 and in air quality standards of Pak-EPA (2012) (SPM: 500 µg/m^3), India-NAQS (2009) (SPM: 500 µg/m^3-Industrial; 200 µg/m^3-Residential), US-NAAQS (2012) (PM10: 150 µg/m^3; PM2.5: 35 µg/m^3), WHO-AAQS (2011) (PM10: 50 µg/m^3; PM2.5: 10 µg/m^3), and ECE-AAQS (2013) (PM10: 50 µg/m^3). The Pb concentrations found in the present study are also much higher than the standard values for Pak-EPA (2012), US-NAAQS (2012) (2 µg/m^3-2011, 24-h

standard; 1.5 µg/m^3-2012, 24-h standard), India-NAQS (2009) (1.0 µg/m^3-24-h standard of 1994), WHO-AAQS (2011) (0.35 µg/m^3, 24-h upper assessment threshold; 0.25 µg/m^3, 24-h lower assessment threshold), and ECE (2013) (0.5 µg/m^3). It needs to be mentioned that the higher concentration of SPM measured in 2003 appears to be due to construction of the ring road around the entire Lahore metropolitan city. The total length of the ring road is around 80 km. As mentioned above, the SPM concentrations before and after 2003 are much lower than the 2003-values.

The study indicates that the major sources of air pollution in Lahore appear to be both natural and anthropogenic; heavy vehicular traffic plying on roads in Lahore and road side dust and several industrial units, small and large, situated around Lahore mostly along 'bund' road part of the ring road and Kot Lakhpat Industrial Estate not only cause higher concentration of SPM but also add Pb and other metals such as: Cd, Ni, Cu, Zn, etc., into the air through burning of fossil fuels and industrial activities. It needs to be mentioned that the vehicle population in Lahore has been growing at the rate of 10% with 72% of vehicles being diesel driven (PEPD, 2000). Air pollution, therefore, appears to be one of the rapidly growing environmental problems in the metropolitan city of Lahore.

Contrary to previous studies, it was found that the SPM samples, collected from different methods, have almost same identified phases and trace metals. This indicates that the environment has its own local zones where the climatology and meteorology has no significant effect on dispersion of SPMs, that is, uniformity and homogeneity of the environment is confirmed. Furthermore, same compositions and trace metals make up of the suspended particulate matter also confirms that the three methods used in this study serve the same purpose. Hence, one can use the method of his own choice, keeping in view the availability of the funds in hand and according to the prevailing conditions of the study. In this way, this study will prove to be a breakthrough towards cost-effectiveness for the under-developed and developing countries, especially, Pakistan (Shahid et al., 2013a, b, c, d, 2014).

Conclusion

Daily eight-hourly mean concentrations of SPM were found to vary from 670 to 1523 µg/m^3 with an average of 1091 µg/m^3. These concentrations are higher than the 24-h standards for Pakistan (550 µg/m^3; 500 µg/m^3 (Pak-EPA, 2012)). These concentrations are found to be much higher than the permissible limits provided in the air quality standards of India, US, and ECE. Minerals like Quartz, Illite, Calcite, etc., were found in all the SPM samples.

Elemental analysis showed an alarmingly high Pb content in the suspended particulate matter, free fall dust, dust of air conditioner filters, and carpet dust. Heavy vehicular traffic and industrial units located along the 'bund' road and in Kot Lakhpat appear to be the contributors to the high Pb content in all types of samples.

In a nutshell, it is possible to conclude that all methods can be used for sample collection. However, the choice must be made between one and the other to obtain specific results. Additional testing and comparison of all methods is proposed to obtain more confidence with results and conclusions.

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