

## Comparison of Two Extraction Methods for Metals from Atmospheric Particulate Matter

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**Summary:** Particulate pollution in ambient air of Lahore is a serious problem. Atmospheric particulates concentrations (PM<sub>10</sub>) were measured at the city centre during February to April 2007, which ranged between 465 and 806 µg/m<sup>3</sup> with an average of 602 µg/m<sup>3</sup>, about an order of magnitude greater than the World Health Organization guideline value of 50 µg/m<sup>3</sup>. Metal and metalloid components of particles have been shown to be of greater health significance, especially the water soluble species. A number of methods have been used to extract the total and water soluble species. In the present study one method each was evaluated for total and water soluble metals (cadmium, chromium, lead, nickel, and mercury), and metalloid species (antimony and arsenic). Segments from the same filter were used for the two methods. Concentrated acids with microwave digestion were used for total concentrations whereas water soluble species were extracted by shaking for 2 hours in one percent HCl solution. The latter method worked as well as the former for cadmium, lead, and antimony, giving about the same concentrations with good correlations. However, for the remaining elements water soluble concentrations were generally lower than the strong acid extractions, indicating lower bioavailability of such elements. Majority of the values for total as well as water soluble cadmium and lead concentrations exceeded the WHO guideline values whereas for other elements the concentrations in both fractions were within acceptable limits.

### Introduction

A number of studies in recent past have found evidence of a link between adverse effects of particulate matter in ambient air and mortality [1-3]. Schwartz *et al.* [4], Touloumi *et al.* [5] and Pope *et al.* [2] reported associations between daily concentrations of airborne particles and daily deaths. Based on the magnitude of the regression coefficients, they concluded that particulate air pollution was responsible for 50,000 to 100,000 early deaths per year in the United States, and for similar numbers in Europe. World Bank [6] also reported the results of two independent analyses, which estimated that urban air pollution in India could be responsible for about 40,000 premature deaths annually primarily due to human exposure to elevated levels of particulate matter. Delhi was identified as the city having the highest mortality figure of about 7,500 deaths per annum.

Quantifying the impact of particulates on mortality, US Environmental Protection Agency (USEPA) [7] reported a 3–8 percent increase in relative risk of death with an increase in the

concentration of PM<sub>10</sub> of 50 µg/m<sup>3</sup>. PM<sub>10</sub> is particulate matter with an aerodynamic diameter of up to 10 µm, *i.e.* the fine and coarse particle fractions combined. Associations with mortality were also observed at mean PM<sub>10</sub> concentrations well below the US National Ambient Air Quality Standard (NAAQS) of 150 µg/m<sup>3</sup> (24-hr average). Other estimates of the overall mortality risk associated with an increase in PM<sub>10</sub> levels of 10 µg/m<sup>3</sup> were reported as 0.74 percent by Maddison [8], 1 percent by Dockery and Pope [9] and 1.23 percent by Ostro [10]. World Bank [11] used an average of 1 percent to estimate the impacts of air pollution on total mortality in Delhi.

The metal content of airborne particulate matter has frequently been implicated as a possible harmful component in toxicological studies. Water soluble metal compounds have been shown to impact health by various pathways, which have been discussed by a number of researchers [12-18]. The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs)

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also list metals and metalloids having soluble TLVs, which are updated and published annually [19]. Similarly, a large number of studies have reported the "total" metal concentration of urban airborne particulates [12, 20-24].

"Total" and "soluble" metals are, in practice, operationally-defined quantities because the measured concentration of metal can depend on the exact method of analysis [12]. Various methods have been used for the determination of such fractions. In the present study, one method each was evaluated for extracting "total" and "water soluble" metals (cadmium, chromium, lead, nickel, and mercury), and metalloid species (antimony and arsenic) from PM<sub>10</sub> collected in Lahore, Pakistan, using segments cut from the same filter. For "total" metals, microwave oven assisted acid extraction was used while the "water soluble" fraction was extracted by 1 percent HCl solution. The former method was based on an earlier study [20] whereas 1 percent HCl solution has been used as extraction solvent for soluble metals in occupational hygiene samples [19].

## Results and Discussion

### PM<sub>10</sub> Concentrations

PM<sub>10</sub> concentrations were measured in the range of 465 µg/m<sup>3</sup> to 806 µg/m<sup>3</sup>, with the average of 12 samples being 602 ± 103 µg/m<sup>3</sup>. The results, along with the weather conditions, during and before sampling, are presented in Table-1. Thus, all the recorded values were about an order of magnitude higher than the 24-hr World Health Organization (WHO) guideline value of 50 µg/m<sup>3</sup> for PM<sub>10</sub> [25]. These values are greater than those reported for Lahore by Zhang *et al.* [26] for year long

measurements during 2007 (158 to 733 µg/m<sup>3</sup> with an average of 361 µg/m<sup>3</sup>) and by Ghauri *et al.* [27] during 2003 to 2004 (average of 200 µg/m<sup>3</sup>). The sampling sites for the latter two studies, however, were different.

### Total and Water Soluble Metals Concentrations in PM<sub>10</sub> Samples

The two extraction methods were evaluated for determining the concentrations of heavy metals cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), and mercury (Hg) and metalloids antimony (Sb) and arsenic (As), using segments cut from the same filter. These elements were selected due to their release into ambient air by various anthropogenic activities (like vehicular traffic and power generation) and their health significance. The concentrations determined in the extracts were translated into concentrations in ambient air, which are shown in Table-2. The health significance of the analysed elements, concentrations obtained by the two extraction methods of each element and the correlations are briefly discussed.

The Agency for Toxic Substances and Disease Registry [28] details health effects for inhaled cadmium, which include possible DNA damage and increased risk of lung cancer and death; intense irritation of respiratory tissue; may accelerate the development of emphysema in smokers; may result in calcium deficiency, osteoporosis, or osteomalacia from long-term occupational exposure to high levels of cadmium. There is very strong evidence that the kidney is the main target organ of cadmium toxicity. It is classified as a probable human carcinogen by USEPA. The WHO guideline value for annual average is 5 ng/m<sup>3</sup> [29].

Table-1: PM<sub>10</sub> Concentrations in ambient Air of Lahore (February to May 2007).

Sampling Date	PM <sub>10</sub> µg/m <sup>3</sup>	Weather Conditions Before and During Sampling*
23-Feb-07	806	Temp. 11.2 - 23 °C; R.H. 37 - 76 %; Wind: Day-calm; Night-W 5 k; Rain - Nil.
01-Mar-07	667	Temp. 12 - 19.7 °C; R.H. 56 - 77 %; Wind: Day-NE 4 k; Night-NW 3 k; Rain - Nil.
07-Mar-07	611	Temp. 12.6 - 24.3 °C; R.H. 29-67%; Wind: Day-NW 5 k; Night-NW 7 k; Rain - Nil.
13-Mar-07	535	Temp. 14.6 - 18 °C; R.H. 68-95 %; Wind: Day-S 2 k; Night-N 4k; Rain - 22.4 mm.
19-Mar-07	563	Temp. 18.7 - 28.2 °C; R.H. 66-81 %; Wind: Day-calm; Night-SE 5 k; Rain - Nil.
25-Mar-07	465	Temp. 17.5 - 28.7 °C; R.H. 37-68 %; Wind: Day-calm; Night-SW 5 k; Rain - Nil.
31-Mar-07	507	Temp. 23.5-35.2 °C; R.H. 36-76 %; Wind: Day-E 3 k; Night-calm; Rain - Nil.
06-Apr-07	590	Temp. 22-33.1 °C; R.H. 28-50 %; Wind: Day-calm; Night-W 4 k; Rain - Nil.
12-Apr-07	590	Temp. 24.4-38.1 °C; R.H. 20-54 %; Wind: Day-W 2 k; Night-SW 3 k; Rain - Nil.
18-Apr-07	703	Temp. 24.2-40.4 °C; R.H. 33-58 %; Wind: Day-NE 9 K; Night-SE 5 K; Rain - Nil.
24-Apr-07	482	Temp. 25.7-38.6 °C; R.H. 21-32 %; Wind: Day-NE 7 k; Night-SW 4 k; Rain - Nil.
30-Apr-07	709	Temp. 27-42.3 °C; R.H. 19-38 %; Wind: Day-calm; Night-NW 7 k; Rain - Nil.
Average	602	
Std Dev	103	

\*Source: Regional Meteorological Department, Jail Road, Lahore.

Table-2: Total and Water Soluble Concentrations of Selected Metals and Metalloids in Ambient PM<sub>10</sub> in Lahore (Feb-May 2007).

DATE	PM <sub>10</sub> µg/m <sup>3</sup>	Cd (ng/m <sup>3</sup> )		Cr (ng/m <sup>3</sup> )		Pb (ng/m <sup>3</sup> )		Sb (ng/m <sup>3</sup> )		As (ng/m <sup>3</sup> )		Ni (ng/m <sup>3</sup> )		Hg (ng/m <sup>3</sup> )	
		ACID	WATER	ACID	WATER	ACID	WATER	ACID	WATER	ACID	WATER	ACID	WATER	ACID	WATER
23-Feb-07	806	2.4	2.6	25.0	21.4	221	276	43.6	8.0	692	343	47.6	15.9	BDL*	24.3
01-Mar-07	667	57.0	55.1	52.5	35.9	520	501	6.6	25.3	813	140	55.4	22.8	0.5	5.3
07-Mar-07	611	11.0	0.1	40.1	28.4	647	786	11.9	12.2	254	162	59.9	27.3	4.8	BDL*
13-Mar-07	535	28.2	38.3	39.0	41.2	1690	2780	57.7	BDL*	165	12	58.3	30.5	9.7	14.5
19-Mar-07	563	19.7	7.5	26.7	11.7	1380	1480	34.2	148	161	186	79.0	46.4	12.6	2.1
25-Mar-07	465	9.3	1.5	16.9	23.1	47	196	143	BDL*	858	305	40.5	12.3	84.8	9.7
31-Mar-07	507	3.4	4.3	23.0	0.0	472	433	194	70.0	83	346	63.3	6.0	87.5	23.3
06-Apr-07	590	45.9	54.7	53.0	8.6	1870	1890	61.0	8.0	323	32	17.6	15.0	78.7	11.7
12-Apr-07	590	12.0	10.9	28.3	5.3	2670	2650	83.5	22.1	963	127	35.0	9.7	64.4	5.1
18-Apr-07	703	58.5	69.3	31.8	11.1	1210	1260	286	195	207	109	84.8	21.7	43.6	48.5
24-Apr-07	482	28.0	34.8	31.8	8.6	1910	1860	286	250	886	130	64.6	26.0	56.4	4.7
30-Apr-07	709	8.3	18.9	30.7	15.7	832	779	364	257	692	343	25.6	10.5	48.5	24.3
AVG	602	23.6	24.8	33.2	17.6	1120	1240	131	82.8	508	186	52.6	20.3	41.0	14.4
STDEV	103	20.2	24.6	11.1	12.6	800	897	123	101	336	120	20.3	11.3	34.1	13.8
CORREL		0.950		0.369		0.939		0.823		0.197		0.605		0.143	

\*BDL – Below detection limit.

The “total” concentration of Cd was measured in the range of 2.4 ng/m<sup>3</sup> to 58.5 ng/m<sup>3</sup> with an average of 23.6 ng/m<sup>3</sup>. Only 2 of the 12 readings were below the WHO guideline value. The “water soluble” concentrations were recorded in the range of 0.1 ng/m<sup>3</sup> to 69.3 ng/m<sup>3</sup>, (the average being 24.8 ng/m<sup>3</sup>) with one-third values being less than 5 ng/m<sup>3</sup>. The average values for the two sets of readings (23.6 ng/m<sup>3</sup> and 24.8 ng/m<sup>3</sup>) are very close and there is also good correlation between the two sets (correlation coefficient of 0.95). Thus, it can be seen that the relatively simple method (1% HCl with 2 hour shaking) is as effective as the more rigorous method using concentrated acids and microwave digestion for the extraction of Cd from airborne PM<sub>10</sub>.

Lead (Pb) is a common toxic pollutant whose health effects are discussed in detail by the Agency for Toxic Substances and Disease Registry [30]. The concentration of “total” lead determined for the 12 samples varied between a minimum of 47 ng/m<sup>3</sup> and 2670 ng/m<sup>3</sup> with the average being 1120 ng/m<sup>3</sup>. The “water soluble” concentrations for Pb ranged between 196 ng/m<sup>3</sup> and 2780 ng/m<sup>3</sup> with the average of 1240 ng/m<sup>3</sup>. Three-fourths of the readings, from each set, exceeded the WHO guideline value in air of 0.5µg/m<sup>3</sup> or 500 ng/m<sup>3</sup> [29]. This is in spite of the discontinuation of lead as an additive in gasoline since 2002. The two averages are fairly close to each other and the two data sets also show a good correlation with coefficient of 0.94.

Antimony (Sb), a metalloid, and its compounds when inhaled may cause a number of health effects including inflammation of the lungs due to the irritation, alterations in pulmonary function

(airway obstruction, bronchospasm, and hyperinflation), increased blood pressure and altered EKG readings, gastro intestinal disorders (abdominal pain, diarrhoea, vomiting, and ulcers) [31]. Occupational Safety & Health Administration (OSHA) and the USEPA have set limits for Sb in air at 0.5 mg/m<sup>3</sup> [31]. The concentration of “total” Sb measured in Lahore samples varied between 7 ng/m<sup>3</sup> and 364 ng/m<sup>3</sup> with an average of 131 ng/m<sup>3</sup>, all values being less than the US limits. The “water soluble” concentrations were measured between BDL (below detection limit) and 257 ng/m<sup>3</sup> with an average value of 83 ng/m<sup>3</sup>. The correlation between two sets of concentrations was quite good at 0.823 indicating that the simpler method could be used for its determination instead of the more rigorous method.

Nickel is considered as possibly carcinogenic to humans (classified in group 2B) and its compounds as carcinogenic to humans (in group 1) by International Agency for Research on Cancer (IARC), and also by the US Department of Health and Human Services [32]. WHO [29] gives cancer risk estimate for a life time exposure to a concentration of 1 µg/m<sup>3</sup> of Ni compounds as unit risk factor of 4.0 x 10<sup>-4</sup>. ACGIH gives a threshold limit value of 1.5 mg/m<sup>3</sup> (8-hr average) for elemental Ni and 0.1 mg/m<sup>3</sup> for soluble inorganic compounds. The concentrations of “total” Ni were measured in the range of 18 ng/m<sup>3</sup> to 85 ng/m<sup>3</sup> with an average of 53 ng/m<sup>3</sup>, whereas “water soluble” concentrations ranged between 6 ng/m<sup>3</sup> and 46 ng/m<sup>3</sup> with an average of 20 ng/m<sup>3</sup>. It is obvious from the results that concentrations obtained by 1 % HCl were generally less than half those obtained by

concentrated acids and microwave digestion. The correlation between 2 sets of data was also not strong (coefficient of 0.61), indicating that "water soluble" fraction cannot be reasonably estimated from the "total" concentration and vice versa.

Chromium is another toxic metal which may cause severe health problems through inhalation. Occupational exposure to Cr(VI) compounds has been associated with increased risk of respiratory system cancers, whereas intermediate- to chronic-duration exposure may cause an increased risk of death due to non-cancer respiratory disease [33]. Other effects such as severe liver damage, asthma, and respiratory distress have also been reported. US EPA lists carcinogenic risk from inhalation exposure for Cr(VI) at  $1.2 \times 10^{-2} \mu\text{g}/\text{m}^3$ , whereas ACGIH and NIOSH (8-hr) limits are  $0.5 \text{ mg}/\text{m}^3$  as Cr [33]. The concentration of "total" Cr measured in Lahore  $\text{PM}_{10}$  varied between  $17 \text{ ng}/\text{m}^3$  and  $53 \text{ ng}/\text{m}^3$  with an average of  $33 \text{ ng}/\text{m}^3$ , whereas "water soluble" concentration ranged from BDL to  $41 \text{ ng}/\text{m}^3$  with an average of  $18 \text{ ng}/\text{m}^3$ . It can be seen that Cr was not adequately extracted by 1% HCl solution. Also, correlation coefficient was only 0.36 indicating that the relative ratio of "soluble" and "insoluble" Cr compounds was not consistent in the particle samples analyzed.

The US EPA has determined that inorganic arsenic is a human carcinogen and has assigned it the cancer classification of Group A. Its quantitative estimates of carcinogenic risk from oral exposures include a cancer slope factor of  $1.5 \text{ mg}/\text{kg}/\text{day}$  and the inhalation unit risk for cancer is  $0.0043 \mu\text{g}/\text{m}^3$  [34]. WHO [29] guideline value is  $1.5 \times 10^{-3}$  unit risk (cancer risk estimates for lifetime exposure to a concentration of  $1 \mu\text{g}/\text{m}^3$ ). The "total" As concentrations in Lahore samples ranged from  $83 \text{ ng}/\text{m}^3$  to  $963 \text{ ng}/\text{m}^3$  (average  $508 \text{ ng}/\text{m}^3$ ) whereas "water soluble" concentration ranged from  $12 \text{ ng}/\text{m}^3$  to  $346 \text{ ng}/\text{m}^3$  (average  $186 \text{ ng}/\text{m}^3$ ). This again indicates relatively poor solubility of As compounds in 1 percent HCl. A correlation coefficient of 0.20 also shows that the two sets of concentrations are very poorly correlated and so one concentration can not be used to get a reasonable estimate of the other.

The last metal analyzed was mercury whose toxicity is well documented with the major target organs being the kidneys and the central nervous system [35]. A guideline value of  $1 \mu\text{g}/\text{m}^3$  is given

by WHO [29]. The concentration of Hg measured in Lahore samples were fairly low ranging from BDL to  $87 \text{ ng}/\text{m}^3$  for "total" and BDL to  $48 \text{ ng}/\text{m}^3$  for "water soluble" fractions, the two averages being  $41 \text{ ng}/\text{m}^3$  and  $14 \text{ ng}/\text{m}^3$ , respectively. The concentrations in the two fractions are also poorly correlated with a coefficient of 0.14.

## Experimental

### Sample Collection

The site selected for collecting air samples was a building at 4 Lytton Road, in the centre of the Lahore city, which housed the Environment Protection Department (EPD). The roads in this area are among the busiest in Lahore with mixed traffic including buses, trucks, cars, rickshaws, and motorcycles. Commercial activities in the general area include denting, painting and repairing of old engines in auto workshops; showrooms of cars and tires; and petrol filling stations. The  $\text{PM}_{10}$  sampler (standard TSP sampler fitted with a  $\text{PM}_{10}$  head made by General Metal Works Inc, 145 S. Miami Ave, Village of Cleves, OH 45002, a subsidiary of Andersen Samplers Inc) was located on the roof of the building, at a height of about 15 metres from the road level. The  $\text{PM}_{10}$  concentrations obtained at this height may have been slightly under-reported as compared to lower heights. However, this was the only suitable location available in the area where power supply and safety of the equipment could be assured.

Twelve samples of  $\text{PM}_{10}$  were collected from mid February to the beginning of May 2007. In addition, one trip blank and one field blank were collected after every 4 samples. The reported mass and metal concentrations are blank corrected. The weather during these months changes from winter to spring to summer. Wind speeds are also generally calm. Sampling was undertaken every sixth day for about 24 hours with the flow rate of the sampler adjusted at  $1 \text{ m}^3/\text{min}$ .

### Gravimetric Analysis

Quartz fibre (PALLFLEX) filters were used for collecting particulate matter. They were pre-baked in an oven at  $550^\circ\text{C}$  for 16 hours along with aluminium foil in which they were wrapped and stored till used for sampling. After sampling, the

filters were again carefully rewrapped in aluminium foil, which were then doubled bagged in self-sealing plastic bags and stored in a freezer for later analysis. The filters were weighed before and after sampling to determine the mass loading.

#### *Extraction of Total Metals*

At the time of analysis the filter was taken out of the freezer, placed on a clean surface, carefully unwrapped, and six circles cut with a specially prepared sharp-edged steel cutter of 2.1 cm diameter. The six cut circles, with combined area of 20.8 cm<sup>2</sup>, were carefully transferred into clean Teflon containers of the bomb calorimeter for acid extraction. The Teflon containers, before use, were soaked in soap water for couple of hours. They were then scrubbed and rinsed with hot water, after which they were washed with distilled de-ionized (DI) water. After rinsing, the containers were soaked overnight in 50 percent HNO<sub>3</sub> acid. They were then again rinsed with DI water and dried in a clean drying cabinet.

The procedure used for the extraction of metals from particulates retained on the quartz fibre filter was taken from an earlier European Union study [20]. It was shown during that study, using standard reference materials that extractions were within standard acceptable limits. The procedure involved additions of 2.0 ml of conc. HNO<sub>3</sub> acid (Merck, technical grade, 65 percent, extra pure), 4.0 ml of conc. HF acid (Merck, technical grade, 38-40 percent, extra pure) and 0.5 ml of H<sub>2</sub>O<sub>2</sub> (hydrogen peroxide) into the Teflon container with filter segments. The Teflon container, with a tight fitting lid was then placed in a Teflon bomb and heated in a micro-wave with heat setting at 350 W for 1 minute. The bombs were cooled to room temperature after which the Teflon container was taken out from it and placed on sand bath for evaporation. When all the liquid in the Teflon container had evaporated, the residue was extracted by adding 5 ml of 2 percent HNO<sub>3</sub>, which was then transferred into a centrifuge tube. The un-dissolved particles including filter residue, were removed from the extract by centrifuging at 3500 rpm for 15 minutes. After centrifuging, the supernatant was filtered through a sterile 0.2 µm polypropylene syringe filter (0.2 µm Whatman PP). The final volume of filtrate was made 50 ml by adding 2 percent HNO<sub>3</sub>. The extracted solution was then transferred into a 50 ml polyethylene bottle. The polyethylene bottle had been

soaked overnight in 2 percent HNO<sub>3</sub> acid and then rinsed with DI water. The sample was then refrigerated till analysis by atomic absorption spectrophotometer.

#### *Extraction of Water Soluble Metals*

Six circles (2.1 cm diameter each) were cut from each of the sampled quartz fibre filter and put in sterile glass conical flask into which 50 ml of 1 percent HCl (Merck, technical grade, 37 percent, extra pure) solution was added to completely immerse the filter segments. The conical flask was shaken for 2 hrs in an automatic shaker at 100 rev/min at 25 °C. The extract was then filtered through a sterile 0.2 micron quartz polypropylene syringe filter. The filtrate volume was made up to 50 ml, transferred to pre-cleaned polyethylene bottle, and stored in refrigerator till further analysis.

#### *Metal Analysis*

The extracted samples were analyzed by atomic absorption spectrophotometer (Shimadzu AA 6800 series) for cadmium, chromium, lead, nickel, mercury, antimony and arsenic. A mixture of air and acetylene gas was used for the analysis. A leak check was done before flame ignition and calibration curves were prepared from the known standards, for each element, covering the expected range of concentrations.

#### **Conclusion**

The study once again reconfirms the very high levels of PM<sub>10</sub> in the ambient air of Lahore, ranging from 465 µg/m<sup>3</sup> to 806 µg/m<sup>3</sup>, which has serious health implications for the residents of this city. The two extraction methods evaluated for metals and metalloids from PM<sub>10</sub> suggest that the method using 1 percent HCl worked very well for Cd, Pb and Sb but not for Ni, Cr, As and Hg. However, the method has its own utility as it gives "water soluble" concentrations, which are considered more "bioavailable" and have greater health significance than "total" concentrations obtained by the more rigorous method using concentrated acids and microwave digestion. The results indicate that majority of measurements as well as the averages of the both the "total" and "water soluble" concentrations of Cd and Pb in PM<sub>10</sub> exceeded the WHO guideline values. However, the concentrations

of Sb, Ni, Cr, As, and Hg were below the limit or guideline values for both fractions.

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