

Understanding sources of airborne water soluble metals in Lahore, Pakistan

TAUSEEF A. QURAIISHI*, JAMES J. SCHAUER** AND YUANXUN
ZHANG***

**IEER, University of Engineering and Technology, Lahore, Pakistan.*

Email: tquraishi@uet.edu.pk

***Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, Wisconsin 53706, U.S.A. Email: jschauer@engr.wisc.edu*

****Center for Air Resources Engineering and Science, Clarkson University, 8 Clarkson Avenue. Portdam, New York, 13699, U.S.A. Email: yzhang@clarkson.edu*

ABSTRACT

Lahore, the second largest city of Pakistan with a population of over 10 million, is growing at a rate of 3.32 percent per year. This is accompanied by a large increase in the number of motor vehicles in recent years (over 37 % average annual increase during the last 5 years) and some industrialization. This air quality study, undertaken from March 13 to April 16, 2006, indicated high levels of PM₁₀ which ranged between 158 and 733 $\mu\text{g}/\text{m}^3$ with an average of 360 $\mu\text{g}/\text{m}^3$. All measurements exceeded the USEPA as well as EU 24-hour standard values. Concentrations of 23 elements in water extracts of PM₁₀ were determined by ICP-OES along with the ions chlorides, nitrates, sulfates, ammonium and potassium by ion chromatography. The concentrations were generally low except for crustal elements of calcium, magnesium and sodium, and toxic metals cadmium, lead and zinc. A higher concentration of crustal elements was expected due to the arid nature of the area, suggesting a greater contribution of wind-blown and re-suspended road dust to PM₁₀. Nitrates, sulfates and ammonium were also measured in relatively high concentrations indicating the contributions by secondary aerosols. Principal Component Analysis showed that the greatest contributors to PM₁₀ were industrial sources followed by secondary aerosols and mobile sources.

Keywords: ICP-OES; Lahore; NEQS; PM₁₀; water-soluble metals.

INTRODUCTION

The increase in air pollution in developing countries is resulting from the expanding use of fossil energy sources and the growth in the manufacture and use of chemicals with scant regard to the associated deterioration in the natural environment. These are necessitated by rapid population increases, shift in population distribution from rural to urban areas, and the desire for improving

the standard of living quickly at minimum cost. The pollutants released into the ambient air are mostly particulates and toxic gases, including organic compounds and metals. They can have direct impacts on human health through inhalation, as well as indirect effects by deposition in environmental media and consequent uptake by plants and animals, resulting in such pollutants also entering the food chain or contaminating drinking water supplies. In many areas air pollution has reached critical levels.

When airborne particles are inhaled they come in contact with mucus lining the respiratory system where they may impact both directly and through uptake into epithelial cells and macrophages (Renwick *et al.* 2001, Stearns *et al.* 2001). According to Brunekreef & Holgate (2002) there is recognition that ultrafine particles (mass median diameter $< 0.1\mu\text{m}$) are more toxic when inhaled than PM_{10} (particles with aerodynamic diameter less than $10\mu\text{m}$), which suggests that their ability to be absorbed into tissues and the circulation might be important factors in determining cardiopulmonary toxicity. Thus, in addition to the direct impact, the particles may also exert an indirect effect through absorption. The health effects, given in literature, and the ambient air standards are generally based on the total concentration of metals, rather than water-soluble fraction. In recent years, however, the bioavailability of toxic compounds in the air particulates has been the focus of many studies (Costa & Dreher 1997, Dye *et al.* 1999, Frampton *et al.* 1999). The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) also list metals and metalloids having soluble TLVs, which are updated and published annually (Ashley & Fairfax 2003). In this context, the present paper targets water-soluble compounds (due to their greater bioavailability) to understand the sources of such metals present in airborne particulates (PM_{10}) collected in Lahore, Pakistan, from March 13 to April 16, 2006.

Lahore, the provincial capital of Punjab, is the second largest city of Pakistan with an area of about 1770 km^2 and a population exceeding 10 million (2006 estimate), which is growing at a rate of 3.32 percent (Lahore City Government 2006). The rapid population growth is accompanied by industrialization and a much larger increase in the number of motor vehicles, factors that are contributing to deteriorating air quality. Lahore, as well as other major cities of Pakistan, has witnessed a large increase in the numbers of motor vehicles in recent years (from 2002), as indicated in Table 1. This is linked directly to the introduction of leasing by financial institutions, besides improvements in the country's economy. Limited capacity of the existing roads, poor maintenance, animal driven carts and carriages on some city roads, including Grand Trunk Road (G.T. Road), and lack of traffic control hinders the smooth flow of traffic, which further enhances the air pollution problem in the provincial metropolis.

In addition, other main sources of air pollution in Lahore (located in the semi arid zone) are natural dust, uncontrolled emissions from industries and smoke arising from the burning of solid waste in community containers and roadside heaps (an illegal but common practice). In spite of the apparent deterioration in the ambient air quality, Pakistan currently does not have any ambient air quality standards. The country’s Environmental Protection Agency did establish emission standards, the National Environmental Quality Standards (NEQS), in 1997, which were revised in 2000. NEQS relating to motor vehicles are shown in Table 2 (GOP 2000), but their enforcement is lax due to political, economical, and technical constraints.

Table 1: Total vehicles registered in Lahore (2000 - 2006)*

Year	Total Vehicles Regd	% Increase from Previous year	Total On-Road Vehicles
2000	45,136	14	790,790
2001	46,413	2	868,000
2002	61,212	33	942,600
2003	101,168	65	1,077,300
2004	153,921	52	1,231,260
2005	166,194	8	1,397,500
2006	212,417	28	1,610,000

* Source: Excise and Taxation, Government of Punjab, Lahore

Table 2: Pakistan’s National Environmental Quality Standards relating to motor vehicles

Sr. No	Parameter	Standard (Maximum Permissible Limit)	Measuring Method				
1.	Smoke	40% or 2 on the Ringelmann scale during engine acceleration mode	To be compared with Ringelmann chart at distance of 6 meters or more				
2.	Carbon Monoxide	<p style="text-align: center;">Emission Standards</p> <table style="margin-left: auto; margin-right: auto;"> <tr> <td style="text-align: center;"><u>New Vehicles</u></td> <td style="text-align: center;"><u>Used Vehicles*</u></td> </tr> <tr> <td style="text-align: center;">4.5%</td> <td style="text-align: center;">6%</td> </tr> </table>	<u>New Vehicles</u>	<u>Used Vehicles*</u>	4.5%	6%	Under idling conditions. Non dispersive infrared detection through gas analyzer
<u>New Vehicles</u>	<u>Used Vehicles*</u>						
4.5%	6%						
3.	Noise	85 dB(A)	Sound meter at 7.5 m from the source				

* 10 year or older models

Some of the previous studies (Quraishi & Hayat 2000, Smith *et al.* 1996, Harrison *et al.* 1994) indicated very high levels for both total suspended particulates (TSP) as well as PM₁₀ for Lahore. During a global air quality monitoring program (1976-1980), the World Health Organization (WHO) identified Lahore as having the highest concentrations of TSP, which averaged 678 $\mu\text{g}/\text{m}^3$ and 749 $\mu\text{g}/\text{m}^3$ at the 2 locations monitored (Smith *et al.* 1996). Based on the results of a European Union sponsored study for the city from 1990 to 1992, Smith *et al.* (1996) reported that concentrations of cadmium, manganese, and vanadium in airborne TSP exceeded WHO guideline values on several occasions, while those of carcinogenic elements arsenic, chromium, and nickel were also reported as relatively high.

The objectives of the present study included the collection of PM₁₀ and analysis of the particles for some water soluble metals, metalloids, ions, organic and element carbon (OC, EC), and more than one hundred organic species. Source apportionment of PM₁₀ OC, EC and mass was performed using a molecular marker based chemical mass balance (CMB) receptor model, published elsewhere (Zhang *et al.* 2008). In this paper, an attempt is made to better understand the sources of such water soluble metals and metalloids, employing the techniques of principal component analysis (PCA) and regression analysis. Pakistan does not currently have ambient air quality standards, so this study, along with others, will help the regulatory and environmental protection agencies to target such sources, which will lead to improvements in urban air quality.

METHODS

Sample Collection

The sampler used for this study was a standard TSP sampler fitted with a PM₁₀ head (made by General Metal Works Inc, 145 S. Miami Ave, Village of Cleves, OH 45002, a subsidiary of Andersen Samplers Inc). It was deployed at a height of about 10 m on the roof of the Institute of Environmental Engineering and Research (IEER) building within the University of Engineering and Technology (UET), Lahore. There were no obstructions or physical structures in the vicinity of the sampler which would interfere with normal flow pattern. The building is two storeys high and is located along the G.T. Road, one of the arterial roads of Lahore. The road has a mix of traffic, including animal driven carts, buses and trucks running on diesel, 2-stroke motor cycles and three-wheelers (rickshaws) running on petrol with lubricating oil added to it, and cars and pick-ups using both petrol and compressed natural gas (CNG). It is also close to a railway workshop (about 1 to 2 km south), the largest in Pakistan, which services diesel

engines, and there is a mix of metallurgical and other small industrial and commercial units in the vicinity as well. The site can be considered as representative for the city of Lahore. The sampler was run for a period of 22 to 24 hours. Flow rate was adjusted at 1 m³/min. Samples were collected almost daily, including field blanks, during the period March 13 to April 16, 2006.

Analytical Methods

Quartz fiber filters (20 x 25 cm) used for the sampling were prepared at University of Wisconsin, Madison (UW-M), USA, where they were baked at a temperature of 550°C for 12 hours, individually wrapped in baked aluminum foil and double packed in zip-lock bags. The filters, with Al wrap, were weighed before and after sampling to get an estimate of particulate loading. They were then triple bagged in zip-lock bags, and sent by courier to UW-M in a cooler with ice packs. The filters were stored in a freezer at UW-M until the time of extraction and analyses. All analytical work was done at UW-M and the Wisconsin State Hygiene Laboratory, Madison, USA, during the summer of 2006.

For metals analysis, a 47 mm diameter segment was taken from each filter and immersed in 37.8 ml of Milli-Q water (> 18.0 MΩ) in a 50 ml sterile plastic centrifuge tube. The tubes were placed in a shaker and agitated for 2 hours. The extracts were then filtered through 0.2 μm polypropylene filters (Whatman 0.2 μm PP), using a new syringe for each sample. The extract was acidified by adding 100 μl of trace-metal grade concentrated HCl (Fisher Scientific) to 9.9 ml extract (making total volume 10 ml). Metal concentrations were obtained from the acidified extracts using inductively coupled plasma - optical emission spectroscopy (ICP-OES) (Perkin Elmer Optima 4300 DV). Most elements were quantified using standard plasma conditions (1300 W power) in the axial view. The SLRS-4 River Water Reference Material for Trace Metals (National Research Council of Canada) was used as standard reference material (SRM) and was analyzed multiple times to verify the calibration curve and to estimate the stability of plasma conditions over the course of the analysis. Propagated uncertainties were calculated from the standard deviations of field blank measurements and the replicate analyses of SRM. Concentrations of twenty three elements were determined by this technique, sixteen of which are reported in Table S1. Concentrations of the remaining 7 elements (As, Co, Cr, Mo, Sc, Se, and V) were mostly insignificant. For cations (NH₄⁺, K⁺) and anions (Cl⁻, NO₃⁻, SO₄⁼) analyses, four segments of 1.45 cm² each for a total filter area of 5.8 cm² were extracted following the method used for soluble metals. Ion concentrations were determined using an Ion Analyzer (DX-500, Dionex Co., U.S.A.).

Table S1: PM₁₀ concentrations of water-soluble species from Lahore, Pakistan (ng/m³)

Date	PM ₁₀ ($\mu\text{g}/\text{m}^3$)	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	K ⁺	B	Ba	Ca	Cd	Cu	Fe
Mar-13(M)	371	6020	8830	15100	5030	1430	14.3	3.40	6520	24.2	56.5	34.7
Mar-14(Tu)	166	5110	5000	15600	3550	823	1.22	1.21	1030	18.7	25.6	5.16
Mar-15(W)	299	10600	6640	10900	2470	1490	5.14	3.35	2870	46.3	3.79	BDL*
Mar-16(Th)	234	7270	7720	8190	2420	1390	5.48	3.34	2390	21.9	2.44	BDL*
Mar-17(F)	376	9440	9330	10100	3310	2090	10.3	11.3	4500	28.1	10.8	5.23
Mar-18(Sa)	458	6460	15400	18400	6340	2730	17.7	8.80	7520	6.19	44.9	31.5
Mar-19(Su)	158	4190	3430	5750	872	941	2.97	5.68	1930	49.0	6.86	BDL*
Mar-21(Tu)	187	6670	6130	8360	2590	2060	5.32	4.37	2550	39.5	16.0	5.32
Mar-22(W)	418	8950	6470	8260	1850	2010	7.22	9.55	4010	35.7	6.28	1.59
Mar-23(Th)	283	9310	7667.4	10900	2100	2270	4.59	4.69	3660	31.4	4.04	0.000
Mar-24(F)	197	10000	5440	5760	1910	1580	2.46	14.0	2680	32.9	5.16	4.46
Mar-25(Sa)	281	2970	3570	6470	1230	1120	3.37	3.73	2970	5.43	11.1	2.15
Mar-26(Su)	411	13100	6150	7130	1390	2180	4.60	13.3	4400	31.9	0.965	BDL*
Mar-27(M)	327	6050	3870	6890	1210	1320	2.46	7.67	3580	16.1	11.0	1.32
Mar-29(W)	316	6620	10300	11500	4920	2120	12.5	3.79	3960	9.25	15.5	9.43
Mar-31(F)	557	3690	8440	12700	4610	2250	10.6	4.84	5530	0.46	24.0	14.8
Apr-01(Sa)	441	11100	8600	12900	2610	2920	3.66	7.10	3870	46.4	5.07	0.570

Date	PM ₁₀ ($\mu\text{g}/\text{m}^3$)	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	K ⁺	B	Ba	Ca	Cd	Cu	Fe
Apr-02(Su)	382	4440	3150	5420	1590	1390	2.43	5.47	2720	13.2	12.0	1.86
Apr-03(M)	240	17900	7470	11300	1620	4610	3.69	9.14	3440	76.6	4.07	BDL*
Apr-04(Tu)	603	15000	8280	11200	2930	3020	5.34	10.5	4500	27.5	9.87	2.81
Apr-06(Th)	454	14020	6110	10200	2510	4090	9.70	13.6	5000	48.2	13.6	1.32
Apr-07(F)	733	8670	5170	8790	2460	2570	6.24	8.95	4000	16.3	5.75	0.380
Apr-08(Sa)	497	4800	5300	9560	2400	2570	7.72	6.53	3440	7.32	14.9	4.23
Apr-09(Su)	347	9140	5690	8930	1720	2580	6.73	17.1	4380	18.7	3.18	2.61
Apr-10(M)	416	6350	3660	4960	1970	1550	2.92	5.73	2060	17.6	2.79	BDL*
Apr-11(Tu)	255	6920	3750	5790	2780	1590	3.10	5.31	1790	23.6	3.51	BDL*
Apr-12(W)	254	15700	5830	7480	5020	2780	6.98	3.59	2130	57.1	3.35	BDL*
Apr-14(F)	412	7430	4190	6760	2300	2140	4.53	5.26	2070	35.5	3.10	BDL*
Apr-15(Sa)	296	5190	4730	8230	1810	2200	4.82	11.0	3290	9.55	8.96	BDL*
Apr-16(Su)	440	6150	3690	8870	2280	2103	3.62	9.19	3300	6.73	11.0	0.130
Average	360	8310	6330	9410	2660	2130	6.06	7.38	3540	27.0	11.5	4.32

BDL* - Below detection limit

Table SI (Continued): PM₁₀ concentrations of water-soluble species from Lahore, Pakistan (ng/m³)

Date	Li	Mg	Mn	Na	Ni	Pb	Sb	Sr	U	Zn
Mar-13(M)	1.44	375	92.8	1830	5.00	201	20.6	24.4	15.0	9700
Mar-14(Tu)	0.636	60.9	32.1	411	1.53	66.8	10.8	3.47	12.9	8600
Mar-15(W)	1.21	162	65.2	1330	1.36	1420	58.8	9.87	20.6	10100
Mar-16(Th)	0.894	159	41.8	1080	0.958	1340	70.0	9.42	12.6	7060
Mar-17(F)	1.63	302	64.3	1970	2.77	51.1	12.0	22.1	8.76	6930
Mar-18(Sa)	1.31	438	83.9	1900	3.47	29.8	8.80	33.9	11.8	2200
Mar-19(Su)	0.677	121	34.4	708	0.582	139	11.9	9.60	13.3	4160
Mar-21(Tu)	0.841	178	33.9	1040	1.64	20.1	6.06	12.6	10.2	4240
Mar-22(W)	1.35	314	70.8	1870	1.36	196	23.1	20.1	16.1	6490
Mar-23(Th)	1.08	229	49.0	1640	1.32	871	18.1	16.1	12.1	7250
Mar-24(F)	1.09	139	49.3	3170	1.38	106	1.83	14.1	4.95	7220
Mar-25(Sa)	0.670	218	41.0	974	1.11	11.1	4.97	15.5	9.12	2010
Mar-26(Su)	1.35	294	99.1	1620	0.929	329	11.9	17.7	BDL*	8320
Mar-27(M)	0.813	237	59.8	1220	1.44	25.4	0.691	17.1	16.4	3780
Mar-29(W)	1.07	278	65.2	1490	2.68	37.5	8.14	18.5	BDL*	3970
Mar-31(F)	0.997	412	46.8	2220	2.50	2.18	4.14	28.1	2.90	189
Apr-01(Sa)	1.71	290	86.9	1970	1.62	940	28.0	17.5	5.36	9560

Date	Li	Mg	Mn	Na	Ni	Pb	Sb	Sr	U	Zn
Apr-02(Su)	0.677	206	36.6	1060	0.821	21.4	5.43	14.5	BDL*	2680
Apr-03(M)	2.00	307	64.0	3470	1.06	1230	20.3	16.7	BDL*	9750
Apr-04(Tu)	1.98	349	68.5	2410	2.04	298	19.2	21.4	0.347	7750
Apr-06(Th)	2.44	457	72.4	4020	1.78	201	8.28	26.2	5.75	6890
Apr-07(F)	2.01	359	53.2	2230	1.96	366	41.1	19.5	4.41	5600
Apr-08(Sa)	1.47	339	58.8	2040	1.74	57.0	10.0	18.7	1.45	3540
Apr-09(Su)	1.61	407	85.5	2380	1.50	78.8	15.2	27.0	3.34	7160
Apr-10(M)	0.906	183	32.8	1460	0.520	547	25.7	10.3	5.91	3530
Apr-11(Tu)	1.07	170	27.0	1220	0.672	821	14.7	9.22	BDL*	3640
Apr-12(W)	1.61	203	43.2	2140	0.606	2580	6.41	9.92	0.06	6980
Apr-14(F)	1.32	194	36.6	1580	0.645	1100	21.4	9.86	1.72	4810
Apr-15(Sa)	0.739	289	47.2	1700	0.709	117	21.2	19.4	6.06	1540
Apr-16(Su)	0.718	276	42.9	1410	0.515	42.5	8.66	18.4	6.19	2100
Average	1.24	265	56.2	1780	1.54	442	17.2	17.0	6.91	5590

BDL* - Below detection limit

RESULTS AND DISCUSSION

PM₁₀ values, given in Table S1, averaged 360 $\mu\text{g}/\text{m}^3$ ranging from 158 $\mu\text{g}/\text{m}^3$ to 733 $\mu\text{g}/\text{m}^3$ (standard deviation of 133 $\mu\text{g}/\text{m}^3$). All measurements exceeded the U.S. Environmental Protection Agency (USEPA) 24-hour value for PM₁₀ of 150 $\mu\text{g}/\text{m}^3$ and European Union 24-hour standard value of 50 $\mu\text{g}/\text{m}^3$ referred to by Brunekreef & Holgate (2002) as well as the WHO annual and 24-hour mean guideline values of 20 $\mu\text{g}/\text{m}^3$ and 50 $\mu\text{g}/\text{m}^3$, respectively (World Health Organization 2006).

International standards and criteria for metals and toxic compounds are based on total concentrations and not on water-soluble component. It is, therefore, not justifiable to compare the values obtained in this study with such standards or with other studies where total concentrations were measured, such as that undertaken by Harrison *et al.* (1994) for Lahore from 1990 to 1992. In the latter study, TSP were measured and the extractions were done by concentrated nitric acid, concentrated hydrofluoric acid, and hydrogen peroxide using a microwave oven as described by Smith *et al.* (1996). It was observed by Harrison *et al.* (1994) that most of the material was soil derived and was trapped possibly in the silica matrix of the filter, which is only partially solubilized by water. This would give much lower values as compared to acid extraction and although the concentrations of some metals in the present study were found to be fairly high, they were generally much less than those reported by Smith *et al.* (1996).

A time series of major PM₁₀ water soluble ions and metals are shown in Figure 1. Relatively large concentrations of sulfates, nitrates, and ammonium ions indicate secondary aerosol formation. Sulfates were in the range of 4,960 to 18,400 ng/m^3 with an average of 9,410 ng/m^3 (STDEV 3,240 ng/m^3); nitrate concentrations varied between 3,150 and 15,400 ng/m^3 with an average of 6,330 ng/m^3 (STDEV 2,610 ng/m^3); and ammonium ranged from 872 to 6,340 ng/m^3 with an average of 2,660 ng/m^3 (STDEV 1,320 ng/m^3). Calcium, magnesium, and sodium, which are major components of crustal material, were among the most abundant of metals measured in PM₁₀ samples. Calcium ranged between 1,030 and 7,520 ng/m^3 with an average of 3,540 ng/m^3 ; Mg varied between 60.9 and 457 ng/m^3 with an average of 265 ng/m^3 ; and Na ranged from 411 to 4,020 ng/m^3 with an average of 1,785 ng/m^3 . Relatively high concentrations of these metals indicate significant contributions of fugitive dust and re-suspended road dust due to moving traffic to PM₁₀. This is understandable given the arid conditions in the area and the lack of grass cover on the exposed median and roadsides. Iron, also a crustal element was, however, measured in low concentrations with a maximum value of 34.7 ng/m^3 and an average of 4.32 ng/m^3 .

Although lead is no longer added to gasoline as an anti-knock agent in Pakistan (phased out in 2002), significant concentrations were still measured in the PM_{10} . These ranged from 2.18 to 2,580 ng/m^3 with an average value of 442 ng/m^3 and standard deviation of 600 ng/m^3 . Thirty percent of daily values exceeded the WHO guideline value for annual average of 0.5 $\mu g/m^3$ (WHO 2000), and one even exceeded the USEPA quarterly standard of 1.5 $\mu g/m^3$, even though the limit values are based on acid extraction rather than water extraction method. Several sources may have contributed, including fuel and motor oil combustion, brake wear, and re-suspension of lead enriched road dust. Another possible source could be lead wheel weights, which drop from vehicle wheels and are pulverized by traffic (Lough *et al.* 2005). The toxicity of lead is widely acknowledged. It can affect almost every organ and system in human body, the main target for its toxicity is the nervous system, both in adults and children. Both USEPA and the International Agency for Research on Cancer (IARC) have determined that lead is a probable human carcinogen (ATSDR 2007).

Zinc was measured in largest concentrations ranging from 189 to 10,100 ng/m^3 with an average of 5,590 ng/m^3 (STDEV of 2,760 ng/m^3). It can be related to tail pipe emissions of motor oil and tire wear (Lough *et al.* 2005), steel production, coal-burning, and burning of wastes (ATSDR 2005b). It may also be emitted by metal industries using Zn alloys, galvanizing iron and other metals, electroplating, metal spraying, electrical fuses, batteries, etc., activities quite common in the city. The main source in Lahore would probably be the high percentage of 2-stroke engine vehicles, including motorcycles and rickshaws, along with metallurgical industries (such as those making cooking utensils of zinc alloy). Motorcycles made up 55% of all vehicles (212,417) registered in the city during 2006 (M.S. Sheikh, Excise and Taxation, Punjab; *pers. comm.*). These use gasoline mixed with lubricating oil. Tire wear from vehicles braking at the road humps across the road in the vicinity of the sampling location could also contribute to high Zn values.

Time series of low concentration PM_{10} water-soluble components is presented in Figure 2. Cadmium was present in relatively high concentrations and was measured in the range of 0.46 to 76.6 ng/m^3 , with an average of 27.0 ng/m^3 , whereas Mn concentrations were in the range of 27.0 to 99.1 ng/m^3 with an average of 56.2 ng/m^3 . Similarly antimony (Sb), which has been suggested as a tracer for brake wear (Lough *et al.* 2005) was also measured in significant quantities ranging from 0.69 to 70.0 ng/m^3 with an average of 17.2 ng/m^3 (STDEV of 15.6 ng/m^3).

To identify the relations between the measured water-soluble species, the correlation matrix of the water-soluble species is listed in Table 3. Accordingly, key species with relative large correlation coefficients are shown in Figure 3 in order to explore their potential source correlations. Lithium shows good correlations with potassium and sodium, with relative coefficients 0.81 and 0.80, respectively. Besides, strontium has good correlations with calcium and magnesium, both with relative coefficients 0.94, which indicates large probability of coming from the same source. Similarly, copper and iron, and nickel and iron also have high relative coefficients which are 0.94 and 0.87, respectively. Some other species also have high correlations, including manganese and strontium ($R^2=0.66$), iron and boron ($R^2=0.80$), zinc and cadmium ($R^2=0.67$), and lead and cadmium ($R^2=0.60$). However, it is difficult to explore the sources according to the correlation matrix as most of the species have multiple sources. Moreover, the aforementioned correlations reflect the relations between the elemental concentrations of the water-soluble species, which should have different tendencies with the relations of acid-soluble species.

To quantitatively identify the source contributions from the principle sources in Lahore, principle component analysis (PCA) was done and the results are shown in Table 4. Four principle components (factors) were derived which combined, explained 83.4 percent of the source variances. Factor contributions were computed following the same procedures previously described by Thurston & Spengler (1985), which applied stepwise regression between the total water-soluble species concentrations and absolute principle components scores, derived by a statistical software, SPSS15.0 (SPSS Inc., Chicago, IL) in this study. The apportioned percentages of summed water-soluble species were listed in Table 4. Only three factors were included which contributed 94 percent of the total water-soluble species. Table 4 shows that factor #1 has positive relations with water-soluble ions, e.g., NO_3^- , SO_4^{2-} and NH_4^+ , as well as boron, copper, iron and nickel. These water-soluble ions are associated with secondary reactions, thus factor #1 is identified as a secondary source. The aforementioned four elements having high correlations with this factor can be particles coated with secondary ions, consisting of relatively small percentages of the total acid-soluble elements. Therefore, factor #1 contributes most of the secondary ions and small fractions of the aforementioned four elements; thus, it was identified as a secondary factor, with total contribution of $32 \pm 18\%$ of the summed water-soluble species. Factor #2 has positive relations with barium and strontium which are associated with vehicle exhaust (Lough *et al.* 2005), as well as some crustal elements such as magnesium, calcium and sodium, etc., which may be introduced from resuspended road dust.

Table 3: Correlation matrix of the measured water-soluble species

	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻	NH ₄ ⁺	K ⁺	B	Ba	Ca	Cd	Cu	Fe	Li	Mg	Mn	Na	Ni	Pb	Sb	Sr	U	Zn	
Cl ⁻	1																					
NO ₃ ⁻	0.21	1																				
SO ₄ ⁻	0.07	<u>0.78</u>	1																			
NH ₄ ⁺	0.001	<u>0.73</u>	<u>0.71</u>	1																		
K ⁺	<u>0.72</u>	0.36	0.27	0.13	1																	
B	-0.02	0.80	<u>0.63</u>	<u>0.78</u>	0.28	1																
Ba	0.40	0.04	-0.14	-0.29	0.46	0.05	1															
Ca	0.10	<u>0.73</u>	<u>0.61</u>	0.49	0.40	0.82	0.36	1														
Cd	<u>0.75</u>	-0.02	-0.08	-0.19	0.43	-0.21	0.07	-0.22	1													
Cu	-0.35	<u>0.52</u>	<u>0.71</u>	<u>0.68</u>	-0.10	<u>0.68</u>	-0.23	<u>0.61</u>	-0.34	1												
Fe	-0.26	<u>0.67</u>	<u>0.69</u>	<u>0.74</u>	-0.05	<u>0.80</u>	-0.14	<u>0.72</u>	-0.31	0.94	1											
Li	<u>0.76</u>	<u>0.34</u>	0.25	0.16	0.81	0.34	0.47	<u>0.44</u>	0.46	-0.07	0.01	1										
Mg	0.21	<u>0.51</u>	0.44	0.33	0.65	0.69	<u>0.51</u>	0.88	-0.18	0.37	0.44	<u>0.63</u>	1									
Mn	0.41	<u>0.58</u>	0.48	0.21	0.42	<u>0.53</u>	<u>0.49</u>	<u>0.76</u>	0.12	0.29	0.40	<u>0.57</u>	0.68	1								
Na	<u>0.66</u>	0.26	0.14	0.08	0.82	0.29	<u>0.63</u>	0.44	0.37	-0.05	0.04	0.80	<u>0.62</u>	0.44	1							
Ni	-0.08	<u>0.72</u>	<u>0.73</u>	<u>0.68</u>	0.09	0.82	-0.03	<u>0.78</u>	-0.22	0.83	0.87	0.29	<u>0.55</u>	0.56	0.20	1						
Pb	<u>0.55</u>	-0.01	-0.10	0.11	0.23	-0.16	-0.31	-0.34	<u>0.60</u>	-0.39	-0.30	0.25	-0.28	-0.11	0.09	-0.33	1					
Sb	0.14	0.09	0.04	-0.10	-0.05	-0.07	-0.20	-0.13	0.17	-0.25	-0.18	0.13	-0.14	0.05	-0.11	-0.07	0.46	1				
Sr	0.06	<u>0.59</u>	0.47	0.36	0.48	<u>0.74</u>	0.94	<u>0.53</u>	-0.30	0.47	<u>0.57</u>	0.43	0.94	<u>0.66</u>	<u>0.53</u>	<u>0.63</u>	-0.44	-0.25	1			
U	-0.29	0.11	0.24	-0.03	-0.46	0.07	-0.27	0.06	0.02	0.29	0.22	-0.33	-0.21	0.05	-0.37	0.23	-0.09	0.33	-0.08	1		
Zn	<u>0.68</u>	0.19	0.26	-0.03	0.23	-0.08	0.10	-0.002	<u>0.67</u>	-0.10	-0.07	<u>0.51</u>	-0.07	0.47	0.28	0.16	0.43	0.41	-0.17	0.18	1	

Values shown in boldface are larger than 0.80, underlined are between 0.5 and 0.8.

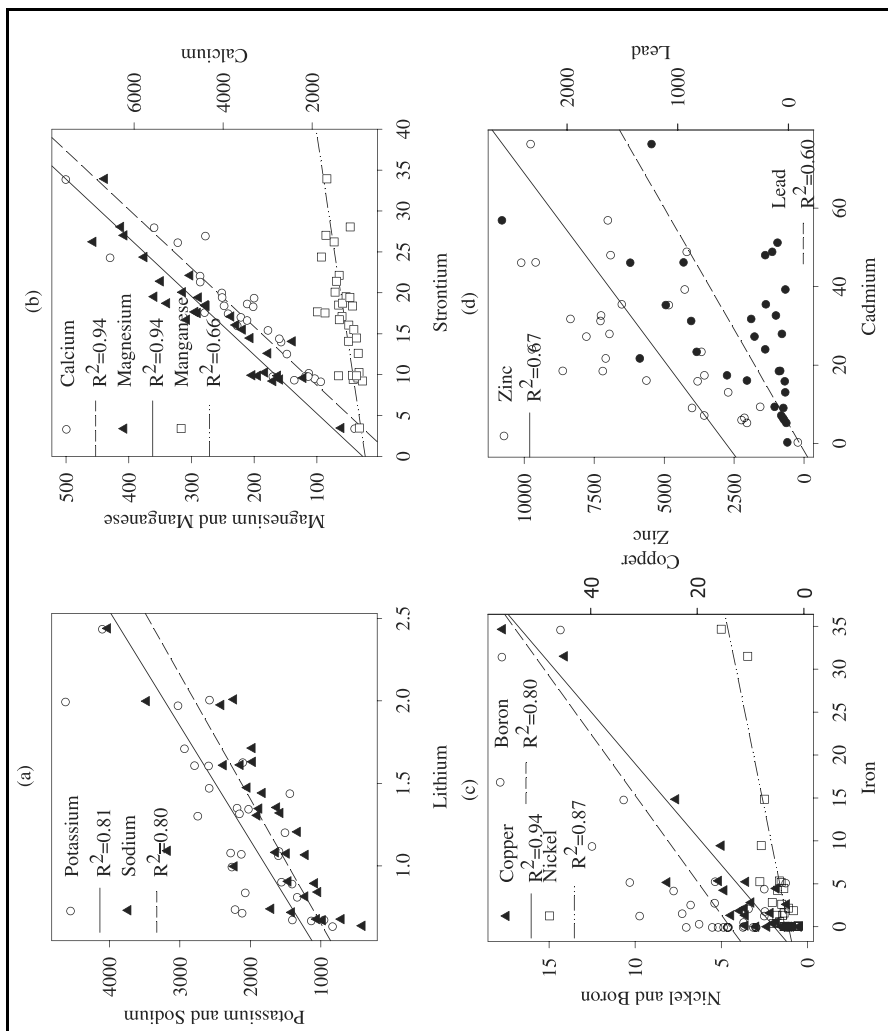


Figure 3: Correlations of key PM₁₀ water-soluble species from Lahore, Pakistan (Unit: ng/m³)

Table 4: Rotate component matrix of PM₁₀ water-soluble species from Lahore, Pakistan

Principle components	1	2	3	4
Cl ⁻	-0.07	0.38	0.86	-0.15
NO ₃ ⁻	0.83	0.22	0.21	0.03
SO ₄ ⁻	0.85	0.09	0.13	0.15
NH ₄ ⁺	0.90	-0.19	0.08	-0.26
K ⁺	0.14	<u>0.58</u>	<u>0.54</u>	-0.47
B	0.88	0.28	-0.06	-0.11
Ba	-0.25	0.88	-0.002	-0.08
Ca	<u>0.72</u>	<u>0.64</u>	-0.11	0.02
Cd	-0.20	0.03	0.83	0.07
Cu	0.85	-0.01	-0.33	0.11
Fe	0.90	0.06	-0.25	0.08
Li	0.19	<u>0.62</u>	<u>0.63</u>	-0.21
Mg	0.48	0.78	-0.04	-0.23
Mn	0.43	<u>0.71</u>	0.23	0.28
Na	0.10	<u>0.70</u>	0.43	-0.35
Ni	0.88	0.25	-0.09	0.19
Pb	-0.08	-0.39	0.81	-0.12
Sb	-0.04	-0.15	0.44	<u>0.50</u>
Sr	<u>0.55</u>	0.76	-0.23	-0.14
U	0.18	-0.17	-0.11	0.83
Zn	0.05	0.14	0.78	0.47
Estimated source variance (%)	32.2	22.4	19.7	9.1
Apportioned Percentages of summed species	32 ± 18%	23 ± 10%	39 ± 19%	-

Values shown in boldface are larger than 0.75, underlined are between 0.50 and 0.75;
 Extraction Method: Principal Component Analysis;
 Rotation Method: Varimax with Kaiser Normalization

Therefore, factor #2 was identified as a mobile associated source with average contribution of 23 ± 10% of the total water-soluble species. The third factor has the largest contribution, which is 39 ± 19% of the total water-soluble species. The dominate elements of factor #3 are lead, cadmium, zinc, chlorine, etc.,

which implicates positive relations between factor #3 and some industrial sources such as coal combustion, waste burning or metal industry emissions. The fourth factor has positive relations with uranium, and does not have significant meanings associated with particular sources. In this case, factor #4 could be an unimportant factor combined with sources with tiny contributions, compared with the other three principle factors.

CONCLUSIONS

The study confirms high air pollution levels in Lahore, as indicated by particulate concentrations in the ambient air. All the PM₁₀ values exceeded the European Union 24-hour standard value of 50 $\mu\text{g}/\text{m}^3$ as well as USEPA 24-hour standard of 150 $\mu\text{g}/\text{m}^3$. Analyses of the collected particulates by ICP-OES show relatively low concentrations of water-extracted metals, especially toxic metals (except cadmium and lead). This, along with relatively higher concentrations of crustal elements would indicate a greater contribution of wind-blown and re-suspended road dust to PM₁₀. Metals, whose concentrations should be a cause of some concern to the relevant environmental protection agencies include cadmium, lead, and zinc. PCA indicated industrial sources as major contributors to PM₁₀ followed by secondary aerosols and mobile sources.

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التعرف على مصادر المعادن الذائبة في الغلاف الجوي في مياه لاهور - باكستان

* توصيف أ. قريشي ، ** جيمس ج. شعير و *** يونكسين جانج

* جامعة الهندسة والتكنولوجيا - لاهور - باكستان

** جامعة ويسكونسن - ماديسون - أمريكا

خلاصة

يتناول هذا البحث فهم مصادر المعادن الذائبة في الغلاف الجوي في مياه لاهور - باكستان، تعد لاهور ثاني أكبر مدينة في باكستان حيث يزيد عدد سكانها على 10 مليون نسمة، وينمو عدد السكان بمعدل 33,32٪ في السنة. ويتوافق مع الزيادة في عدد السكان، زيادة في التصنيع والمركبات المتحركة والتي بلغ متوسط الزيادة السنوية فيها أكثر من 37٪ خلال الخمس سنوات الماضية.

دلت دراسة جودة الهواء، التي أجريت خلال أشهر مارس، نيسان، وأبريل 2006 على مستوى عال من الـ PM_{10} والتي تراوحت قيمتها ما بين 158 و $733 \mu g/m^3$ وبمتوسط $360 \mu g/m^3$. ووجد أن كل القياسات تزيد على القيم القياسية للهيئة العامة للبيئة الأمريكية والاتحاد الأوروبي في 24 ساعة. لقد تم تحديد تراكيز 23 عنصراً لمستخلصات المياه PM_{10} باستخدام جهاز ICP-OES بالإضافة إلى تعيين عناصر الكلوريدات، النترات، الكبريتات، الأمونيا والبوتاسيوم باستخدام جهاز الكروموتوجراف. وعموماً وجد أن التراكيز منخفضة ما عدا عناصر القشرة الأرضية من مثل الكالسيوم، الماغنيسيوم، الصوديوم والمعادن السامة مثل الكاديوم والرصاص والزنك. كان من المتوقع ارتفاع تركيز عناصر القشرة الأرضية بسبب الطبيعة القاحلة للمنطقة، مما يشير إلى مساهمة كبيرة لهبوب الرياح، وإعادة تراب الطرق المعلقة لـ PM_{10} . كما تم قياس تركيزات عالية للنترات، الكبريتات والأمونيا مما يدل على مساهمة البخاخات الثانوية. كما أظهر تحليل العنصر الأساسي أن المساهمات الكبرى لـ PM_{10} كانت من المصادر الصناعية تليها البخاخات الثانوية والمركبات.