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The Study of PM_{10} Concentration and Trace Metal Content in Different Areas of Karachi, Pakistan

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Abstract. Atmospheric particulate matter may exert serious health hazards because of its chemical characteristics. Aim of this study was to determine the concentrations of particulate matter (PM) with an aerodynamic diameter ≤10 µm (PM10), and air transmitted particulate trace metals in different areas of Karachi's ambient air, for the period of 01 year *viz.* June 2011 to June 2012. Furthermore, the present work compares the levels of particulate matter and trace metals with the proposed limiting values from the U.S. Environmental Protection Agency (65 µg/m^3 for PM10). The sampling for PM_{10} was performed by using a high volume air sampler. The PM_{10} levels were determined by gravimetry and the metals by graphite furnace. Arithmetic means of 361.0 µg/m^3 was determined for PM_{10} in commercial areas, 275.0 µg/m^3 in residential areas, 438.0 µg/m^3 in industrial areas and 68.9 µg/m^3 in background areas of Karachi. Trace metal content in PM_{10}, such as lead (Pb) and cadmium (Cd) were also analysed separately during the same period using atomic absorption spectrometry. The average concentration of Pb were found in commercial zone 1.36 µg/m^3, in residential zone 1.0 µg/m^3, in industrial zone 1.46 µg/m^3 and in urban background zone 0.6 µg/m^3, whereas; Cd concentration in commercial zone 0.10 µg/m^3, in residential zone 0.02 µg/m^3, in industrial zone 0.25 µg/m^3 and in urban background zone 0.01 µg/m^3, respectively.

Keywords: trace metal, atmospheric particulate matter, ambient air, Karachi

Introduction

Airborne particulate matter composed of wide range of chemically and physically diverse substances variable in size, chemical composition, formation, origin and concentration, and is variable across space and time. The particulates may include a broad range of chemical species, ranging from metals to organic and inorganic compounds (Park and Kim, 2005; Tsai and Cheng, 2004). The sources, characteristics, and potential health effects of particulate matter with aerodynamic diameter less than 10 µm (PM_{10}) are very different. The particulate emitted by stationary and mobile sources have a range of health effects that are known for a long period of time (Sharma and Maloo, 2005). One of the most important components of the air pollution mixture that contributes in a various adverse health outcomes as well as general environmental effects is urban particulate matter (PM) (Van Der Zee *et al*., 1998). Regarding the size of urban particulate matter, it tends to be divided into three principal groups: coarse, fine, and ultrafine particles. Particulate matter air pollution has both natural and anthropogenic sources.

Coarse particles normally divided into rural and natural crustal material for example dust due to 1) kicked up by vehicles (called resuspended dust), 2) construction and demolition, 3) industries, and 4) biological sources. It contains biological matter, hydrocarbons, both organic and inorganic compounds, acid deposition and several trace metals (de Kok *et al*., 2006). Fine particles may be emitted directly as a result of combustion process or may be due to some chemical reactions of different gases such as nitrogen dioxide, sulphur dioxide and some of organic gases.

A number of epidemiological studies show strong relation between elevated concentrations of inhalable particles (PM_{10}) and increased mortality and morbidity (Namdeo and Bell, 2005). Health hazards associated with particulate matter (PM_{10}) are linked to pulmonary and cardiovascular diseases (Callen *et al*., 2009). It is demonstrated that trace metal content of PM_{10} can be toxic to living organism at certain levels. They occur naturally and also emitted from different sources such as industrial emission, mining industries, fossil fuels burning, solid waste incineration, garbage dumping, tobacco smoke and transportation. Several trace metals, such as Cd, Pb, Co, Cu, and Cr, are considered to be very harmful that can accumulate in the human body, with a relatively long half-life. For example, it has been stated that Cd has a half-life of 10 years in the human body. Cadmium can produce acute toxic effects on

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various organs such as the kidney, liver, pancreas, and lung (by inhalation) and the toxicity of lead may largely be explained by its interference with different enzyme systems; lead inactivates these enzymes by binding to SH-groups of its proteins or by displacing other essential metal ions (Benoff *et al*., 2000).

Several researches have been conducted on Pb, Cd, Cr, Hg, and other trace metal levels in air and their toxic effects (Onder and Dursun, 2006), which shows a wide inconsistency in the intake of some metals through air by breathing, drinking water and food (e.g., seafood). High concentration of airborne trace metals such as Pb, Cd, other trace metals and organic pollutants may also cause neuro-developmental and behavioural defects in children. Thus, in this study, the levels of PM_{10}, and two most important trace metals (Pb and Cd) have been investigated in the atmospheric air in Karachi. Also, the trace metal content of PM_{10} has been compared with other parts of the world.

Materials and Methods

Study area. Karachi lies between 24°45′N in longitude and 66°37′E in latitude. It has an area of 3,640 km² and is located along the cost of the Arabian sea. It is the largest metropolitan city of Pakistan, has an estimated population of over 23.5 million people as reported in 2013. With respect to the population, Karachi is the 2nd largest city in the world. Karachi has a moderately temperate climate with a generally high relative humidity that varies from 58% in December (the driest month) to 85% in August (the wettest month). In winter, the average temperature of the city is about 21°C while in summer it reaches up to 35°C. Karachi receives about 256 mm of average annual rainfall (Sajjad *et al*., 2010).

Karachi is the financial and commercial capital of Pakistan as well as the major sea port. It plays an important role in the economy of Pakistan and is considered as the economic and financial gateway of Pakistan. Karachi has several large industrial zones such as Karachi export processing zone (KEPZ), Sindh industrial trading estate SITE, Korangi industrial area (KIA), Landhi industrial trading estate, Northern by-pass industrial zone (NIZ), Bin Qasim and North Karachi industrial zone (KNIZ), located on the fringes of the main city (Sajjad *et al*., 2010). Its primary industries are textiles, pharmaceuticals, steel, and auto-mobiles. Due to industrialisation, business activities and employment opportunities Karachi has been facing mass scale rural-urban migration from all over Pakistan.

Ambient monitoring. *Sampling*. Sampling was carried out at one hundred eight (108) locations consisting of main roads, side road, round abouts, and open places along the busy roads of Karachi (Fig. 1) from 2011 to 2012 for PM_{10}. Selected locations were categorized as commercial, residential, industrial and background areas of the Karachi. Samples were collected on glass fibre filters (203×254 mm) by using high volume air sampler with an average flow rate of 1.0 m^3/min. Eight hour average sampling was done in duplicate at each location during the year 2011 to 2012. The high volume is considered a reliable instrument for measuring the weight of PM_{10} in ambient air (USEPA-Method 40 CFR). Relevant features of air quality stations are shown in Table 1.

Mass concentration. In addition to the determination of elemental concentrations, airborne particle masses of PM_{10} samples were measured using analytical balance (KERN, ALS 220-4). The filter papers were weighed under controlled conditions of humidity and temperature before and after collection of particulate matter. Weights for the blank filters were also recorded. Prior to weighing, all filter papers (glass fiber filter paper) were left to equilibrate their humidity and temperature conditions for at least 24 h in a desiccators. The collected particle mass was calculated by subtracting pre–weight from post–weight of the filter.

Sample analysis. Acid digestion method for metals determination by atomic absorption spectrophotometer (Hitachi Z-8000), with Zeeman effect background correction was carried out according to a standard procedure. Acid digestion was performed by following these steps: (1) samples of dry filters were dissolved in

Table 1. Relevant feature of the air quality stations

Location code	Remarks
C-01 to C-54	Vehicular movement and other commercial activities. Road traffic and commercial activities
R-01 to R-36	Railway siding, vehicular movement, transport on paved road and unpaved road, haul road and exposed dump/ exposed pit surface, domestic waste burning and residential activities etc.
I-01 to I-14	Vehicular emission, waste incineration, Stack emissions and other industrial activities.
UB-01 to UB-04	Low vehicular movement and transport on unpaved road and solid waste dumping.

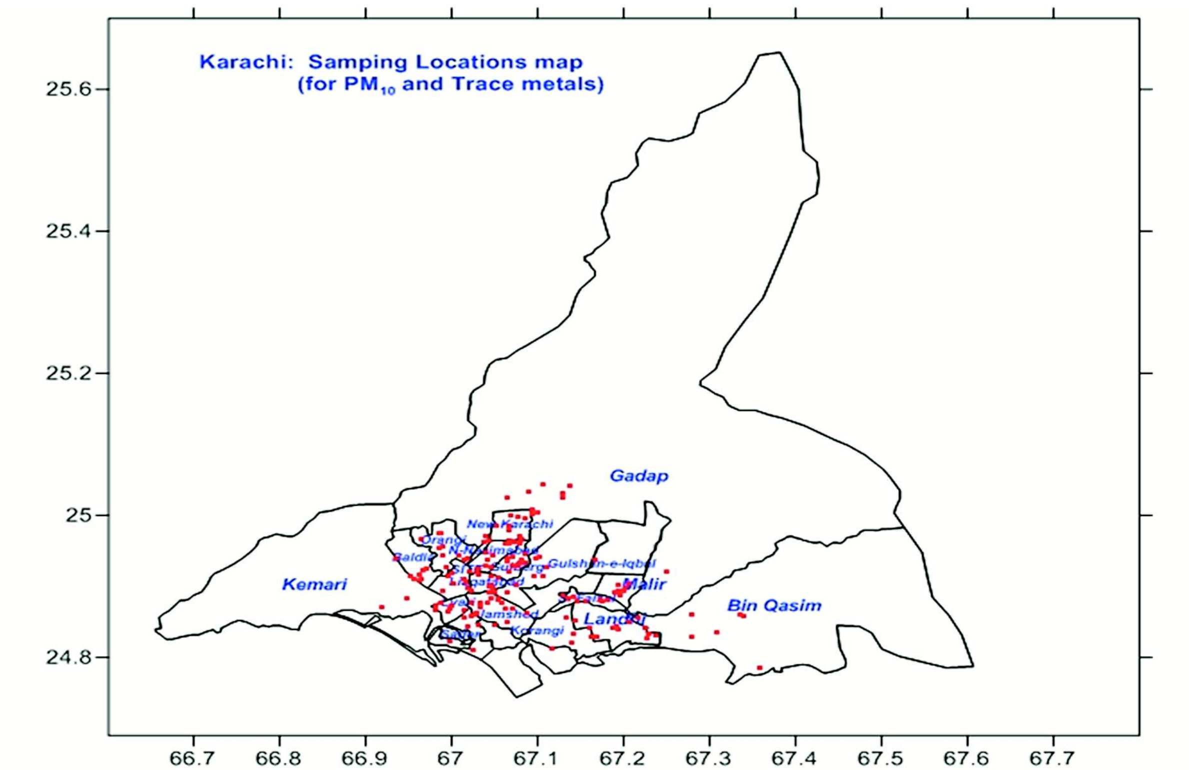

Fig. 1. Location map.

nitric acid and perchloric acid (10:4), (2) digestates were evaporated till white fumes arose and reduced to 2-3 mL, (3) the content was filtered through a Whatman filter 42 and the final volume was make up to 50 mL by double distilled water.

A series of blanks were prepared using the same digestion method. Metals and reagents used for standard solutions were of AR grade. The reagents used were HNO_3 71% (specific gravity=1.41, Pb and Fe=0.00002%, Mn=0.00004%, while Cu=0.00001%) and $HClO_4$ 40% (specific gravity 1.13). The filtrates were analysed for trace metals using AAS. The trace metal amounts in the samples were calculated by subtracting the blank value for the respective metal. The detection limit of various trace metals for the AAS were Pb (0.01 ppm) and Cd (0.004 ppm).

Before analysing the samples, the instrument was calibrated for Pb and Cd. As per the USEPA method 40 CFR, stock solutions (BDH, 1,000 ppm) were used and diluted to the range of working standards for individual metal just before their utilisation. Using these working standards, the calibration graphs were prepared in the linear range of the optical density (0.04-0.8). The instrument was calibrated at three different levels (0.5, 1.0, and 1.5ppm) for both metals. Exactly the same extraction and analysis procedure was employed for PM_{10} filter papers in order to examine the trace metal content of blank filter paper.

Quality assurance. Precision and accuracy of the results were confirmed through an average value of three replicates for each reading and cross checking of the blank or standard at ten sample intervals. The calibration curves of standard solutions of metals were used to justify the quantification. The minimum detection limit for Pb and Cd is 0.30 and 0.01 µg/m^3, respectively. The precision of the analysis of standard solution was better than 5% in all the readings.

Results and Discussion

PM_{10} concentration. The statistical distribution parameters for PM_{10} and trace metals (Pb and Cd) for commercial, residential, industrial and background areas are given in Table 2. The particulate matter concentrations varied from 68.3-719.3 µg/m^3 for commercial areas, 69.1-491.4 µg/m^3 for residential areas, 109.6-736.6 µg/m^3 for industrial areas, while 47.2-98.3 µg/m^3 for background areas. In commercial areas PM_{10} concentrations were higher at locations C-6, C-7, C-28

Table 2. Statistical distribution of PM_{10} and trace metals levels (μg/m^3) in particulate matter of study areas

Pollutants	Range (μg/m^3)	Arithmetic mean	Median
Commercial areas			
PM_{10}	68.3-719.3	361.0	325.9
Pb	0.182-2.46	1.36	1.35
Cd	0.008-0.723	0.10	0.052
Residential areas			
PM_{10}	69.1-491.4	275.0	297.0
Pb	0.30-1.80	1.0	1.06
Cd	0.003-0.073	0.023	0.017
Industrial areas			
PM_{10}	109.6-736.6	438.0	479.35
Pb	0.844-2.15	1.46	1.39
Cd	0.038-0.944	0.25	0.1045
Background areas			
PM_{10}	47.2-98.3	68.9	65.0
Pb	0.40-0.70	0.60	0.006
Cd	0.00-0.01	0.01	0.5

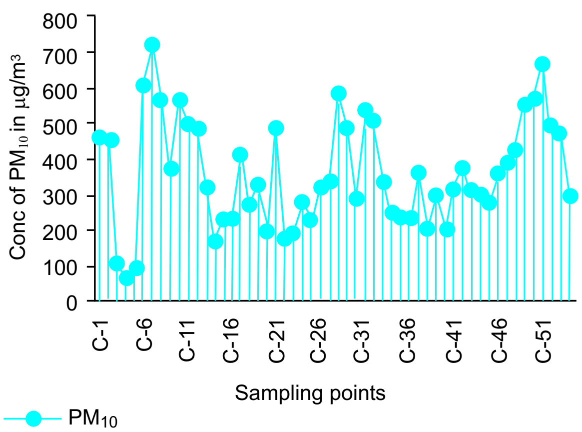

Fig. 2. Concentration of PM_{10} in commercial areas.

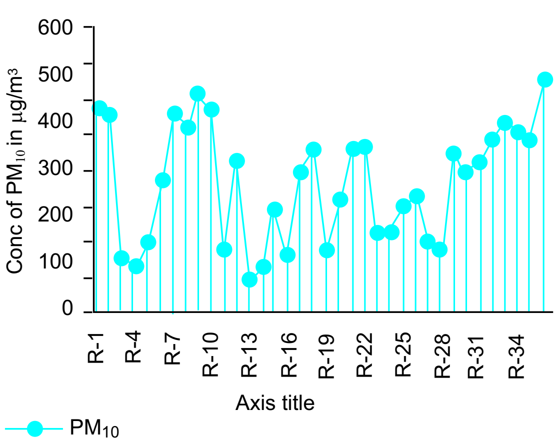

Fig. 3. Concentration of PM_{10} in residential areas.

and C-51. These locations are surrounded by roundabouts having automobile repairing shops, unplanned rickshaws stand and they are receiving higher emissions due to vehicles and commercial activities (Fig. 2). In residential areas PM_{10} concentrations were higher at locations R-1, R-2, R-7, R-9, R-10 and R-36, surrounded by shopping centers with food court producing emission due to

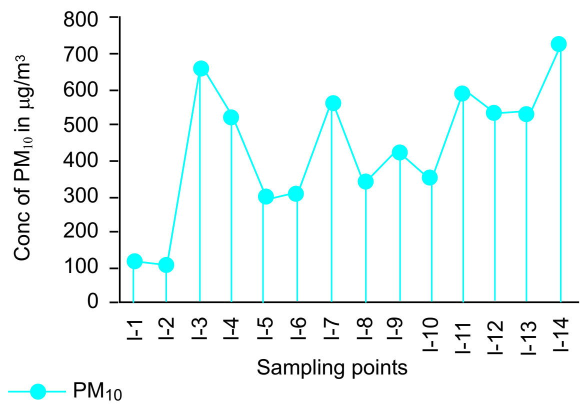

Fig. 4. Concentration of PM_{10} in industrial areas.

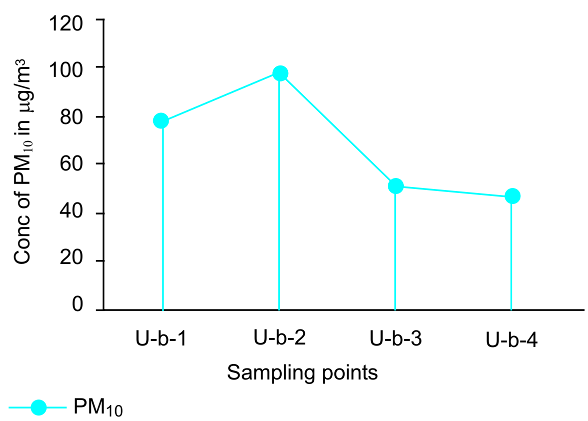

Fig. 5. Concentration of PM_{10} in background areas.

commercial activities (Fig. 3). In industrial areas PM_{10} concentrations were higher at locations I-3, I-7, I-11 and I-14 and receiving higher emissions due to industrial and vehicular emission (Fig. 4) whereas in background areas PM_{10} concentrations were higher at location UB-2 due to impact of vehicular emission from nearby superhighway (Fig. 5). Mean concentration of PM_{10} at various locations of commercial, residential, industrial and background areas were 361.0, 275.0, 438.0 and

68.9 μg/m^3, respectively (Table 2), giving an overall mean of 285.7 μg/m^3 for Karachi region.

Elemental concentrations. Average concentrations for trace metals (Pb and Cd) at various locations (commercial, residential, industrial and background areas) are shown in Fig. 6-9 for the study areas**.** The highest mean concentration of Pb (Table 2) was found 2.46 μg/m^3 in commercial area, 1.83μg/m^3 in residential area, 2.15μg/m^3 in industrial area and, 0.7μg/m^3 in urban background area and Whereas highest mean concentration of Cd (Table 2) was found 0.72 μg/m^3 in commercial area, 0.073μg/m^3 in residential area, 0.94 μg/m^3 in industrial area and, 0.01μg/m^3 in urban background area, respectively. On the average, the decreasing elemental concentration trend for Pb and Cd in Karachi was: commercial > industrial > residential >urban background areas.

Source apportionment. One hundred eight (54+36+14+4) samples of particulate matter were collected from the main roads, side road, round about, and open places along the busy roads of Karachi (Fig. 1), and these locations were categorised as commercial (54 locations), residential (36 locations), industrial (14 locations) and urban background zones (04 locations) of the Karachi city. Analysis of these particulate matter samples were carried out for lead and cadmium, respectively.

Figure 6 shows the concentration of lead and cadmium in commercial areas of Karachi. Maximum average concentration of lead and cadmium found at location C-52 (2.46 μg/m^3 Pb) and (0.723 μg/m^3 Cd), respectively. These high concentrations of lead and cadmium may be due to the large parking place for hundreds of vehicles near this round about with very high traffic density. Moreover; the roads are narrow and congested with high traffic density. The lowest concentration of lead and cadmium in commercial areas was found at location C-4 (0.18 μg/m^3 Pb) and (0.008 μg/m^3 Cd), respectively. The low concentration at this location may be because this is an open place on wide road having low traffic density with low emissions. All the sampling points in commercial areas were on the busiest intersections in Karachi and are surrounded by multistoried buildings both for commercial offices and residential buildings on main roads and round about having high traffic density.

Figure 7 shows the concentration of lead and cadmium at 36 locations in residential areas of Karachi. Maximum concentration of lead and cadmium found at location R-11 (1.8 μg/m^3 Pb) and (0.073μg/m^3 Cd), respectively. The factors responsible for high values at R-11 are multistoried buildings located at both sides of the roads which produce tunnel effect in this area and high traffic density, whereas, the lowest concentration of lead and cadmium found at location R-3 (0.3μg/m^3 Pb) and (0.003 μg/m^3 Cd), respectively due to open place with low vehicular emissions. Residential areas are densely populated having high traffic density. The sampling points in residential areas are also covered with the busiest intersections in Karachi and surrounded by single and mostly multistoried buildings for residence. The populations living around the selected locations were middle and high income group and also have high emission of vehicles.

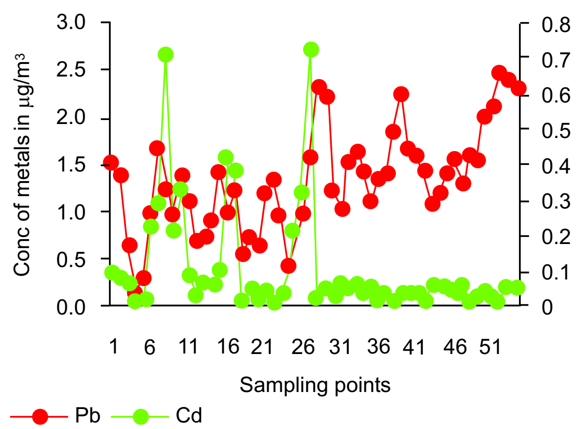

Fig. 6. Concentration of Pb and Cd in commercial area.

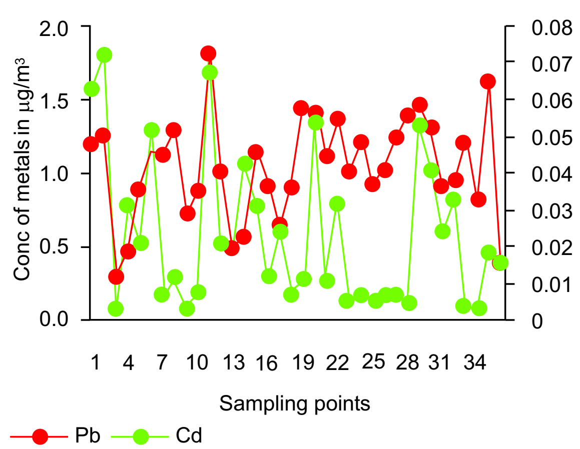

Fig. 7. Concentration of Pb and Cd in residential areas.

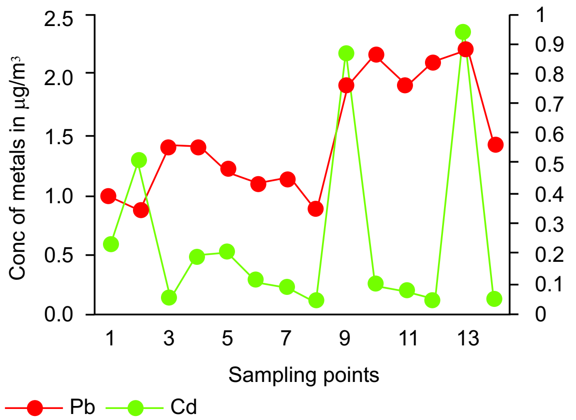

Fig. 8. Concentration of Pb and Cd in industrial areas.

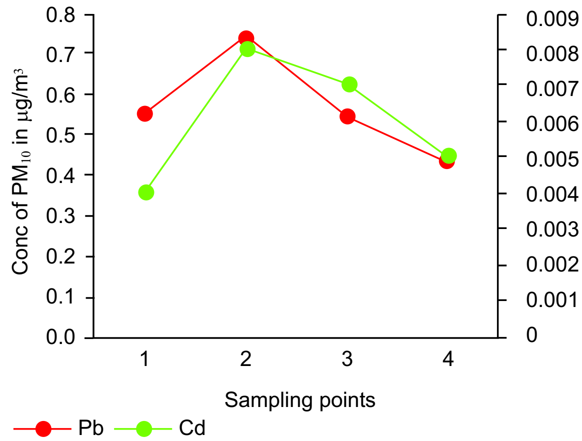

Fig. 9. Concentration of Pb and Cd in industrial areas.

Figure 8 shows the concentration of lead and cadmium at 14 locations in industrial areas of Karachi. Maximum concentration of lead and cadmium found at location I-13 (2.2 µg/m^3 Pb) and (0.944 µg/m^3 Cd), respectively. Increase in trace metal pollution at this location may be due to high traffic density and emission from the industries which are located on main roads of the city. Whereas, lowest concentrations of lead and cadmium found at location 1-8 (0.84 µg/m^3 Pb) and (0.038 µg/m^3 Cd), respectively. The low values found here may be because these industrial areas have relatively open place and situated on the intersection of very wide road. The sampling points in industrial areas have different types of industries. The areas covered are SITE, LITE, KIA and Port Qasim. Approximately 60% of the industries are textile mills, while other involve pharmaceuticals, chemicals, detergents, iron and steel, sulphur refining, vegetable oil, beverages and food products.

Figure 9 shows lead and cadmium concentrations at 04 locations in background areas of Karachi. Maximum concentrations of lead and cadmium in urban background areas was found at location U-B-2 (0.7 µg/m^3 Pb) and (0.008 µg/m^3 Cd) whereas, minimum concentration was found at location U-B-4 (0.4 µg/m^3 Pb) and (0.004 µg/m^3 Cd), respectively. The low values found here may be due to the locations selected in urban background areas are relatively open places and situated on wide roads having low traffic density. The sampling points UB-2 and UB-3 in urban background areas are 390 km away from the main super highway whereas UB-1 and UB-4 are situated on wide road. The areas around the sampling site are sparsely populated having low vehicular traffic.

Lead has been found to be one of the major toxic elements generated through the motor vehicle exhaust using leaded gasoline. It is non degraded pollutant and it not only accumulates in the body but also modifies itself as it moves through biological cycles and food chain. The relatively high lead concentration in Karachi could predominantly originate from burning of solid waste and from large number of vehicles. Emission from road or wind-blown dust, or other industries may also have significant contribution to the lead pollution in Karachi city. Previously, much attention has been paid towards lead in the atmosphere due to wide spreads use as an anti-knocking agent in gasoline (Jones, 1991). Presently, however, after the introduction of the regulations requiring the reduction in the lead content in gasoline markedly decreased from 0.64 g/L in 1966 to 0.14 g/L in 1986, this decrease of lead concentration in gasoline also decrease the addition of lead to the environment by using it in the motor vehicles. Whereas, previously deposited lead concentration in the environment is a main source of lead in present environment. Even though the concentration of lead decreases in the gasoline but due to increase of vehicles in the city also increase the emission of lead in the environment of the city.

The average concentration of cadmium at some points exceeded the WHO guidelines value (0.005 µg/m^3) in commercial and industrial areas at selected points in Karachi. The higher cadmium concentration in industrial areas of Karachi may be due to the release of cadmium from different industrial and mechanical processes. Whereas in commercial areas may be due to the vehicular traffic. The sources of cadmium are diesel and lubricating motor oil, tyres and galvanized part of the vehicles. Diesel oil contains 0.07 to 0.1 ppm of Cd, whereas lubricating oil contains 0.26 ppm. The wear and tear of automobile tyres, which contain 20-90 ppm Cd, is main source of Cd pollution (Qureshi, 2000). However, the cadmium concentration has the lowest concentration than the measured concentration of lead in this study. Care should be taken about the sources and remedy of the high level of cadmium pollution in Karachi as it has serious impact on human health.

Table 3 shows that various studies on trace metals (lead and cadmium) level in PM_{10} samples have been undertaken in different countries of the world. Khillare and Sarkar (2012) reported the Pb concentration in particulate matter in urban residential areas within the range 0.27 to 0.46 µg/m^3. In the present study (Table 3) average concentration of lead in residential areas was recorded 0.96 µg/m^3 which is higher from Delhi, India (Shridhar *et al*., 2010), Coimbatore, India (Vijayanand *et al*., 2008), Beijing China (Khan *et al*., 2010) and Tocopilla, Chile (Jorquera, 2009). In urban background areas, was recorded as 0.01 µg/m^3, which is higher than that reported for urban background of Italy (Contini *et al*., 2010) and UK (Heal *et al*., 2005). Level of lead and cadmium also analysed in the samples collected from industrial and commercial areas of Karachi city. The average concentration of lead in industrial areas was found to be 1.46 µg/m^3 whereas in commercial areas of Karachi was found to be 1.36 µg/m^3, respectively. Khillare and Sarkar (2012) also

Table 3. Comparison of metal concentrations (µg/m^3) in Karachi with other parts of the world

Location/Site type	Typography	Cd	Pb	References
Karachi, Pakistan	Commercial	0.10	1.36	Present study
	Residential	0.03	0.96	
	Industrial	0.25	1.46	
	U-background	0.01	0.6	
Delhi, India,	Residential	0.01-0.02	0.27-0.46	Khillare and Sarkar (2012)
Coimbatore, India	Residential	BDL	0.21-0.62	Vijayanand *et al*. (2008)
Agra, India	Urban	NR	1.1	Kulshrestha *et al*. (2009)
Delhi, India	Urban	0.01	0.44	Shridhar *et al*. (2010)
Lahore, Pakistan	Urban	0.08	4.4	von Schneidemesser *et al*. (2010)
Beijing, China	Residential	0.005	0.33	Khan *et al*. (2010)
Tocopilla, Chile	Residential	NR	0.01	Jorquera (2009)[a]
Istanbul, Turkey	Urban	0.001	0.07	Theodosi *et al*. (2010)
Lecce, Italy	Urban background	NR	0.008	Contini *et al*. (2010)
Vienna, Austria	Urban	0.0005	0.01	Limbeck *et al*. (2009)
Bratislava, Slovakia	Urban	0.0001	0.02	Meresova *et al*. (2008)
Huelva, Spain	Urban	0.0006	0.02	Sanchez de la Campa *et al*. (2007)
Edinburgh, UK	Urban background	0.0003	0.01	Heal *et al*. (2005)[b]
Los Angeles, USA	Urban	NR	0.002	Singh *et al*. (2002)

NR=not reported; BDL=below detection limit; a=sampling in March-April 2006; b=median values

Table 4. Comparison of metal concentrations (µg/m^3) with USEPA and WHO guidelines

Metals	Commercial (present study)	Residential (present study)	Industrial (present study)	U-background (present study)	WHO	USEPA
	(µg/m^3)	(µg/m^3)	(µg/m^3)	(µg/m^3)	(µg/m^3)	(µg/m^3)
Pb	1.36	0.96	1.46	0.6	0.500	1.500
Cd	0.008	0.10	0.03	0.25	0.01	0.006

reported the concentration of cadmium in particulate matter range from 0.01 to 0.02 µg/m^3. Table 3 shows that in the present study the average concentration of Cd in residential areas was recorded as 0.03 µg/m^3 which is higher from Delhi, India (Shridhar *et al*., 2010), Coimbatore, India (Vijayanand *et al*., 2008), Beijing China (Khan *et al*., 2010) and Tocopilla, Chile (Jorquera, 2009), in urban background areas was recorded as 0.60 µg/m^3 which is higher than that reported for urban background of Italy (Contini *et al*., 2010) and UK (Heal *et al*., 2005), in industrial areas was found to be 0.25 µg/m^3 whereas in commercial areas of Karachi was found to be 0.10 µg/m^3, respectively.

In the atmospheric air, toxic metals cannot be destroyed or shattered and can be inhaled during breathing. Various studies on atmospheric metal concentration and their health hazards have been carried out in different cities of the world which shows variation in the concentration of toxic elements like lead and cadmium (Freitas *et al*., 2010). Both these toxic metals causes different types of health hazards as slowing of heart rate, different types of cancer, bronchitis and leukemia (Khillare and Sarkar, 2012; Jorquera, 2009). Lead is one of the well known man made environmental pollutant and causes chronic obstructive pulmonary diseases, lungs cancer, bronchitis and chief source of asthma both in young and older citizens even a very small amount of lead exposure becomes physiologically active and results into its accumulation in the food chain. Adverse health effects on humans particularly on infants' central nervous system (CNS) have been well established.

Cadmium is carcinogenic to human body and inhalation of Cd, causes lung cancer, different types of cardio-vascular diseases, acute and chronic kidney diseases etc. Other effects due to cadmium exposure due to breathing for a long time are lung damage and fragile bones (Järup and Alfvén, 2004).

Conclusion

The study area covers a substantial portion of Karachi (as commercial, residential, industrial and background areas). The characterisation of trace metal sources in the study area is quite challenging due to a large number of vehicles, industries and commercial activities. Trace metals (Pb and Cd) associated with PM_{10} were characterised at one hundred eight locations in different areas of Karachi to identify and quantify their major sources. The findings of this study may provide a comprehensive database for framing an appropriate strategy for necessary mitigative/preventive measures for the sake of human health.

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