The study of TSP and PM₁₀ concentration and their heavy metal content in central area of Tehran, Iran

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Abstract Atmospheric particulate matter may exert serious health hazards because of its chemical characteristics. The main objective of this study is to assess the concentrations of total suspended particles (TSP), particulate matter (PM) with an aerodynamic diameter $\leq 10 \mu\text{m}$ (PM₁₀), and air-transmitted particulate trace metals in Tehran University (a central location in Tehran, capital of Iran) ambient air, for the period of 5 months viz. February–June 2007. Furthermore, the present work examines the daily levels of fine particles in comparison with the proposed limiting values from the U.S. Environmental Protection Agency ($65 \mu\text{g m}^{-3}$ for PM₁₀). The sampling for TSP and PM₁₀ was performed using a high-volume sampler. The TSP and PM₁₀ levels were determined by gravimetry and the metals by flame atomic absorption spectrometry. Arithmetic means of $151 \pm 44 \mu\text{g m}^{-3}$ and $90 \pm 38 \mu\text{g m}^{-3}$ were determined for TSP and PM₁₀, respectively. Comparing with EPA primary and secondary air quality standards, only PM₁₀ concentrations in 3 days were higher than the standard values. Heavy metal content of both TSP and PM₁₀, such as chromium (Cr), cadmium (Cd), and lead (Pb), were also analyzed separately during the same period using atomic absorption spectrometry. The average concentrations of heavy metal in TSP were Pb: $183.63 \pm 147.81 \text{ ng m}^{-3}$; Cr: $13.72 \pm 2.40 \text{ ng m}^{-3}$; and Cd: $6.80 \pm 1.97 \text{ ng m}^{-3}$ and for PM₁₀ were: Pb: $150.36 \pm 157.01 \text{ ng m}^{-3}$; Cr: $9.12 \pm 2.14 \text{ ng m}^{-3}$ and Cd: $6.87 \pm 2.22 \text{ ng m}^{-3}$.

Keywords TSP · PM · PM₁₀ · Heavy metals · FAA

Introduction

The sources, characteristics, and potential health effects of total suspended particles (TSP) and particles with aerodynamic diameter less than $10 \mu\text{m}$ (PM₁₀) are very different. The aerosols emitted by the fixed and mobile sources have a variety 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 air pollution has a both anthropogenic (man-made) and natural sources. Fine particles can be emitted directly, for example, as a result of combustion processes, or can form from chemical reactions of gases such as sulfur dioxide, nitrogen dioxide, and some organic gases. Coarse particles can be generally divided into rural, natural crustal material such as dust and urban particles such as road dust kicked up by traffic (called resuspended dust), construction and demolition, industries, and biological sources. It contains hydrocarbons, biological matter, organic and inorganic compounds, acid aerosols, and metals attached to a carbonaceous core (de Kok et al. 2006).

The relations between ambient particulate matter and heart disease were recognized in the nineteenth century when evidence showed that the number of hospital admissions increased on days that the ambient air concentrations of particulate matter was higher than the other days (Peters 2005). Many atmospheric processes including cloud formation, visibility variation, and solar radiation transfer can be influenced by atmospheric aerosols. The gaseous and particulate components of atmospheric aerosol have a

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noticeably role in the deterioration of air quality (Wu et al. 2002).

It is demonstrated that heavy metal content of TSP and PM_{10} can be toxic to living things at certain levels. Although they occur naturally but they can come from many different sources such as some mining industries, fossil fuels burners, garbage or tobacco burners, and even forest fires. Thus, as a result of industrialization, current environmental levels of metals can be elevated relative to naturally occurring levels. Several heavy metals, such as Pb, Co, Cd, Cu, and Cr, are considered hazardous contaminants 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. Furthermore, metals are associated with a variety of health effects. For example, in experimental animals, cadmium can produce acute toxic effects on various organs such as the kidney, liver, pancreas, and lung (by inhalation); chromium (VI) compounds can cause chrome ulcers, corrosive reactions on the nasal septum, acute irritative dermatitis, and allergic eczematous dermatitis among subjects who have been exposed; 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 (WHO 2000).

The analyses conducted in many industrial countries have consistently shown that changes in daily death rates are linked with short-term changes in air pollution levels. Causing serious environmental risks, its effect has been examined extensively (Onder and Dursun 2006). Some studies show that total suspended particles (TSP) and metal concentrations follow a similar pattern but Beceiro-Gonzalez et al. (1997) found that, for the same area, TSP and PM_{10} metal distribution patterns were different (O'Donnell et al. 1976). There are many investigations on Pb, Cd, Hg, and other heavy metal levels in air and their toxic effects (Onder and Dursun 2006). This may result in a wide variability in the intake of some metals through food (e.g., seafood), drinking water, or air. High levels of airborne heavy metals such as Pb, Cd, and certain persistent organic pollutants may also cause neurodevelopmental and behavioral defects in children. Thus, in this study, we investigated the levels of TSP, PM_{10} , and three most important heavy metals (Pb, Cd, and Cr) in the air. Also, we compared the differences between heavy metal content of TSP and PM_{10} .

Materials and methods

Air-transmitted particulate matter (including TSP and PM_{10}) was collected during the period of February 2007–June 2007 at one site located on the central part of the

Tehran (35°45'20.90"N, 51°23'40.40"E, and 1,200 m above sea level). A large number of bookshops, workshops, and some educational institutions (e.g., Tehran University), schools, and colleges are located near this site (the map of sampling sites is shown in Fig. 1). The emissions from public and commercial transportation are the main source of air pollution at this site. The selection of the points and the sampling procedure to estimate the interest parameters took into account the Environmental Protection Agency recommendations (EPA 1997).

Forty-one ambient air samples of TSP and PM_{10} particles were collected on the glass fiber filters (203×254 mm) by using high-volume air samplers (GMV Inc., average flow rate $1.40 \pm 0.05 \text{ m}^3 \text{ min}^{-1}$ for TSP and $1.39 \pm 0.04 \text{ m}^3 \text{ min}^{-1}$ for PM_{10}) for the analysis. The high volume is considered a reliable instrument for measuring the weight of TSP and PM_{10} in ambient air (USEPA—Method IO-2.1 1999). Two high-volume apparatus (one of them coupled with size-selective (cyclone) inlet for PM_{10}) were used for sampling. The main difference between these two devices refers to the size of the particles that can reach the filter surface. The TSP sampler allows trapping the whole particulate, while in the PM_{10} system, only particles with a size $\leq 10 \text{ }\mu\text{m}$ can be collected. With using glass fiber filters, the particles with 0.1–100 μm diameter or less are ordinarily collected. With a size-select inlet, particles with 10 μm diameter or less are collected on the quartz filter. Ambient samples were collected at a height of about 10 m (USEPA 1998) above the ground level. Pre-field filters are conditioned in a room of constant relative humidity and temperature and are gravimetrically tared (USEPA—Method IO-3.1 1999). The duration of each sampling period was 24 h starting at midnight (USEPA—Method IO-3.2 1999).

After air samples were collected, the loaded filters were returned to the laboratory and conditioned as before and then particle mass was gravimetrically determined by weighing filters after drying for 48 h in a desiccator. To measure the heavy metal content of TSP and PM_{10} , the weighted filters were divided into two equal pieces using a cutter, and then the collected samples on glass fiber filters were extracted by acid extraction procedure (USEPA—Method IO-3.1 1999). The selection and preparation of filters, extraction, and analysis of heavy metals were carried out based on the USEPA method IO-3.1 and IO-3.2 (USEPA—Method IO-3.1 1999; USEPA—Method IO-3.2 1999). According to these procedures, the inorganics collected on glass fiber filters were extracted from one of the pieces of the filter strip with 50 ml of hydrochloric and nitric acid mixture (3:1) using a hot acid extraction procedure (USEPA—Method IO-3.1 1999).

After cooling, the three digestates were mixed and filtered with 0.45-mm Acrodisc syringe filters to remove any insoluble material. The heavy metal concentrations in

Fig. 1 Map of the sampling site

Table 1 TSP, PM₁₀, and their heavy metal concentrations in the sampling area

Parameters	Minimum	Maximum	Mean $\pm$ SD
TSP($\mu\text{g m}^{-3}$)	75.72	271.66	151.60 $\pm$ 44.24
Pb (ng m^{-3})	58.45	553.17	169.33 $\pm$ 104.35
Cd (ng m^{-3})	3.33	10.92	6.80 $\pm$ 1.97
Cr (ng m^{-3})	9.87	19.83	13.72 $\pm$ 2.40
PM ₁₀ ($\mu\text{g m}^{-3}$)	21.47	187.83	90.56 $\pm$ 38.54
Pb (ng m^{-3})	39.68	485.33	132.53 $\pm$ 109.34
Cd (ng m^{-3})	3.38	10.64	6.87 $\pm$ 2.22
Cr (ng m^{-3})	5.08	15.82	9.12 $\pm$ 2.14

each sample were determined by atomic absorption spectrometry according to standard analytical procedures (atomic absorption spectrophotometry is capable of quantitatively determining most metals at levels that are required by federal, state, and local regulatory agencies; USEPA—Method IO-3.2 1999).

Before analyzing the samples, the instrument was calibrated for Pb, Cd, and Cr. As per the USEPA method, stock solutions (of 1,000 ppm) were prepared and diluted to the range of working standards for individual metal just before their utilization. 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 (0.1, 10, and 100 ppm) for each metal. Exactly the same extraction and analysis procedure was employed for TSP and PM₁₀ filter papers in order to examine the background heavy metal

content of blank filter paper. As suggested in the method and to verify reproducibility and low background metal concentrations of reagent and filters, 5% of the total number of samples were taken as blank and analyzed for presence of specific metals. The filter blanks were found to have all metals higher than the minimum detectable limits (for Pb, Cd, and Cr were 2.2, 0.2, and 0.7 ng m^{-3} , respectively; USEPA—Method IO-3.2 1999). The concentration of metals in sampled filter papers was found to be much higher than in blank filters.

The one-way analysis of variance (ANOVA) procedure was used to search for significant variabilities among the results. All statistical evaluations were performed with SPSS (SPSS Inc., ver. 11.0.5).

Results and discussion

The total concentrations of TSP, PM₁₀, and their heavy metal content (mean $\pm$ SD) determined in this study are presented in Table 1. As shown in this table, both TSP and PM₁₀ average concentrations are lower than EPA daily standards (EPA 1997) that are used in Iran. Furthermore, the higher concentrations obtained from April to June are lower than those were founded by El Desouky (1988). The average monthly temperatures, rainfalls, and mean TSP and PM₁₀ concentration for the period of sampling are displayed in Figs. 2 and 3. As shown in the figures, good linear correlation ($R^2=0.79$) was observed between the mean TSP concentrations and the mean monthly temperatures. The increase in photochemical activity

Fig. 2 Average monthly temperature, rainfall, and mean TSP concentration for the period of sampling

Fig. 3 Average monthly temperature, rainfall, and mean PM₁₀ concentration for the period of sampling

during days due to increased solar intensity can cause it (Chaloulakou et al. 2003). But monthly precipitations and TSP concentrations show a quite poor correlation ($R^2=0.0092$); this correlation has been shown by Simone Lorena Quiterio et al. (2004).

In order to compare the measured concentrations of interest parameters between various days of the week, the data from the study were divided into the following three groups: holidays, 1 day after holidays, and the other days. Variabilities between all three groups (including TSP and

Table 2 The differences between concentration and content of ambient TSP and PM₁₀ in holidays, 1 day after holidays, and the other days

		Minimum	Maximum	Mean	Standard deviation
The other days	TSP ($\mu\text{g m}^{-3}$)	76.91	271.66	151.28	42.05
	Pb (ng m^{-3})	58.45	553.17	178.04	112.55
	Cd (ng m^{-3})	3.33	10.81	6.63	1.99
	Cr (ng m^{-3})	9.87	19.83	13.56	2.25
	PM ₁₀ ($\mu\text{g m}^{-3}$)	35.90	185.76	92.34	36.32
	Pb (ng m^{-3})	39.68	485.33	127.84	117.30
	Cd (ng m^{-3})	3.38	10.64	6.65	2.06
	Cr (ng m^{-3})	5.08	15.82	9.46	2.26
Holidays	TSP ($\mu\text{g m}^{-3}$)	75.72	187.97	132.86	37.14
	Pb (ng m^{-3})	61.40	278.09	146.43	71.81
	Cd (ng m^{-3})	4.14	10.92	7.33	2.09
	Cr (ng m^{-3})	9.93	17.82	14.41	3.09
	PM ₁₀ ($\mu\text{g m}^{-3}$)	21.47	127.03	70.52	40.39
	Pb (ng m^{-3})	47.02	264.67	146.28	66.39
	Cd (ng m^{-3})	6.29	9.01	5.89	1.69
	Cr (ng m^{-3})	4.00	11.13	8.28	1.69
1 day after holidays	TSP ($\mu\text{g m}^{-3}$)	112.60	243.41	178.02	55.99
	Pb (ng m^{-3})	61.10	341.52	160.69	112.60
	Cd (ng m^{-3})	4.35	9.23	6.88	1.92
	Cr (ng m^{-3})	10.69	17.22	13.53	2.32
	PM ₁₀ ($\mu\text{g m}^{-3}$)	72.45	187.83	106.78	42.15
	Pb (ng m^{-3})	45.97	395.76	135.25	130.83
	Cd (ng m^{-3})	3.96	10.52	8.90	2.45
	Cr (ng m^{-3})	5.97	12.40	8.74	2.12

Fig. 4 Time series of daily mean TSP and PM₁₀ levels recorded during the sampling period

PM₁₀) were not significant at the 0.05 level, but variability between groups was significant ($P=0.032$) for Cd content of PM₁₀. Although no significant differences were seen for other parameters, the mean concentrations of TSP and

PM₁₀ in 1 day after holidays were found higher compared with the other days (Table 2). The total concentrations of heavy metals found in this study are well in line with those previously reported for the Asian urban area (Fang et al.

Fig. 5 Variation in Pb content of TSP and PM₁₀ during the sampling period

Fig. 6 Variation in Cd content of TSP and PM₁₀ during the sampling period

2005). Mean lead concentrations were well below the both WHO standards (WHO 2000) and EPA ambient air quality standards (EPA 1997). As previously mentioned, the one-way ANOVA procedure was used to search for significant variabilities among these groups. Using this procedure, it was observed that variabilities between

groups (holidays, 1 day after holidays, and workdays) were not significant at the 0.05 level (with the exception of Cd). The results of grouped data for TSP, PM₁₀, and total metal concentrations are presented in Table 2. Variation of TSP and PM₁₀ mean concentration recorded during the sampling period are presented in Fig. 4.

Fig. 7 Variation in Cr content of TSP and PM₁₀ during the sampling period

According to this figure, average PM_{10} concentrations in 3 days were higher than NAAQS.¹ Results of the present study also showed that the Pb, Cd, and Cr content (an arithmetic mean) of TSP were 169.33 ng m^{-3} (0.1253% of TSP), 6.80 ng m^{-3} (0.0050% of TSP), and 13.72 ng m^{-3} (0.0098% of TSP), respectively. Similarly, the Pb, Cd, and Cr content (an arithmetic mean) of PM_{10} were 132.53 ng m^{-3} (0.1824% of PM_{10}), 6.87 ng m^{-3} (0.0093% of PM_{10}), and 9.12 ng m^{-3} (0.0124% of PM_{10}), respectively (Table 1). Variations in heavy metal content of TSP and PM_{10} during the sampling period are shown in Figs. 5, 6, and 7. As implied from Fig. 6, 77% of TSP and 79% of PM_{10} samples have Cd content higher than WHO annual average guideline ($0.005 \text{ } \mu\text{g m}^{-3}$) while concentrations of Cr in all samples were higher than the value of 2.5 ng m^{-3} (that corresponds to an excess of lifetime risk of 1:10,000) (WHO 2000).

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¹ National Ambient Air Quality Standards.