Concentrations and Source Assessment of Some Atmospheric Trace Elements in Northwestern Region of Tehran, Iran

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Abstract Outdoor concentrations of some elements such as iron, aluminum, magnesium, titanium, copper, zinc, lead, manganese, sulfur, chromium and arsenic in PM_{10} and $PM_{2.5}$, was evaluated at four points in north-western part of Tehran in winter 2007. The total concentration of the elements in PM_{10} and $PM_{2.5}$ at the north Karegar avenue found to be as high as 82.05 and 60.64 $\mu g/m^3$, respectively, while at the Arjantin square it was measured to be 34.30 and 28.03 $\mu g/m^3$. The emission sources of the trace elements were attributed to the adjoining local industries in the west parts of Tehran.

Keywords Trace elements \cdot PM₁₀ \cdot PM_{2.5} \cdot Tehran air pollution

Tehran, the capital city of Iran with over 10 million populations, is facing great risk from various pollutants, especially suspended particulate matters (Madanipour 2006; Atash 2007). Many of clinical and epidemiological studies have stimulated to find the cause of adverse effects of particulate matter (PM) on human respiratory system. Epidemiological studies also have shown an association between respiratory-related mortality and morbidity to the levels of ambient PM having diameter of <10 μ m or PM₁₀ (Dockery et al. 1993; Adler and Fischer 1994; Gillies et al. 2001; Pope III et al. 2002). The United States Environmental Protection

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R. M. Darbani Faculty of Environment, Tehran University, P.O. Box 14155-6135, Tehran, Iran Agency (US-EPA) classified fine particulate matter as a criteria air pollutant and added new annual (15 $\mu g/m^3$) and 24 h (65 $\mu g/m^3$) standards of ambient $PM_{2.5}$ (particles with aerodynamic mean diameters at or below 2.5 μm) mass concentration to the National Ambient Air Quality Standard (NAAQS 2003). Designing control strategies to bring the $PM_{2.5}$, PM_{10} levels into compliance with the NAAQS will require knowledge of the aerosol chemical composition and source contribution.

Knowledge of the size distribution of atmospheric particles, which contain trace elements, is not only vital in understanding PM adverse effects on human health, but also controls the extent to which metals may be dispersed via atmospheric transport and hence is a prerequisite for the determination of rates of deposition of elements to the earth's surface (Allen et al. 2001). It is well established that these inhalable particles carry higher concentrations of many potentially toxic trace elements such as Pb, Cd, V, Fe, Zn, Cr, Ni and Mn (Hlavay et al. 1992; liu et al. 2000; Harrison and Yin 2000).

Earlier efforts in this direction include a study in Spain by Espinosa et al. (2001) describing size distribution of metals content of aerosol and variability of airborne trace metals in urban aerosols in Argentina. Some studies report on the size distribution of metals in atmospheric aerosols measured at rural and semi-rural locations in Brazil (Quiterio et al. 2005), England (Allen et al. 2001; Cass et al. 2000), Japan (Wang et al. 2005), Syria (Al-Masri et al. 2006), China (Wu et al. 2008), Turkey (Bakirdere and Yaman 2008), and USA (Abbott et al. 2004).

Trace elements are released into the atmosphere by human activities, such as combustion of fossil fuels and industrial activities; and natural sources such as forest fires, oceans and volcanoes (Samara et al. 2003; Querol et al. 2007; Rajsic et al. 2008; Yatkin and Bayram 2008).



The concentration of particulate matter in Tehran increases drastically in the winter time and as the result, Tehran experiences such days quite often, forcing schools to close and people with heart and lung problems to stay home. In this study, the experiments were carried out to determine the concentration of PM trace elements, as well as elements characterization of PM and source assessment in four different areas in the north-western parts of Tehran in the winter time. This part of Tehran is highly populated and jammed with traffic and also many schools, universities, commercial areas, terminals, and hospitals are involved in their daily activities.

Materials and Methods

The sampling area in the north-western part of Tehran is illustrated in Fig. 1. This area is approximately 18.5 km², spreading from the north west of Tehran, all the way along the west central parts of this city. The 40 km highly industrial area is in contact with this region, directing toward the west.

 $\textbf{Fig. 1} \ \ \text{The sampling area}$

Selection of the sampling stations was based on population, density of traffic and urbanization character, characteristic of which are summarized in Table 1.

All the samples were collected during January, February and March 2007. Daily 24 h sampling started at 8:00 A.M. Sampling height was chosen according to average height of Iranian people which is 1.65 m (Haghdoost et al. 2008).

 PM_{10} and $PM_{2.5}$ collections were done using cascade impactors (Sierra Instruments, USA) with the rate of 30.5 m³/h. Wathman glass fiber filters (type GF/A) were used for collecting the samples. Filters were weighted up to 0.1 mg (after equilibration) before and after sample collection. After each collection, the filters were dried in a 105° C oven for 2–3 h and kept over P_2O_5 in a desicator prior to weighing. All the samples were acid digested according to the method adapted by EPA-3051 Test Method (2003), using microwave oven (Mile Stone – ATC – FO 300 – Italy).

A quarter of each filter paper was cut and placed inside a pressure controlled sample bottle. Proper amount of Aqueo regia solution was then added (9 mL conc. $HNO_3 + 3$ mL conc. HCl) to each sample and digested according to the EPA-3051 Test Method (2003). The samples were cooled to

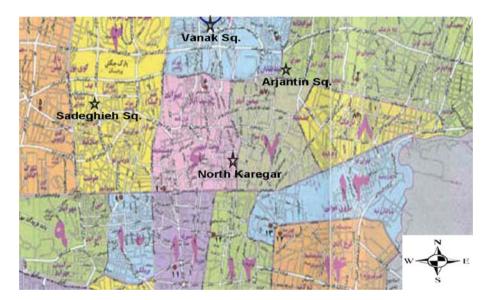


Table 1 Characteristics of the sites

Site (abb.)	Description
Vanak square (VS)	Close to some commercial areas, close to Tehran large Mellat Park, many hospitals are located in this area
Arjantin square (AS)	Close to Hemmat and some other highways and expressways, a large bus terminal is located in this square
Sadeghieh square (SS) North Karegar ave. (NK)	Near large residential areas; heavy-trafficked neighborhood, close to a main bus terminal, close to some commercial areas, close to a large Tehran subway station, many schools are in this area
	Highly populated with university students, in contact with large Laleh Park, many major hospitals are located in this area, highly commercial activities, highly populated area, many schools are located in this area



Table 2 Limits of detection (LOD) for the elements (mg/L)

	Zn	Fe	Pb	Mg	Al	Cu	S	Ti	Mn	Cr	As
LOD	0.001	0.0005	0.01	0.00002	0.02	0.0003	1	0.1	0.0001	0.002	0.05

the ambient temperature outside the microwave oven and filtered on Wathman 41 filter paper. The filtrates were diluted with deionized water to 50 mL and then analyzed for the elements, according to EPA-6010 Test Method (2003), using Inductive Coupling Plasma instrument (ICP-ARL 3410, Switzerland).

Various dilutions of standard solutions were used to obtain calibration curves for each run. Depending on the nature of elements, mean extraction recovery for particulate elements was calculated to be 88%, ranging from 81% to 96%. Five-point calibration curves for all the target analysis were obtained (r > 0.97). The limit of detection (LOD) for each element, listed in Table 2, was obtained by measuring sequentially diluted standard solutions of the elements by ICP.

Results and Discussion

Mean outdoor PM_{10} and $PM_{2.5}$ concentrations for each of the sampling sites are shown in Fig. 2. As it can be seen, the total average PM_{10} concentration at the sites was 336.7 μ g/m³, while $PM_{2.5}$ summed up to 210.5 μ g/m³. It is worth noting that $PM_{2.5}$ concentration accounted for 60% of total particulate matter and is considered to be high enough to elevate lung and other respiratory diseases. This figure also suggests that the concentrations of the particles in this region are highly vacillated.

The highest PM_{10} and $PM_{2.5}$ concentrations were found at NK site, while the least values attributed to AS site. Referring to Table 1, it is noticed that many major hospitals are located at NK region and also it is densely populated with students.

The second highest concentrations of PM_{10} and $PM_{2.5}$ belongs to SS site, where the main bus terminal is located.

This area is considered as a heavy trafficked as well as a large commercial center of Tehran. The concentrations of both PM_{10} and $PM_{2.5}$ were also high at VS site, where some main commercial areas are in contact with this region. Regarding the data obtained from Fig. 2, it could be noticed that the order of PM concentrations in four different stations is NK > SS > VS > AS. The accordance between measured and standard PM concentrations was good in AS station, but the concentrations of both PM_{10} and $PM_{2.5}$ for the rest of the stations were much higher than the permitted standard values ($PM_{10} = 150 \ \mu g/m^3$; $PM_{2.5} = 65 \ \mu g/m^3$).

Results of elemental analysis of PM_{10} and $PM_{2.5}$ obtained at the sites are presented in Figs. 3, 4, 5 and 6. The orders of abundance of the elements at the four sites are listed in Table 3.

As it is noticed in Table 3, the order of PM elemental concentration in different sites is: NK > VS > SS > AS. It is noticed from Figs. 3, 4, 5 and 6 that the concentrations of the three elements Zn, Mg and Fe are much higher than the other elements. The percent values of these three elements carried by PM_{10} and $PM_{2.5}$ in the sites are summarized in Table 4.

Results shown in Table 4 indicate that the concentrations of Zn and Mg in PM_{10} at VS and SS stations are more or less the same. It could be also noticed from the data listed in Table 4 that the percent concentrations of Fe related to PM_{10} at different sites are approximately the same as the total concentrations of the other eight elements.

Table 5 lists the average concentrations of different elements on PM_{10} and $PM_{2.5}$. The list suggests that the tendency of PM_{10} and $PM_{2.5}$ in combining with the elements is different. For example, trace elements such as Cr and Zn are more combined with $PM_{2.5}$, while PM_{10} contained more S and Fe. The total concentrations of all the

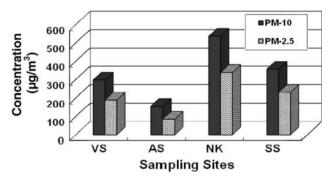


Fig. 2 PM concentrations measured in different sites

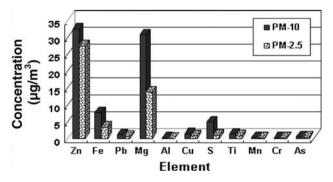


Fig. 3 Elements concentrations (Vanak Site)

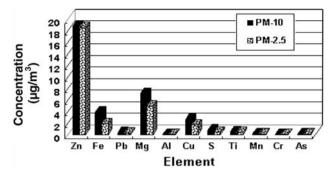


Fig. 4 Elements concentrations (Arjantin Site)

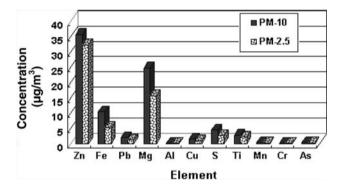


Fig. 5 Elements concentrations (North Karegar Site)

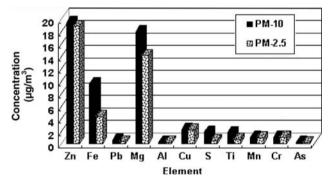


Fig. 6 Elements concentrations (Sadeghieh Site)

trace elements attributed with PM_{10} averaged to be 63.17 µg/m³, while for $PM_{2.5}$ was 44.98 µg/m³. This lead to the ratio of $C(PM_{2.5})/C(PM_{10}) = 0.71$, which suggests that more trace elements in Tehran atmosphere are combined with smaller particulate matter. Since the smaller particles can accumulate deeper in lungs, therefore the

smaller the size of the particles the more dangerous they become for human health.

As it was discussed, among the trace elements, the concentration of Zn content of PM_{10} and $PM_{2.5}$ in the sites in the western parts of Tehran was the highest. The input of Zn in the aerosols could be emitted from two sources: anthropogenic and natural sources. Many large and small industries located within the 40 km westward of Tehran, use Zn, ZnO and other compounds of this element as one of their feed. In addition of anthropic sources of Zn, which considered as the main sources of PM_{10} and $PM_{2.5}$ Zn contamination, natural sources of this element in the soil can be other sources of Zn pollution in air and carry this element with the prevailing westward wind in this region.

Atmospheric outdoor transport of highly concentrated particulate matter with zinc in this urban area of Tehran where many hospitals, universities, houses and commercials are located, could cause serious health problems. Human high concentration intake of this element could cause headache, nausea, digestive spasm and etc. Absorption of 100–300 mg/d of this element may cause cellular anemia in human and hence decrease the absorption of necessary body intake of zinc (Fernandez et al. 2005; Fischer Walker et al. 2008).

Although magnesium and its salts in controlled doses could be beneficial in treatment of some diseases and is considered as a necessary element for human health, but exposure to high concentrations of this element could cause irritation to skin, eyes and respiratory tract (Tanaka et al. 2006; Bintz and Butcher 2007). This element has been found to be as the second highest trace element in this study. Magnesium and its salts have various applications in different field of industry, agriculture and medicine. In addition of these sources of emission from the 40 km western zone of Tehran, this element can be found as the carbonate compound in the soils around this city.

The third abundant element in PM_{10} and $PM_{2.5}$ was found to be iron. The sources of this element are considered to be the 40 km various industrial plants and agricultural activities adjoin to this region of Tehran. In addition, iron could be found as one of the constituents of soil in the various forms of its salts. Exposure to high concentrations of this element and its salts could cause haemokramotosis in human.

Table 3 The order of abundance of the elements at the sites in Tehran

Site	Range of mean conc. of elements (µg/m³)	Order of abundance of the elements on PM_{10} and $PM_{2.5}$
VS	0.12–32.39	Zn>Mg>Fe>S>Cu>Ti>Pb>As>Mn>Cr>Al
AS	0.04-18.83	Zn>Mg>Fe>Cu>S>Ti>Pb>Mn>As>Cr>Al
NK	0.09-35.71	Zn>Mg>Fe>S>Ti>Pb>Cu>Mn>As>Al>Cr
SS	0.21–19.47	Zn>Mg>Fe>Cu>S>Ti>Cr>Mn>Pb>Al>As



 Table 4
 Percentages of concentrations of the main three pollutant elements

Site	Zn Conc. (%) (PM ₁₀ –PM _{2.5})	Mg Conc. (%) (PM ₁₀ –PM _{2.5})	Fe Conc. (%) (PM ₁₀ –PM _{2.5})	Other elements Conc. (%) (PM ₁₀ –PM _{2.5})
VS	40.32–56.75	38.24–28.38	9.52-7.06	11.92–7.81
AS	54.90-66.15	20.85-17.46	11.33-6.72	12.92-9.64
NK	43.52-53.37	30.15-25.75	12.63-8.72	13.70-12.16
SS	34.78-43.64	32.14–32.78	17.15–10.12	15.93–13.46

Table 5 Average concentrations of different elements on PM₁₀ and PM_{2.5} (μg/m³)

	Zn	Fe	Pb	Mg	Al	Cu	S	Ti	Mn	Cr	As	SUM
PM_{10}	26.60	7.87	0.94	20.15	0.12	1.92	3.00	1.56	0.42	0.33	0.27	63.17
$PM_{2.5}$	24.26	3.73	0.58	12.08	0.08	1.37	1.11	0.96	0.32	0.30	0.20	44.98

The concentrations of the other elements compared to the three main elements, Zn, Mg and Fe are low and could be considered as anthropic sources emitted mostly from the industrial activities. The total concentration of these elements in PM_{10} and $PM_{2.5}$ is more or less the same to the concentration of Fe alone in the particulates. Among these elements, As and Mn have more health risk in human. It is known that arsenic decreases DNA repair process and, hence, enhances susceptibility to cancer and noncancerrelated diseases (Duker et al. 2005). Arsenic contamination also could be a serious concern especially for babies (Kim et al. 2009). Long term exposure to Manganese may pose a significant risk for human central system (Elsner and Spangler 2005).

The emission sources of these trace elements in this part of Tehran are mostly attributed also to the large and small industries.

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