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LEVELS OF $PM_{2.5}$ - ASSOCIATED HEAVY METALS IN THE AMBIENT AIR OF SINA HOSPITAL DISTRICT, TEHRAN, IRAN

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ABSTRACT

Introduction: A broad spectrum of adverse health endpoint has been reported because of short- and long-term exposure to particles. Furthermore, various studies which have been indicated correlation between health effects and particle matter characterization such as chemical composition and heavy metals.
Materials and methods: $PM_{2.5}$ samples were collected in the ambient air of Sina hospital in Tehran, Iran, during the springtime 2013. The concentrations of target heavy metals (Pb, Cd, Cr, Ni, Hg, As and Zn) in $PM_{2.5}$ particles were quantified. The $PM_{2.5}$ levels were determined by gravimetric analysis and sample analysis for their heavy metals was done by ICP-AES (Arcous model, Germany) after total digestion.
Result: The results showed that $PM_{2.5}$ levels with an average of 41.19 µg/m^3 were higher than outdoor $PM_{2.5}$ standard of 35 µg/m^3 recommended by USEPA. Total target heavy metals accounted for 0.3 % of $PM_{2.5}$ by mass. The mean values in 31 $PM_{2.5}$ particles samples also were found to be: Pb: 38.05 ng/m^3, Cd: 18.2 ng/m^3, Cr:4.24 ng/m^3, Ni:4.19 ng/m^3, Hg: Not detection, As:1.34 ng/m^3 and Zn:69:92 ng/m^3. Correlations between $PM_{2.5}$ concentrations and toxic elements in various days of the week including: holidays, 1 day after holidays, and the other days have been extracted.
Conclusion: This work describes the levels of $PM_{2.5}$ and their heavy metals. The average concentration of $PM_{2.5}$ were higher than $PM_{2.5}$ standard that recommended by USEPA. The mean concentrations of $PM_{2.5}$ and heavy metals in 1 day after holidays were found higher in comparison with other two groups.

INTRODUCTION

Epidemiological literature of the recent decades disclosed surprisingly large public health effects related with the pollution levels in the world. Especially, the health effects of PM_{10} and $PM_{2.5}$are more serious than previously assumed [1-5]. than previously assumed. Particles with smaller size due to their greater ability to penetrate deeper into the airways and lungs of a person who is breathing have serious health impacts [6-8]. In this regard, in the past decades, PM_{10} and $PM_{2.5}$ have attracted much attention because they have been shown to be harmful to human health [9, 10]. However some epidemiological studies have demonstrated a rise in risk of lung cancer particularly associated with exposure to PM_{10} and

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$PM_{2.5}$[11, 12]. The other studies have shown an increase in respiratory disease is associated especially with $PM_{2.5}$ or secondary particles such as sulfates [13-15]. Moreover, many other studies have attempted link health impacts or toxicity measurements with certain features of particles such as particle size, number , concentration, and chemical composition, including relations with PM chemical constituents such as sulfate, trace elements and metals such as Si, V, Fe, Pb, Cd, Ni, and Zn and elemental carbon [16-19] At the same relationship, it has been demonstrated that heavy metal contents of aerosols can be toxic to humans and other organisms at certain concentrations and there are many studies on Pb, Cd, Hg, and other heavy metal levels in air and their toxic impacts [20, 21].The nature of the PM could be Metal ware, organic, or a mixture of them. Among the mineral constituent of PM, heavy metals are an important group that have caused more and more considerations because they have been shown to be detrimental to human health. These pollutants are formed from various environmental Resources. Some of these metals, such as As, Pb, Cd, Hg, Zn, Ni and Cr are remarkable due to their toxicity. Considering there were no available data concerning these elements for Tehran atmosphere, the purpose of this study is to assess for the first time the air quality of Tehran, regarding the $PM_{2.5}$ and its trace elements content. Therefore, in the work reported here, seven heavy metals including Pb, Cd, Cr, Ni, Hg, As and Zn related to $PM_{2.5}$ particles in the Ambient Air of Sina Hospital District, Tehran will be reported. Furthermore, correlations between $PM_{2.5}$ concentrations and toxic elements in various days of the week including: holidays, 1 day after holidays, and the other days have been extracted.

MATERIALS AND METHODS

Sampling

The sampling was conducted in the Sina hospital district, Tehran (35° 45' 20. 90" N, 51° 23'40. 40"E, and 1,200 above sea level). Air samples were taken from an urban background area in the city on the roof top of the Sina hospital security building characterized by residential and commercial buildings. The emissions from public and commercial transportation are the major source of air pollution at this location. $PM_{2.5}$ samples were collected using a frmOMNI^{tm} Ambient Air Sampler operated at 5 l/m. The PTFE filters of 47mm of diameter from Sartorius Stedim Biotech GmbH (Germany) were used. 31 $PM_{2.5}$ samples were collected every three day from 21 March to 22 June, 2013. Sampling duration was 24 h, yielding sample volumes 7.2 m^3. After the sampling, particle concentrations were obtained by gravimetric method. The filters wrapped in aluminum foil, and stored in freezer at -20 ºC until analysis.

Analysis of heavy metals

In order to determine the heavy metals concentrations, one-fourth of each PTFE filter digested twice with 5mL of concentrated HNO3 and 5ml of $HCLO_4$ in a Teflon bomb to solubilize the metals in ionic form, after that heating almost to dryness(4 hours at 170 ° C) and rinsing with 2.5 ml HNO_3 1N and then rising distilled–deionized water (with a resistivity of 18 Ω) up to a final volume of 25mL with the aim of analyzing their content in Pb, Cd, Cr, Ni, Hg, As and Zn by ICP-AES (Arcous model, Germany) [22, 23] .Each compound was quantified under specific wavelength conditions with the corresponding dilutions using Milli-Q water, in order to be into the quantification range of each compound, and using standards which were simultaneously analyzed with experimental samples. The instrument deviation was checked at the beginning and at the end of each measured trace elements. In order to determination the background values of each species during the study period, blank samples (i.e., unexposed control filters) were chemically analyzed routinely. Then, the real concentration of each species was calculated by subtracting the blank values from the results of the chemical analysis conducted on the exposed filters.

RESULTS AND DISCUSSION

Particles mass and heavy metals concentrations

Mass concentration of $PM_{2.5}$ and its heavy metal content (mean ± SD) determined in this study are shown in Table 1.

Table1. Particles mass and heavy metals concentrations obtained urban site of Tehran, Iran

Components	Mean ± SD	Median	Range
$PM_{2.5}$ (μg/m^3)	41.19 ± 11.9	37.98	17.98-76.45
Pb (ng/m^3)	38.05 ± 11.96	37.98	14.98-66.51
Cd	18.20 ± 6.13	19.04	5.97-33.26
Cr	4.24 ± 1.44	4.43	1.40-7.80
Ni	4.19 ± 1.38	4.33	1.35-7.49
Hg	ND	ND	ND[a]
As	1.34 ± 0.99	1.23	0.12-3.65
Zn	63.92 ± 19.94	61.33	22.24-109.27

[a]Not detection

As shown in Table 1, the $PM_{2.5}$ concentrations range from 17.98 to 76.45 μg m^{-3} at Tehran during sampling period with a mean concentration of 41.19 μg m^{-3}. It is noteworthy that in some days the $PM_{2.5}$ concentrations observed in the present study are upper than EPA daily standards that are used in Iran [24]. In comparison with other studies, these levels fall in the low to moderate range [25-29]. Total target heavy metals accounted for 0.3 % of $PM_{2.5}$ by mass that is a small amount $PM_{2.5}$.The mean concentrations of metals measured in this study following order: Zn > Pb > Cd > Ni> As. As can be seen, the most abundant heavy metal species in the $PM_{2.5}$ fraction were Zn and Pb respectively. The As, Ni and Cr showed a lower contribution to the total heavy metal content, with average concentrations lower than 5ng/m^3. Results obtained by Khaiwal Ravindra, Marianne Stranger & Rene Van Grieken in Menen, Belgium also shown that Ni and Cr were classified as trace elements with mean concentrations below 10 ng m^{-3} [30]. Hg was not found in our study. Mean lead concentrations were well below the both WHO standards [31] and EPA ambient air quality standards [24].

$PM_{2.5}$-related heavy metals levels could be compared with other studies. According to Thomaidis et al study in Athen, higher Pb levels and slightly lower values of other metals were observed. (Means in ng/m3: Pb=190; Ni=6.5; As=2.9; Cd=1.0). The heavy metal concentration in the Athens study follow in order Pb>Ni>As>Cd. [28]. The authors of mentioned study proposed that As and Ni were produced largely by metals industries in Athens such as steel industry and smelters, together emissions associated with diesel, oil and coal burning. Zn production was associated with abrasion and incineration of the tire, brake pads and engine oil [32]; Pb in urban sites was related to emission from motors and the wear of construction materials such as brick, metal, wood and paint. Cu and Cd were related to brake pad wear, diesel emissions of diesel and motor oil [32].

Heavy metals levels in $PM_{2.5}$ found were higher than those reported by Philadelphia and Phoenix in the USA in 1994 [33], Spain in 2003–2006 [22] and Turkey in 2007-2008 (Table 2) [34]. This variety observed, especially about Pb and Cd could be attributed to the large number of vehicles and industries in Tehran.

Due to plenty of pollution sources and restricted control, it seems difficult to determine the particular sources of these metals. It is guesstimated that the emissions are associated with the consume of fossil fuels (coal, oil and etc) for energy and the metal industries.

Table 2. Mean concentrations (ng/m^3) of 7 heavy metals measured in urban background $PM_{2.5}$ in Tehran over the period March to June 2013 and compared with other studies.

literatures	Pb	Cd	Cr	Ni	Hg	As	Zn
Our study	38.05	18.2	4.24	4.19	ND	1.34	63.92
Urban USA[a]	28	-	1.4	8.5	-	0.4	56
Urban Spain[b]	26	0.5	6	6	-	1.1	103
Urban Turkey[c]	32	1.3	9.4	7.7	-	4	215

[a] Philadelphia, USA in 1994 [33] [b] Metal concentrations in PM_{10} in Barcelona, Spain during 2003–2006 [22]
[c] Metal concentrations in $PM_{2.5}$ in Bursa, Turkey during 2007-2008 [34]

Comparison the pollution various days of the week

For comparison the measured levels of considered parameters between various days of the week the data from the study classified into the following three categories: holidays, 1 day after holidays, and the other days.

The results of grouped data for $PM_{2.5}$, and total metal concentrations are presented in Table 3.As shown the $PM_{2.5}$ and their heavy metals concentration in 1 day after holidays were found higher compared other 2 groups. This can be attributed to the accumulation of vehicles in these days.

The one-way ANOVA procedure was used to search for significant variability's among these groups. Using this procedure, it was found that variability's between groups (holidays, 1 day after holidays, and workdays) were significant at the 0.05 level. Exception is Hg (P_{value}=0.238) and Zn (P_{value}=0.177). The total levels of Pb, Cd and Cr obtained in this work are lower than those previously reported for TSP and PM_{10} in the in central area of Tehran [35, 36] and other Asian urban area [37].

Table3.The differences between concentration and content of ambient $PM_{2.5}$ in holidays, 1 day after holidays, and the other days

The days of the study	Components	Mean ± SD	Median	Min-Max
The other days	$PM_{2.5}$ (µg/m^3)	36.91 ± 7.46	37.65	24.67-52.12
	Pb (ng/m^3)	35.74 ± 9.58	37.79	21.46-58.68
	Cd	17.87 ± 4.79	18.90	10.73-29.34
	Cr	4.19 ± 1.12	4.43	2.52-6.88
	Ni	4.03 ± 1.08	4.26	2.42-6.61
	Hg	ND	ND	ND
	As	1.23 ± 0.92	0.98	0.12-2.98
	Zn	66.99 ± 17.37	70.37	39.97-109.27
Holidays	$PM_{2.5}$ (µg/m^3)	38.68 ± 12.37	39.10	17.98-52.93
	Pb (ng/m^3)	37.23 ± 13.73	37.32	14.98-57.76
	Cd	14.03 ± 6.2	14.16	5.97-21.07
	Cr	3.29 ± 1.45	3.32	1.4-4.94
	Ni	3.16 ± 1.4	3.90	1.35-4.75
	Hg	ND	ND	ND
	As	1.21 ± 0.83	1.29	0.23-2.45
	Zn	52.26 ± 223.10	52.72	22.24-78.46
1 day after holidays	$PM_{2.5}$ (µg/m^3)	57.99 ± 11.63	57.34	47.87-76.45
	Pb (ng/m^3)	44.62 ± 16.76	42.06	20.70-66.51
	Cd	20.70 ± 7.70	21.03	12.32-33.26
	Cr	5.14 ± 1.96	4.88	2.54-7.8
	Ni	4.92 ± 1.96	4.74	2.14-7.49
	Hg	ND	ND	ND
	As	1.74 ± 1.48	1.23	0.23-3.65
	Zn	58.87 ± 18.41	54.92	37.92-78.31

The results of grouped data for total metal concentrations are presented in Fig.1 According to this figure, the mean concentrations of $PM_{2.5}$ in 1 day after holidays were found higher compared other two groups. also the mean levels of heavy metals in 1 day after holidays were found higher compared other two groups (except Zn). also the mean levels of heavy metals in holidays found lower compared other two groups.

CONCLUSIONS

As a result, the average concentration of the $PM_{2.5}$ for the sampling period is 41.19 µg/m^3, which is 1.64 and1.2 times higher than the WHO guidelines [38] and EPA ambient air quality standards [24], respectively. This result is likely due to considering contribution of automotive emissions and industrial and mining activities, solid waste burning, industrial refuse and lack of basic

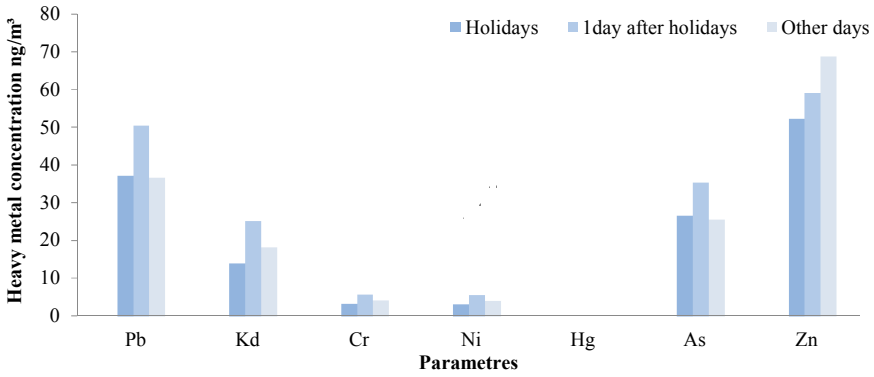

Fig.1. measured levels of heavy metals between various days of the week

substructure. In general heavy metal concentrations in atmospheric $PM_{2.5}$ collected at Tehran are lower than several reported values for other urban areas with high or medium vehicular traffic and/or industrial inputs. Values are also lower than those previously reported for TSP and PM_{10} in Tehran.

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COMPETING INTERESTS

The authors declare they have no potential or actual competing financial or personal interests.

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ETHICAL CONSIDERATIONS

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

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