

On the nature of heavy metals in particulate matter $(PM_{10}, PM_{2.5})$ and their health impact assessment for a desert city in Iran, Birjand

Adeleh Esform¹, Mohammad Sadegh Hassanvand², Ali Naghizadeh^{3,*} Alireza Amirabadizadeh⁴, Sajad Lashkari¹

¹ Department of Environmental Health Engineering, Student Research Committee, Faculty of Health, Birjand University of Medical Sciences, Birjand, Iran

² Center for Air Pollution Research (CAPR), Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran ³ Medical Toxicology and Drug Abuse Research Center (MTDRC), Birjand University of Medical Sciences, Birjand, Iran

⁴ Cardiovascular Diseases Research Center, Birjand University of Medical Sciences, Birjand, Iran

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CORRESPONDING AUTHOR:

al.naghizadeh@yahoo.com Tel : (+98 56) 32381665 Fax :(+98 56) 32440117

ABSTRACT

Introduction: Air pollution is the leading environmental risk factor for
health. This study aimed to assess heavy metals in Particulate Matter (PM ₁₀ ,
PM _{2.5}) and their health impact assessment for a desert city in Iran, Birjand.
Materials and methods: In this study, the concentrations of PM_{10} and
PM _{2.5} were measured from September 2019 to March 2020. Measurements
were performed once every six days for 24 h using high-volume samplers.
Moreover, health-related effects attributed to the suspended particles were
estimated using the AirQ2.2.3.
Results: Mean and standard deviation of PM_{10} and $PM_{2.5}$ concentrations
were 97.5 \pm 38.7 µg/m ³ and 36.3 \pm 19.1 µg/m ³ , respectively. The mean metal
concentrations in PM2.5 were in the Co>Cd>Ce>V order, while the metal
concentrations in PM ₁₀ were in the Cd>As>Ce>V order. The lowest and
highest number of deaths attributed to PM2.5 per 100,000 persons were related
to ischemic heart disease (1.73) and chronic respiratory disease (18.35). The
highest number of deaths attributed to PM ₁₀ per 100,000 persons was related
to chronic bronchitis in adults (35.74).

Conclusion: This study revealed that particle-based air pollution negatively affects health as caused by heavy metals, whereas further research is required to determine the effects of bacterial and fungal bioaerosols on human health. Monitoring the elemental composition of atmospheric particles can contribute to better air quality management.

Introduction

Air pollution is one of the world's principal health and environmental problems. Air pollution exists at varying degrees wherever we live on the planet. It includes a mixture of gases and solid or liquid particles suspended in the atmosphere [1]. Major air pollutants include Carbon monoxide

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(CO), Formaldehyde (HCHO), Nitrogen Oxides (NOx), Sulfur dioxide (SO₂), Ozone (O₃), and suspended particles. Among them, Particulate Matters (PMs) are important as they significantly affect human health, atmospheric chemistry, and global climate change [2]. According to the World Health Organization (WHO), seven million deaths occur yearly due to air pollution [3]. PMs in the atmosphere are major contributors to air pollution in the city [4]. Studies have revealed that air pollution, especially PM, increases hospitalization and mortality and changes the body's physiological function, especially respiratory and cardiovascular function [5]. PM with an aerodynamic diameter of 10 μ m and smaller (PM₁₀) has the greatest health effects due to the ability to penetrate the pulmonary alveoli. It is divided into two categories: coarse $(2.5-10 \,\mu\text{m})$ and fine $(\text{PM}_{25}; \text{PM} \text{ with aerodynamic})$ diameter 2.5 µm and smaller) [6]. Currently, the WHO's air quality guidelines set a threshold for PM of 50 μ g/m³ for PM₁₀ and 25 μ g/m³ for PM₂₅ [7]. Several studies have considered the increase in lung cancer associated with long-term exposure to $PM_{2.5}$ and PM_{10} [8]. Many epidemiological studies demonstrate that when inhaled and deposited in the lungs, PM_{25} (particle diameter smaller than 2.5 μ m) can cause respiratory and cardiovascular disease in humans. Thus, exposure to high concentrations of PM₂₅ increases morbidity and mortality [9].

Research indicates that exposure to PM has increased the number of respiratory and cardiovascular diseases as well as the PM-related mortality rate [10, 11]. In addition to PM, heavy metals such as lead, cadmium, mercury, and other heavy metals are considered important air pollutants due to their carcinogenic and mutagenic properties [12]. Unlike other pollutants, heavy metals have toxic properties and a bioaccumulative potential in plants and animals. Their introduction into the food chain has multiplied the dangers they pose and has numerous ecological effects [13]. They can also damage the nervous system and internal organs [14]. Heavy metals are released into the atmosphere through various processes such as natural resources (ores, volcanic dust, etc.) and synthetics (dyeing industry, metal plating, battery making, etc.). In recent years, many studies have been conducted to determine the content of heavy metals on respirable particles [15].

A study investigated the concentration of PM_{2.5}related heavy metals in the air and assessed their potential risk to human health. The results indicated that the concentration of lead metals and cadmium particles was higher than the standard and that the concentration of particles in winter and spring was higher than in summer and autumn. Human health risk assessment has demonstrated that the total potential cancer risk for adults and children is above the safe range recommended by the United States Environmental Protection Agency (US EPA) [16].

Many recent studies have been conducted to determine the content of heavy metals and their contamination in street dust worldwide [14]. Informing decision-makers and the general public about the health effects of air pollution is the first essential step in developing successful pollution control strategies. Quantifying the health effects of air pollution is an important guide for community decision-makers. The health effects of air pollution are estimated via quantification, and the priority of air pollution control compared to other risk factors is determined. However, no study has been conducted so far on the content of heavy metals in the dust and the pollution rate of the streets in downtown Birjand. This study focused on the nature of heavy metals in PM (PM₁₀ and PM₂₅) and their health impact assessment for a desert city in Iran: Birjand. This study is to inform the public debate better, assist authorities in defining local programs for air quality management, and raise awareness.

Materials and methods

Location of the sampling site

Birjand city is the capital of South Khorasan province in eastern Iran. The city has a semi-



Fig. 1. The geographical location of Birjand city

desert climate with cold winters and hot and dry summers. With a population of 220,671 people and an area of 35 Km², the city is located on the geographical coordinates of 32 degrees and 87 min north latitude and 59 degrees and 21 min east longitude. One of the buildings affiliated with Birjand University of Medical Sciences in the city center was selected as the sampling site. The sampling site is specified in Fig. 1.

Sampling

The sampling period was from the 24th of September 2019 to the 19th of March 2020, and PM was measured according to the US EPA method at intervals of once every 6 days for 24 h [17]. Sixty samples were measured. A sampling of outdoor PM was performed using the highvolume sampler with an AMS analytical model made in France that featured a flow rate of 1.1-1.7 cubic m³/min and a duration of 24 h. In order to determine the concentration of PM before and after sampling, France-made Millipore Filters (micro glass fiber filters) of the MMP model were placed inside the desiccator. After 24 h, the filters were weighed by a laboratory scale (AND HR200, made in Japan) with an accuracy of 0.0001 g and were placed inside the filter of the device holder. After sampling, the filters were weighed, and the particle concentration (PM_{25}) and PM_{10}) was determined according to Eq. 1, considering the difference between the primary and secondary weights and the volume of the passage air [18].

 $pm_{2.5} = \frac{(w_f - w_t) \times 10^6}{v} \quad pm_{10} = \frac{(w_f - w_t) \times 10^6}{v}$ (1)

Where, $PM_{2.5}$ and PM_{10} represent the concentration of PM with aerodynamic diameters 2.5 µm and smaller in µg/m³, wf represents the weight of the filter at the end of sampling in g, wt denotes the weight of the filter before sampling in g, and v is the volume of the air passage in m³.

Determination of heavy metal components

After sampling using micro-glass fiber filters, the filters were crushed and poured into Teflon containers to determine the heavy metal components. Acids (HNO₃, HClO₄, and HF) were added, and the containers were placed in the oven at 417 °C for four hours [19]. Subsequently, the device was turned off for about 30 min so that the Teflon containers cooled off. The lids were removed, and the containers were placed on a hot plate at a temperature of 90-100 °C until the contents of the Teflon container were completely dry. After drying, the contents of Teflon containers, nitric acid, and double distilled water were added. The sample was filtered by passing through Whatman paper filters 0.42, and an ICP device was used to determine the metals in the samples.

Meteorological data

The meteorological data pertaining to the wind speed, including temperature, relative humidity, precipitation, and prevailing wind direction, were also received from the South Khorasan Meteorological Organization to investigate the effect of meteorological factors on PM concentration.

Statistical analysis

Statistical analysis was performed using SPSS (version 22). ANOVA and Pearson correlation analysis was used to investigate the relationships between changes in heavy metal concentrations.

AirQ 2.2.3

The WHO has proposed the AirQ2.2.3 model to assess the possible effects of specific air pollutants in the atmosphere on the health of people living in a given place and period [20]. Health impact assessment of air pollutants is based on Attributable Proportion (AP) calculation, that is, the portion of the health effect on a specified inhabitant exposed for a certain time to a specific atmospheric pollutant. The AP can be estimated using Eq. 2:

$$AP = \frac{\sum\{[RR(c-1)] \times P(c)\}}{\sum[RR(c) \times P(c)]}$$
(2)

Where RR (c) is the relative risk of health outcome in group c and p (c) is the proportion of the population in the group (c). In selected groups (I) in the target community, the amount attributed to population contact (or several items per unit population) (IE) can be calculated as follows:

$$IE = I \times AP \tag{3}$$

Where IE and I represent the rates of the health impact attributable to the exposure and the BI of the health effect on investigated inhabitants, respectively. Lastly, the number of cases attributable to the exposure can be estimated using Eq. 4, when the size of the population is known:

$$NE = IE \times N \tag{4}$$

(1)

Where NE is the number of excess persons associated with the contact, and N is the number of people studied [21].

Results and discussion

$PM_{2.5}$ and PM_{10} concentrations

Fig. 2 compares the mean concentrations of $PM_{2.5}$ and PM_{10} vis-à-vis air quality guidelines and standards [22]. The results revealed that the mean and standard deviation of $PM_{2.5}$ concentrations was $36.3\pm19.1 \ \mu\text{g/m}^3$ and the mean and standard deviation of PM_{10} concentration was $97.5\pm38.7 \ \mu\text{g/m}^3$, which exceed the 24 h WHO guidelines. According to 24 h WHO guidelines, the mean concentrations of $PM_{2.5}$ and PM_{10} are, respectively, $15 \ \mu\text{g/m}^3$ and $45 \ \mu\text{g/m}^3$.





Monthly variations of $PM_{2.5}$ and PM_{10} concentration

Fig. 3 displays the mean concentrations of $PM_{2.5}$ during the monthly period. According to the results of Fig. 3, the concentration of $PM_{2.5}$ was higher in February. A study investigating the concentration of heavy metals in the air associated with $PM_{2.5}$ and assessing their potential risk to human health concluded that the concentration of $PM_{2.5}$ was 49.9 g/m³ and that the concentration of PM was higher in winter and spring than in summer and fall, consistent with the findings of this study [16].

According to Fig. 3, the concentration of PM_{10} was higher in December and September. Our study's results comply with other research findings indicating that the concentration of PM_{10} was highest in December and September [23]. A study examined the relationship between central nervous system biomarkers and short-term exposure to PM_{10} -bound metals during dust storms, concluding that the concentration of PM_{10} on stormy days and dust (309.8±22.9 µg/m³) was three times higher than on normal days when the concentration of PM was 86.1±14.4 µg/m³[24].

Relationship between $PM_{2.5}$ and PM_{10} concentrations and meteorological parameters

Studies have shown that air pollution is caused by two factors: PM and meteorological factors [25]. PM stability in the atmosphere is mainly influenced by meteorological factors such as transport by wind, precipitation, and dispersion. In addition, photochemical reactions depend on temperature, percentage of humidity, solar radiation, and other factors; the accumulation and transport of PM are closely related to the synoptic system and air circulation [26].

Table 1 presents the correlation between airborne PM concentrations and meteorological parameters. A direct relationship has been established between temperature and PM_{2.5} concentration, where the concentration of PM25 increased with an increase in the temperature. This result is similar to the study in Hong Kong [27]. Additionally, negative results have been found between temperature and PM25 concentration [28]. Table 1 presents the direct relationship between humidity and PM₂₅ concentration so that the concentration of PM_{25} increased with increasing humidity in September,



Fig. 3. Monthly mean values of PM_{2.5}, PM₁₀ concentration during the period

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December, January, and February.

The correlation between wind speed and $PM_{2.5}$ is an inverse one. $PM_{2.5}$ concentration measured near a road in Paris was inversely related to the wind speed [29]. There is a positive link between temperature and PM_{10} concentration, such that the PM_{10} concentration decreases with decreasing temperature. Research [25, 30-32] exhibits a positive relationship between temperature and the PM_{10} concentration.

Also, there is an inverse relationship between the parameter of humidity and PM_{10} concentration, so that with decreasing humidity in September, the concentration of PM_{10} increased, and with increasing humidity in December and January, the concentration of PM_{10} decreased. On the other hand, one study found no difference between $PM_{2.5}$ and PM_{10} concentrations, as both negatively correlated with humidity [33]. There was no significant relationship between wind speed parameters and PM_{10} concentration. According to Table 1, there was no relationship between precipitation and PM concentration, which is associated with the low rainfall due to the semi-desert climatic conditions of the region.

Metals in PM_{2.5} and PM₁₀

Table 2 exhibits the (mean) concentrations of heavy metals in PM₂₅ and PM₁₀ samples. According to Table 2, which indicates the mean concentration of heavy metals in PM_{10} , the lowest amount of heavy metals in PM₁₀ was related to As, Ce, and V with a value of 0.001> $\mu g/m^3$, and the highest amount was related to Cd with a value of 9.588 μ g/m³. Besides, the lowest content of heavy metals in PM_{2.5} was related to Co, Cd, Ce, and V with 0.001> μ g/ m³. The mean total PM_{10} and PM_{25} were 11.4 $\mu g/m^3$ and 4.6 $\mu g/m^3$, respectively. A study in Tehran found that the concentration of heavy metals in the PM_{25} level was less than 5.5 µm [34]. In another study, the number of heavy metals on the surface of suspended particles in an industrial area (grams per square meter) and the accumulation of heavy metals (lead, copper, and zinc) (mg per square meter) was 15 and 54-8 times higher than in urban areas, respectively [35].

Variable	$PM_{10}(\mu g/m^3)$	PM _{2.5} (µg/m ³)	
Temperature	0.21	0.38	
Humidity	-0.01	0.023	
Rainfall	0.518	0.326	
wind speed	0.031	0.012	

Table 1. Correlation between airborne particulate matter concentrations and meteorological parameters

Heavy metal	PM ₁₀ (µg/m ³)	PM _{2.5} (µg/m ³)
Со	0.224	<0.001
As	<0.001	<0.001
Ni	0.006	0.007
Cd	9.588	<0.001
Zn	0.716	0.714
Ce	< 0.001	<0.001
Cu	0.006	0.008
Mn	0.029	0.024
Cr	0.006	0.005
Pb	0.004	0.003
V	<0.001	<0.001
Total	11.4	4.6

Table 2. Heavy metal (mean) concentration levels in $PM_{2.5}$ and PM_{10} samples (n=60)

This study used the Pearson correlation test, which is a suitable and verified measure to describe the sources of suspended aerosols and heavy metals. Tables 3 and 4 present the Pearson linear correlation results for samples of heavy metals in $PM_{2.5}$ and PM_{10} . The relationship of PM22.5 with Ni, Zn, Cu, Mn, and Cr metals was significant (P<0.05), such that metal contents increased with increasing PM_{25} levels. Table 3 indicates that PM_{10} has a significant relationship with Co, Cu, and Cr metals (P < 0.05), so that with increasing PM_{10} , the level of Co, Cu, and Cr metals decreased. PM_{10} correlated significantly with Pb (P<0.05), such that the particle concentration increased with increasing particle level. The results indicate that these metals are transported by outdoor PM. Likewise, Table 4 demonstrates a strong interrelationship between heavy metals.

However, according to the Pearson correlation test, this relationship is weaker between some metals; for example, there is a weaker relationship between chromium and barium or between boron and zinc. There is also a stronger relationship between chromium and nickel or copper and potassium. The correlation between chromium and nickel in this study is consistent with the findings related to the Shanghai-Nanjing expressway [36]. In another study, there was no significant correlation between lead and chromium, which is similar to the results of this study [37]. Table 3 presents the relationship between metals in PM_{10} . As the table shows, there is a strong relationship between silicon and nickel, copper, manganese, chromium, and lead. There is also a weak correlation between copper and aluminum, potassium and barium, and sodium and zinc.

V	Рь	Cr	Mn	Cu	Ce	Zn	Cd	Ni	As	Co	PM _{2.5}	Heavy Me
0.686	-0.055	0.415	0.504	0.569	0.704	0.554	-0.342	0.381	-0.342	-0.210	1	ral PM _{2.5}
-0.406	-0.389	0.067	-0.576	-0.017	-0.414	-0.277	-0.116	-0.175	-0.116	1		C.
0.440	0.422	-0.495	-0.258	-0.375*	0.094	-0.004	1.000	-0.129	1			As
0.157	0.753	0.866	0.877	0.283	0.133	-0.359	-0.129	-1				<u>N</u> :
0.044	0.422	495	-0.258	-0.375	0.094	-0.004	1					Cd
-0.110	-0.518	-0.387	-0.1	0.238	0.769	1						Zn
0.694	0.009	0.089	0.326	0.651	1							Ce
0.988	-0.003	0.575	0.339	1								Cu
0.349	0.654	0.742	1									Mn
0.165	0.459											Ç
0.040	-											РЬ
-												<

Table 3. Pearson linear correlation of heavy metal samples in $PM_{2.5}$ (n=30)

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[Unit of heavy metal µg/m³]

												-
РЬ											1	-0.173
Ċ										1	0.143	-0.051
ЧИ									1	0.665	0.289	0.148
Cr								1	0.530	0.0946	-0.106	0.513
Ce							1	-0.001	0.316	-0.062	0.170	0.875
Zn						1	0.246	-0.367	-0.094	-0.515	-0.141	0.750
Cd					1	0.373	0.258	-0.687	-0.409	-0.595	0.6418	-0.079
ï				1	-0.278	-0.249	0.031	0.706	0.895	0.845	0.494	0.0398
As			1	0.384	-0.207	0.769	0.883	0.226	0.486	0.131	-0.018	0.995
C		1	0.864	0.387	-0.277	0.551	0.8388	0.369	0.492	0.277	-0.166	0.086
PM ₁₀	1	-0.497	-0.460	-3.00	0.558	-0.161	-0.257	-0.547	-0.357	-0.394	0.395	-0.502
Heavy Metal	PM ₁₀	Co	As	Ni	Cd	Zn	Ce	Cu	Mn	Ċ	Pb	>

Table 4. Pearson linear correlation of heavy metal samples in PM_{10} (n=30)

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[Unit of heavy metal $\mu g/m^3$]

Incidence of chronic bronchitis in adults		Health consequences (PM ₁₀) Age cat			Death due to stroke			Death due to ischemic heart disease			Death due to lung cancer			Death due to respiratory disease (ALRI)			Chronic respiratory disease				Natural death		Health consequences $(PM_{2.5})$ Age		
	>25		ouroPorres	categories			>25			>25			>30			0-5			>30					categories (year)	THOID UT
Estimated number of attributable cases per 100.000 population at risk	Estimated number of attributable cases	Estimated attributable proportion (%)		Criteria		Estimated number of attributable cases per 100.000 population at risk	Estimated number of attributable cases	Estimated attributable proportion (%)	Estimated number of attributable cases per 100.000 population at risk	Estimated number of attributable cases	Estimated attributable proportion (%)	Estimated number of attributable cases per 100.000 population at risk	Estimated number of attributable cases	Estimated attributable proportion (%)	Estimated number of attributable cases per 100.000 population at risk	Estimated number of attributable cases	Estimated attributable proportion (%)	Estimated number of attributable cases per 100.000 population at risk	Estimated number of attributable cases	Estimated attributable proportion (%)	Estimated number of attributable cases per 100,000 population at risk	Estimated number of attributable cases	Estimated attributable proportion (%)	Criteria	
13.31	29	29.07	lower			1.57	S	8.61	0.57	1	11.41	1.30	1	9.81	1.19	з	12.76	7.62	17	9.9	41.38	91	9.81] lower	10
28.42	63	62.06	central	Number of deaths		2.82	6	15.46	0.88	2	17.59	0.63	ω	20.03	1.79	4	19.21	12.33	27	16.03	61.78	136	14.65	Number of deaths central	
35.74	79	78.05	upper			4.41	10	24.22	1.73	4	34.46	1.87	4	29.15	2.33	S	24.92	18.35	41	23.86	79.88	176	18.94	upper	

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Health effects

The health effects and long-term consequences attributed to $PM_{2.5}$ and PM_{10} in the air of Birjand city are detailed in Table 5. According to Table 5, the highest and lowest natural mortality rates attributed to $PM_{2.5}$ were 18.92% and 9.8%, respectively. The lowest and highest number of deaths attributed to PM_{25} per 100,000 were related to ischemic heart disease (1.73) and chronic respiratory disease (18.35), respectively. The highest number of deaths attributed to PM_{10} per 100,000 were related to chronic bronchitis in adults (35.74). A study in Taiwan reported that long-term exposure to PM_{2.5} resulted in 2,244 and 645 deaths from ischemic heart disease and Chronic Obstructive Pulmonary Disease (COPD), respectively [38]. A metaanalysis study revealed that long-term exposure to PM_{2,5} in amounts greater than 10 micrograms/ m³could increase the risk of COPD mortality by 2.5% [39]. A study in Shiraz reported that the harmful effects of PM₁₀ on health would increase significantly at concentrations of more than 40 $\mu g/m^3$. The results showed that the number of deaths from respiratory and cardiovascular diseases attributed to PM₁₀ in Shiraz in 2019 was 92 and 22, respectively, which accounted for 2.4% of the total deaths in Shiraz [40]. In a study in Hamadan, the mortality rate due to cardiovascular disease and respiratory diseases attributed to PM_{25} and PM_{10} pollutants was 3.37% and 1.75%, respectively. In addition, cardiovascular mortality had a higher share than respiratory mortality. Moreover, PM₂₅ was found to have the greatest health effects on citizens [41]. The mortality rate in our study was lower than in a study conducted in Tehran, possibly because Tehran has a higher population density and, as a result, more people are exposed to the particles than in birjand city. In addition, a study conducted in Tehran revealed that 5,073 deaths were caused by exposure to PM_{25} particles [42]. Lastly, studies in San Diego, Chile, and Hong Kong have reported a significant association

between air pollution and respiratory disease [43].

Conclusion

This study investigated the concentration of heavy metals in ambient PM $(PM_{10} \text{ and } PM_{25})$ and assessed their health effects in Birjand. According to the results of this study, the mean scores and standard deviations of PM₂₅ and PM_{10} concentrations were 36.3±19.1 µg/ m³ and 97.5 \pm 38.7 µg/m³, respectively. The PM level in a region with a semi-desert climate varies according to rainfall, wind speed, humidity, and temperature. Indeed, the PM level increases as wind speed, humidity, and precipitation decrease. AirQ software also revealed a high mortality rate caused by PM₂ related respiratory diseases and the incidence of chronic bronchitis in PM₁₀-related adults in Birjand. Hence, the necessary strategies to control PM should be considered. In addition, the results of the study suggest that particlebased air pollution has a negative impact on health in terms of heavy metals. The health effects of bacterial and fungal bioaerosols must be determined through additional research into this particle property. Because this survey was conducted during a specific season, it is necessary to conduct similar surveys during other seasons.

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Competing interests

The authors declare that no conflict of interest would prejudice the impartiality of this scientific work.

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Ethical considerations

Ethical issues (including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication, and/ or submission, redundancy, etc.) have been completely observed by the authors.

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