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Heavy Metal Risk Assessment in Particulate Matter (PM_{2.5} and PM₁₀) Emissions from a Cement Factory in Bojnord, Iran

Sima Yekta^a, Alireza Pardakhti^{b,*}, Mohammad Ali Zahed^c

Email Address: *Alirezap@ut.ac.ir

^a College of Environment, University of Tehran (Kish International Campus), Kish, Iran

^b Department of Environmental engineering, University of Tehran, Tehran, Iran

^c Faculty of Biological Sciences, Kharazmi University, Tehran, Iran

Abstract

The present study is an attempt to investigate the heavy metals (Nickel and Chromium) existing in various types of particulate matters (PMs) emitted from a cement factory located in Bojnord-Iran. The research specifically focused on the improvement of health and environmental indexes thus, this research purposed to evaluate the contamination levels and spatial distribution of PMs for estimating cancer and non-cancer risks owing to the exposure of heavy metals in the residents surrounding the cement factory. For this purpose, three main axes with nine stations were determined by considering the wind prevailing and the location of electro filters and mills in the cement factory for comparing heavy metal contamination levels in both PM_{2.5} and PM₁₀ pollutant. The obtained results proved that PM₁₀ concentration is much higher than PM_{2.5} in all points especially the stations located on the third axis. Moreover, it can be concluded that some processes such as the abrasion of raw materials in the cement production line had the largest contribution to the production of PM₁₀. According to the results, cancer and non-cancer risk values attained for Cr and Ni in all stations were in the negligible range, indicating no health risk exists in the present situation. However, controlling and monitoring PM levels in the area are still required to prevent destructive impacts in the future.

Keywords: PM; Heavy metals; Cancer; Health risk; Air pollution

Introduction

Air pollutant emission from the industrial sectors has become a serious challenge worldwide, especially in developing countries [1,2]. A variety of industrial air pollution sources such as fossil fuels-based power plants, chemical industries, metallurgy, machine-building, mining, etc. irreparably change the environment and pose significant health risks to surrounding residents [3-5]. Among these facilities, the cement industry is very important due to its decisive role in the development of the world economy and has attracted the

extended attention of many scholars in recent years [6-8]. The cement sector is the third largest industrial source of pollution, emitting more than 0.000,000 tons per year of greenhouse gas [9]. In addition to carbon emissions that lead to the increase in global warming, this sector emits particulate matter that carries various pollutants including, heavy metals (HMs), Sulfur dioxide, and Nitrogen dioxide [10,11]. Therefore, due to the proximity of cities and residential areas to these units, continuous monitoring of these pollutants is undeniable. Among these pollutants, HMs such

as Pb, Ni, Cr, As, Cd, Al, etc. have been recognized as one of the most significant health concerns in recent years due to their widespread presence in the atmosphere and high toxicity [12,13]. The mechanism of action of heavy metals is very complex, and the lack of metabolism of these metals affects not only human health but also the structure of the ecosystem [14-16]. HMs enter the body directly through the inhalation of polluted air or indirectly through the food chain and cause various diseases and complications in citizens' immune system, especially children [17]. However, the study of heavy metals' behavior and destructive impacts of their release in different cement production units is still limited [18-20]. Health risk assessment is currently considered an effective tool for identifying the hazards of HMs, assessing the risks posed to health hazards, and determining appropriate mitigation, control, and compensation measures. Hence, many research efforts have been focused on the human health risk assessment [21-23]. For example, Goudarzi et al., compare the health effects of HMs for citizens in different urban areas. Based on their results, the areas close to industrial sectors have a higher health risk than high-traffic urban areas [24]. Zhou et al. identified the health assessment of trace elements in different parts of particulate matter (PM_{2.5} and PM₁₀) in industrial areas in China. The obtained results showed that particulate matter (PM) in places close to industrial areas is associated with a wide range of toxic trace elements, especially chromium, cadmium, and nickel, and carries significant health risks for humans [25]. Alfaro et al. analyzed the concentration level of Ni, Cr and Pb in areas contaminated by slag from an abandoned steel plant in Havana, Cuba. Based on the results, even with negligible Cr concentration, it leads to agricultural food contamination and increasing cancer risk for residents [26]. Mallongi et al. evaluated the levels and spatial distribution of fine particulate matter surrounding the cement industry in Indonesia. Furthermore, they assessed cancer and non-cancer health risks for residents based on the United States Environmental Protection Agency (EPA). They found that, health risks of residents in the studied area are considerably

dependent on exposure duration and pollutant concentration [27]. According to the aforementioned literature review, health risk assessment as the most suitable methods has been successful in monitoring HMs in various industrial activities and it can overcome the uncertainty related to their harmful effects.

Our aim in this research is to investigate the amount of heavy metal pollution bound to particles including nickel (Ni) and chromium (Cr) in different locations of a cement factory in Bojnord-Iran. In addition, special emphasis is placed on the use of health risk assessment in determining the effects of chromium and nickel contamination. For this purpose, sampling was performed in order to determine the concentration of studied heavy metals in PM_{2.5} and PM₁₀ in 9 stations. In the following, first, the method used in this project is explained in section 2, including sampling and how to obtain or evaluate the concentration of heavy metals in PM samples. In section 3, the results obtained for health risk assessment are analyzed and finally, conclusions are drawn in section 4.

2. Materials and Methods

2.1. Studied Area

In this study, the contamination level of air pollution and health risk assessment in the Bojnord cement factory has been investigated. This unit with a capacity of 2000 tons/day, is known as one of the important units of cement production in Iran. Due to the effects of climate indicators on the sampling and degree of concentration intensity of pollutants [28], climate data such as wind direction was received from the meteorological department of North Khorasan Province.

2.2. Sample Collection

All stages regarding collecting and analyzing all samples were performed according to EPA methods. The PM_{2.5} and PM₁₀ levels were analyzed in three main axes which were determined according to the wind direction and the location of electrofilters and mills in the cement factory. Each axis has three main stations which are located west and southwest of the factory, approximately between 500 m to 1 km from the major industrial activities. It is worth highlighting that the all measurements at this stage were performed using a PARTICLE MASS COUNTER (model TES 2000) with the

ability to directly measure the concentration of PM₁₀ and PM_{2.5}.



Fig 1. Location of axes and their stations around the cement factory

2.3. Pre-treatment and Data Analysis

The amount of heavy metals (Cr and Ni) in the study area is based on active sampling methods

Table 2. Input parameters to characterize CDI_{inhal} values [33]

Index	Definition	Unit	Amount
C	Concentration	mg/m ³	-
EF	Exposure Factor	Days/year	300
ED	Exposure Duration	Years	30
AT	Average Time	days	360 × ED
ET	Exposure Time	hours	1

using pumps (SKC) and low flow using a 37 mm membrane filter made of fiberglass. The filters' weight was measured separately, and during sampling, the filters were placed in their special guards and installed on the pump. The pump flow for sampling was adjusted to 1.0 liter/min using a calibration device. The average sampling time in this method was between 40 and 60 minutes. The collected filters were transported by unique holders to the laboratory site using the acid digestion method and induction coupled plasma mass spectrometry (ICP-MS). The heavy metals were measured separately by the device with Model Perkin-Elmer, 9000 Elan USA. Besides, the quality assurance and quality control (QA/QC) index included field blanks, parallel samples, and samples' duplicate measurements. The QA/QC outputs display no sign of contamination in all the analyses. All steps

were carried out in compliance with OSHA-120G standard [30].

Table 1. Temperature program and time schedule of the microwave for digesting samples

Program No.	Temp (°C)	Time (min)	Energy (%)
#1	100	12	100
#2	110	24	100
#3	120	24	100

2.4. Risk Assessment Methods

After measuring the concentrations of Ni and Cr in the collected samples, a model developed by the US Environmental Protection Agency (EPA) was used to assess the health risk of heavy metals Ni and Cr for residents [31].

In this regard, the inhaled dose (CDI_{inhal}) is

evaluated to identify the concentration that consumers might be exposed to heavy metals. Some factors such as average time, exposure factor, and exposure duration determine the amount of inhaled dose. Based on the defined model, the CDI_{inhal} of heavy metals in the air is derived using Equation 1 [32].

$$CDI_{inhal} = \frac{C \cdot EF \cdot ED \cdot ET}{24 \cdot At} \quad (1)$$

Hazard Quotient (HQ) and Hazard index (HI) are analyzed to evaluate non-cancerous effects. HQ was calculated for both the lead and cadmium metals according to Equation 2. Reference concentrations (RfCs) for acute and chronic are used to estimate the effects of inhalation of non-carcinogenic substances. HI was also calculated for all substances with non-cancerous health effects based on Equation 3 [34,35].

$$HQ = \frac{CDI_{inhal}}{RFC} \quad (2)$$

$$HI = \sum HQ \quad (3)$$

The amount of RFC (mg/m³) for Ni in chronic and acute states is 9 × 10⁻⁵, and 6 × 10⁻³, respectively. RFC_{chronic} also has a value of 1 × 10⁻⁴ for Cr [36]. If HI > 1 represents non-cancer side effects of concern in calculating the Hazard Index, HI < 1 is acceptable [37].

Cancer risk Index (RI) is calculated using the Inhalation Unit Risk (IUR), which is used to examine and analyze carcinogenic infections. According to the EPA, If RI is less than 1 × 10⁻⁶, the carcinogenic adverse effect due to this exposure pathway is assumed to be negligible, while if RI is above than 1 × 10⁻⁴, it can be dangerous to human health. Moreover, If the RI is among the numbers listed, it indicates an acceptable or tolerable risk [38]. The RI value for the heavy metals is presented in equation 4 [39].

$$IR = CDI_{inhal} * IUR \quad (4)$$

IUR (μg/m³)⁻¹ value for Ni and Cr are 2, 5 × 10⁻⁷, 1, 5 × 10⁻⁷, respectively.

2. Results and Discussion

2.1. Mass Concentration

2.1.1. PM Concentration

The variation in the size of PM is an important factor that influences the heavy metals concentration. In this investigation, heavy metal contamination levels in both PM_{2.5} and PM₁₀ have been evaluated to compare in all stations. The concentration of PMs with various diameters is listed in Table 2. The results illustrated that the concentration of PM differed at each station. The concentration of PM_{2.5} has lower than PM₁₀ in all stations due to the role of emission sources in this region, as shown in Table 1. Based on the results obtained from previous studies [40, 41], the main factor in increasing the concentration of PMs with small diameters (PM₁ and PM_{2.5}) is the combustion of engines and vehicles, while some process such as abrasion of raw materials in the cement production line plays a significant role in increasing the concentration of PM₁₀. This

finding is generally consistent with similar studies have been conducted in the past [42, 43].

Table 2. The concentration of PMs measured based on the diameter of the particles

Axis	Station	PM ₁	PM _{2.5}	PM ₇	PM ₁₀	TSP (μg/m ³)
1	1	2	9	72	148	231
	2	1	13	59	172	245
	3	8	21	70	124	218
2	1	5	14	45	107	220
	2	6	20	50	187	268
	3	7	17	77	153	244
3	1	10	19	59	158	247
	2	9	28	83	191	311
	3	7	23	77	176	283

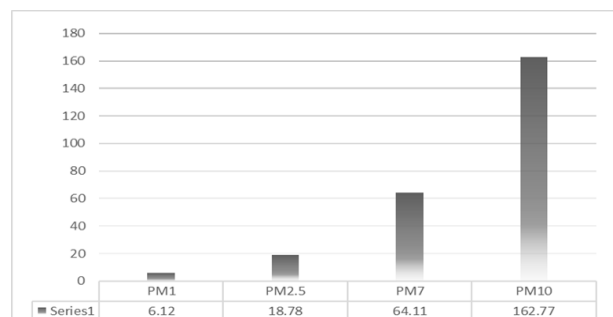


Figure 1. The average concentration of PMs based on size (μg/m³)

Different sizes were observed in the structure of PMs around the studied area, as illustrated in Fig. 1. As can be seen, PM₁ and PM₁₀ has the minimum and maximum rate among all types with 60% and 2%, respectively (Fig. 2). Furthermore, the results illustrated that the concentration of PM₁₀ on axis 2 and 3 mostly exceeds WHO's standard. The provided report also indicated that the cement factory had the largest contribution to the production of PM₁₀ and PM₇. The lowest amount of PMs (PM_{2.5} and PM₁₀) is found in the stations of axis 1. The main reason for this result can be explained by wind direction and the distance of the stations located on this axis from the road. Moreover, it can be concluded that the highest

amount of PMs was in the southwest part of the factory (stations located in Axis 3).

The increase in PMs is basically due to the direction of the prevailing winds in the area and the stations' distance from the road, as described for Axis 1.

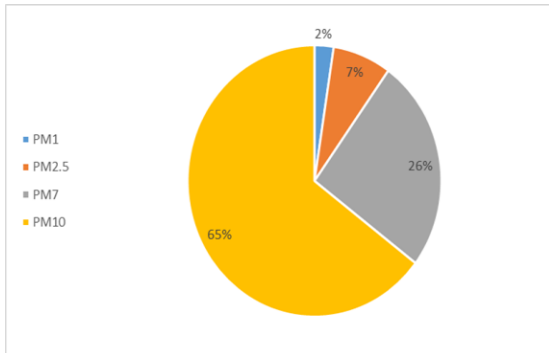


Figure 3. The average concentration of PMs based on size (µg/m³)

3.1.2. Heavy metals Concentration

In this section, the total concentration of heavy metals Cr and Ni in both PM_{2.5} and PM₁₀ are shown in Figs (3) and (4), respectively

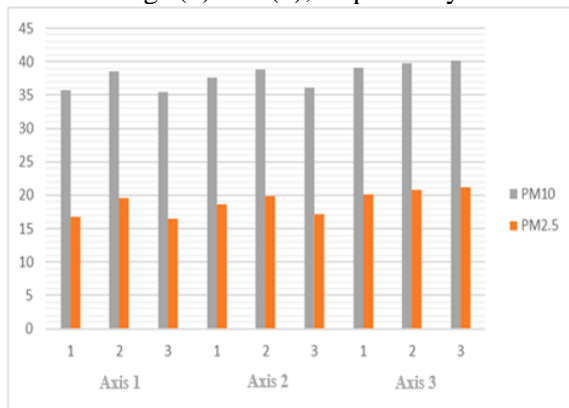


Figure 4. The amount of Cr concentration in the studied stations (ng/m³)

it is clearly observed that there is a significant difference between the concentration of Cr in both PM_{2.5} and PM₁₀ in different stations in axis one, two and three, so the highest concentration of Cr in PM₁₀ was obtained in axis 3. Moreover, the concentration of Cr in PM_{2.5} in station 3 (axis three) and station 2 (axis two) have the highest level among all studied areas while, station 1 (axis one) has the

lowest amount of Cr in all measurement stations.

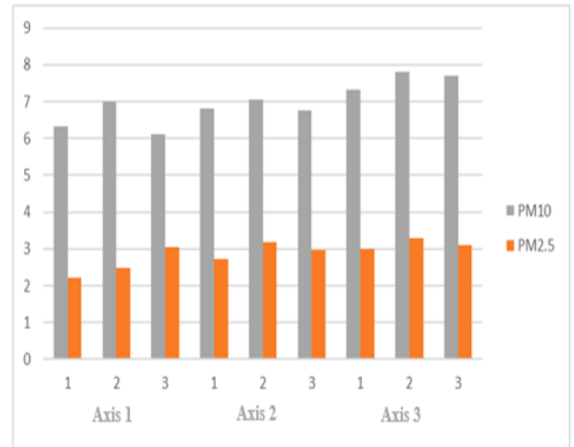


Figure 5. The amount of Ni concentration in the studied stations (ng/m³)

By comparing the measured Ni for both PM_{2.5} and PM₁₀, it can be concluded that Ni concentration in both PM_{2.5} and PM₁₀ fitted proportionately with Cr trend in the whole stations, while the two pollutants were difference in contamination levels (Fig. 5). Therefore, it should be highlighted that contamination levels of studied pollutants were based on wind direction and the distance from polluting sources. In the following, the concentration of Ni and Cr (the maximum, minimum, and average values) in PM_{2.5} and PM₁₀ are presented in Table 4.

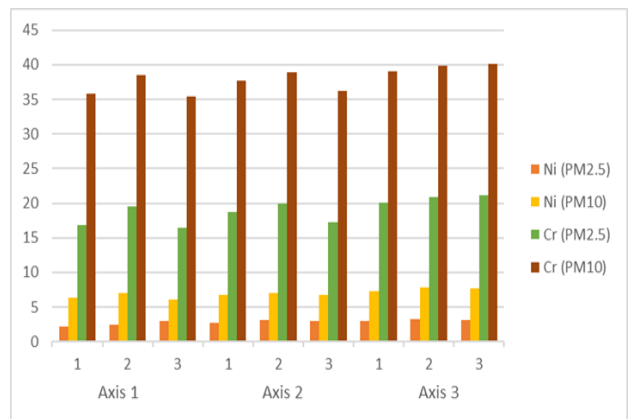


Figure 6. Comparison of studied heavy metals concentrations in PM_{2.5} and PM₁₀

According to the obtained results, due to the prevailing wind, the maximum amount of heavy metals was observed in axis 3, while the minimum total amount of heavy metals was reported in the stations next to the factory in the

first axis. The results (Table 4) are in line with the confirmation of previous studies [44,45].

3.2. Health Risk Assessment

3.2.1. Non-Cancer Risk Assessment

The health risk assessment is one of the main effective indicators in air pollution monitoring. In this investigation, health risk assessment including non-cancer risk and cancer risk was hired to analyze the contamination levels of HMs emitted by the cement unit. The constant values of RFC (acute and chronic) required to assess the HQ and HI rate is presented in Table 5. According to the obtained results, the HI index for Cr and Ni is estimated to be less than the safe level (HI < 1) therefore, the risk of non-cancerous diseases in the studied area is considered acceptable. Moreover, the non-carcinogenicity index of Cr is higher than Ni, which means that the Cr poses a higher risk

than Ni in predisposing to non-cancerous diseases. Therefore, Cr must be paid more attention to the high Hazard Index as well. This result is consistent with earlier researches [46].

3.2.2. Cancer Risk Assessment

cancer risk assessment is known as an appropriate tool that can be reliably used to assess cancer-based diseases.

Hence, the cancer risk implications of Cr and Ni in PM_{2.5} and PM₁₀ were assessed by using EPA standard, as can be seen in Table 6.

Table 4. Concentration (maximum, minimum and average) of heavy metals in PM_{2.5} and PM₁₀.

Axis	Stations	Cr (ng/m ³)		Ni (ng/m ³)	
		1. PM _{2.5}	2. PM ₁₀	PM _{2.5}	PM ₁₀
1	1	16,82	30,78	2,21	6,34
	2	19,00	38,01	2,47	7,01
	3	16,43	30,39	3,00	6,11
2	1	18,67	37,63	2,73	6,82
	2	19,88	38,84	3,19	7,06
	3	17,23	36,19	2,96	6,77
3	1	20,09	39,00	2,99	7,33
	2	21,14	39,80	3,28	7,80
	3	20,84	40,11	3,11	7,69
Minimum		16,43	30,39	2,21	6,11
Maximum		21,14	40,11	3,28	7,80
Average		6,67	37,92	2,88	6,99

Table 5. Non-cancer risk assessment of Cr and Ni by using HQ and HI indicators

Index	Cr (PM _{2.5})	Cr (PM ₁₀)	Ni (PM _{2.5})	Ni (PM ₁₀)
Average Concentration (µg/m ³)	0,01896	0,03792	0,0288	0,0769
CDI _{inhal}	0,00194	0,01389	0,00789	0,01910
RFC _{Acute} (mg/m ³)	-	-	6 * 10 ⁻⁷	6 * 10 ⁻⁷
RFC _{chronic} (mg/m ³)	1 * 10 ⁻²	1 * 10 ⁻²	9 * 10 ⁻²	9 * 10 ⁻²
HQ _{Acute}	-	-	0,00131	0,00319
HQ _{chronic}	0,0194	0,01389	0,08766	0,21277
HI	0,0194	0,01389	0,08897	0,21096

Table 6. Cancer risk assessment of Cr and Ni by using IUR and RI indicators

Index	Cr (PM _{2.5})	Cr (PM ₁₀)	Ni (PM _{2.5})	Ni (PM ₁₀)
Average Concentration (µg/m ³)	0.01896	0.03792	0.0288	0.0669
CDI _{inhal}	0.00194	0.0389	0.00789	0.01910
IUR (µg/m ³)	0.12	0.12	0.024	0.024
RI	0.000223	0.00124	1.89 * 10 ⁻⁷	4.79 * 10 ⁻⁷
Total risk	18.79 * 10 ⁻⁶			

4. Conclusion

The contamination level and health risk assessment of HMs existing in various types of particulate matters (PMs) emitted from a cement factory in Bojnourd (Iran) were studied. In this regard, Sampling from 9 stations in three axes was conducted to analyze the concentration of Ni and Cr existing in PM_{2.5} and PM₁₀. The sample points were selected based on the prevailing wind in the region and the location of electrofilters and mills in the cement factory. After measuring the concentrations of Ni and Cr in the collected samples, a model developed by the EPA was hired to assess the health risk of heavy metals Ni and Cr for residents. The data acquired from the measurements indicated that PM₁₀ concentration is much higher than PM_{2.5} in all stations especially the stations located on the third axis, while the minimum total amount of heavy metals was reported in the stations next to the factory in the first axis. Moreover, it can be concluded that non-cancer risk for Ni and Cr was lower than standard levels, likewise cancer risk of studied pollutants was in acceptable range in this region. However, controlling and monitoring PM levels in the area are still required to prevent destructive impacts in the future.

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