



# Ecological Risk Assessment of Heavy Metals in the Atmospheric Dry Deposition in Hamedan City

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## Abstract

**Background:** Dust pollution can cause serious ecological problems. Therefore, the current study aimed to carry out the ecological risk assessment of heavy metals (Co, Cr, and Mn) in the atmospheric dry deposition in Hamedan city, Iran.

**Methods:** In the current study, 36 samples of atmospheric dry deposition were collected from three regions of Hamedan city from September to October 2014. After sample digestion in the laboratory, the content of the metals was determined using inductively coupled plasma-optical emission spectrometer (ICP-OES). All statistical analyses were performed using the SPSS statistical package.

**Results:** The results showed that the average contents ( $\text{mg kg}^{-1}$ ) of Co, Cr, and Mn in the studied samples were  $0.23 \pm 0.06$ ,  $0.89 \pm 0.20$ , and  $8.10 \pm 0.70$ , respectively. The results of the potential ecological risk analysis of heavy metal pollution in the atmospheric dry deposition in Hamedan city demonstrated that the risk index (RI) of stations A, B, and C with an average of 0.13 is at low ecological risk levels.

**Conclusions:** In present study the potential ecological risk of Co, Cr, and Mn was at low levels. Also, the results showed that the Co and Mn contents in the atmospheric dry deposition collected from the stations with heavy traffic intensity were significantly higher than that in the other stations. Therefore, control of the anthropogenic sources that cause discharge of hazardous compounds, particularly toxic heavy metals, into the atmosphere is recommended.

**Keywords:** Atmospheric Dry Deposition, Heavy Metals, Ecological Risk Assessment, Hamedan City

## 1. Background

Natural and anthropogenic sources, such as soil erosion, sea spray, mining, industrial activities, urbanization, agriculture, power generations, construction activities, and fossil fuel combustion, can cause emissions of particles and gases into the atmosphere through dry deposition pathway (1, 2).

Since the heavy metals are indestructible, they are not easily biodegradable in the environment and accumulate in the biota and have toxic effects on living organisms; therefore, heavy metals are of great importance among the thousands of inorganic and organic matter discharged into the environment. The pollution of the natural environment by toxic heavy metals is a worldwide problem (3-6). In this regard, heavy metal contents in wet and dry atmospheric depositions, particularly respirable dust particles, have been significantly affected by anthropogenic sources. Since airborne particulate matter (PM), especially the fine particle, is a potential source of toxic heavy metals for urban residents via inhalation, oral (ingestion), and

also dermal absorption, they can cause adverse effects on human health. So, in recent years, concern about the quality of dust and atmospheric depositions has been growing around the world (7-11).

It has been proven that the contents of the PMs airborne aerosols in the urban atmospheres are related to traffic pollutants (e.g., heavy metals and organic compounds), caused by combustion of fuel and depreciation of vehicle parts. Also, the dispersion and distribution of environmentally sensitive elements depend heavily on the particle size and the surface properties of the substrate on which the metals are deposited (12-14).

Cobalt as an essential nutrient is beneficial for humans, being an integral part of vitamin B12, and is necessary for proper endocrine functioning, especially thyroid, and has an important role in the regulation of blood pressure. However, exposure to high amounts of this element can cause serious effects on the lungs, including asthma, wheezing, and pneumonia (15-18).

Chromium (III), similar to cobalt, is an essential min-

eral that is widely distributed in the human body tissues in extremely low and variable quantity. This element can help the body utilize lipid, protein, and also carbohydrates (16, 19). Hexavalent chromium (VI) compounds are toxic and known human carcinogens. Breathing high levels of this element can cause adverse effects on human health (e.g., irritation to the lining of the nose, nose ulcers, running nose, cough, asthma, shortness of breath, or wheezing) (20).

Manganese is known as an essential element, but the toxicity of Mn has been reported via occupational and dietary overexposure. The exposure to high levels of Mn can cause adverse health effects, especially effects on the central nervous system, liver, lung, heart, and reproductive system. Also, neurotoxicity of Mn can cause a progressive disorder of the extrapyramidal system similar to Parkinson's disease (21).

Atmospheric dry deposition as an important carrier of contaminants is a typical non-point source (22). Therefore, studying the characteristics of atmospheric dry deposition pollution is an important aspect of urban environmental quality assessment and also human health risk assessment. In this regard, risk index (RI) proposed by Håkanson indicates the sensitivity of the biological community to the toxic heavy metals and illustrates the potential ecological risk caused by the overall contamination (23, 24).

The determination of trace elements in dry atmospheric depositions has been reported by several authors. In this regard, Zheng et al. (2005) analyzed fourteen major and trace elements in dry and wet deposition samples collected in Hong Kong (1). Al-Momani et al. (2008) determined the content of some major and trace elements in the atmospheric deposition in Amman, Jordan (8). In another study, some heavy metal concentrations in falling dust were measured in eastern Mazowieckie Province, Poland (25). Abah et al. (2014) reported some trace metal content in atmospheric dust deposition in Katima Mulilo metropolis, Namibia (26). Also, Tabatabaei et al. (2015) studied the geospatial patterns and background levels of heavy metals in the deposited PM in Bushehr, Iran (27).

Nowadays, due to population explosion, urbanization, and industrialization, the urban environments of developing countries like Iran are experiencing unprecedented environmental challenges. In this regard, since no studies have been carried out for the ecological risk assessment of heavy metals in atmospheric dry deposition in Hamedan city, the current study aimed to analyze and assess the ecological and health risk of heavy metals (Co, Cr, and Mn) in atmospheric dry deposition in regions with different traffic intensities in Hamedan city in 2014.

## 2. Methods

### 2.1. Study Area

Hamedan city, the capital of Hamedan province, is one of the biggest cities in the western part of Iran, located in the northern part of Alvand mountain at an altitude of 1850 m above sea level and lies between longitude 48° 31' E and latitude 34° 48' N with an urban area of about 56 km<sup>2</sup> and population of 581,925. The climate of Hamedan is favorable, with four distinct seasons. Hamedan has cold winters, and there is usually rainfall in the winter and spring. The annual average temperature and annual average precipitation of this city are 11.3°C and 317.7 mm, respectively (28).

### 2.2. Reagents

In the current study, standard stock solutions were of analytical grade (Merck, Darmstadt, Germany). They were used to prepare working solutions after appropriate dilution for analyzing the elemental ions at the concentration of 1000 µg L<sup>-1</sup>. Also, distilled deionized water was used in all the dilution procedures.

### 2.3. Sampling and Sample Analysis

In this descriptive study, according to the Cochran's sample size formula and also considering the financial and time constraints, 36 atmospheric dry deposition samples were collected over a five days interval from mid-September to mid-October, 2014. The samples were collected from the residential areas of three regions of Hamedan city with high (A), moderate (B), and low/light (C) traffic intensity by placing high-density polyethylene bucket of 30 cm diameter on an elevated tripod stand (1 m) above the ground surface to minimize contamination from resuspended particles generated by natural wind and induced by traffic. The geographic coordinates of the sampling sites are presented in Table 1. For sample digestion, after transferring 1.0 g of each sieved sample into a digestion vessel and adding 10 mL of nitric acid 65% (Sigma-Aldrich, Spain), the solution was covered with a watch glass. Then, the samples were heated to 90°C and refluxed at this temperature for 15 minutes after which they were allowed to cool for 10 minutes at 20°C. After that, 5 mL of concentrated HNO<sub>3</sub> was added to each solution, covered, and refluxed again at 90°C for 30 minutes. Then, the solutions were allowed to evaporate without boiling to approximately 5 mL each and cooled again for 10 minutes at room temperature. This was followed by the addition of 2 mL of double-distilled water and 3 mL of H<sub>2</sub>O<sub>2</sub> (30%) to each solution. For the start of peroxide reaction, the digestion vessels were covered and heated just enough to warm the solutions.

This process was continued until effervescence subsided, and the solutions were cooled (1, 8, 28). Finally, the content of the elements was analyzed using inductively coupled plasma-optical emission spectrometer (710-ES, Varian, Australia) at wavelengths of 228.615 nm for Co, 267.716 nm for Cr, and 257.610 nm for Mn.

**Table 1.** Geographic Coordinates of the Sampling Sites

Sampling Station	Geographic Coordinates
A	34°51'23" N; 48°46'51" E
B	34°59'22" N; 48°53'07" E
C	34°58'59" N; 48°58'49" E

#### 2.4. Potential Ecological Risk Assessment

Potential ecological RI of heavy metal levels in the atmospheric dry deposition in Hamedan city was assessed in accordance with Equation 1 (29, 30):

$$RI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n TiC_f^i = \sum_{i=1}^n Ti \frac{C_s^i}{C_b^i} \quad (1)$$

where  $E_r^i$  represents the potential ecological risk factor of metal  $i$ ;  $Ti$  indicates the toxic response factor of metal  $i$  (1, 2, and 5 for Mn, Cr, and Co, respectively);  $C_f^i$ ,  $C_s^i$ , and  $C_b^i$  represent the pollution factor of the metal  $i$ , the content of the metal  $i$  in the atmospheric dry deposition samples, and the background value of the metal  $i$  (19 for Co, 31 for Cr, and 850 for Mn), respectively (30-33).

According to Hakanson (1980),  $E_r^i < 40$ ,  $40 < E_r^i \leq 80$ ,  $80 < E_r^i \leq 160$ ,  $160 < E_r^i \leq 320$ , and  $E_r^i > 320$  indicate low ecological risk, moderate ecological risk, appreciable ecological risk, high ecological risk, and serious ecological risk, respectively. Also, RI is classified into four categories as follows:  $RI < 150$  represents low ecological risk;  $150 < RI < 300$  indicates moderate ecological risk;  $300 < RI < 600$  represents high ecological risk; and  $RI \geq 600$  indicates significantly high ecological risk (29).

#### 2.5. Statistical Analysis

The statistical analysis of the obtained results consisted first of Shapiro-Wilk normality test followed by the study of the variance homogeneity using a parametric test, ANOVA, with a DMS post hoc and Duncan multiple range test. The mean levels of the elements in the atmospheric dry deposition were compared with maximum permissible concentrations (MPC) using a one-sample t-test. Finally, to study the correlation between the metals in the different samples, the 2-tailed test of Pearson correlation was performed.

### 3. Results

#### 3.1. Heavy Metal Concentration

The mean content of heavy metals in the atmospheric dry deposition is presented in Table 2. The data in Table 2 shows that the Co content ( $\text{mg kg}^{-1}$ ) in the analyzed samples ranged from 0.17 to 0.34 with an average of  $0.23 \pm 0.06$ . The chromium content ( $\text{mg kg}^{-1}$ ) in the analyzed samples ranged from 0.61 to 1.21 with an average of  $0.89 \pm 0.20$ . Also, the Mn content ( $\text{mg kg}^{-1}$ ) in the analyzed samples ranged from 7.19 to 8.95 with an average of  $8.10 \pm 0.70$ .

**Table 2.** Heavy Metal Analysis of Atmospheric Dry Deposition ( $\text{mg kg}^{-1}$ )<sup>a</sup>

Sampling Station	Metal Concentration		
	Co	Cr	Mn
A	$0.29 \pm 0.04^a$	$1.01 \pm 0.01^a$	$8.82 \pm 0.11^a$
B	$0.21 \pm 0.04^b$	$1.02 \pm 0.17^a$	$8.24 \pm 0.09^b$
C	$0.19 \pm 0.03^b$	$0.65 \pm 0.05^b$	$7.23 \pm 0.03^c$
Min.	0.17	0.61	7.19
Max.	0.34	1.21	8.95
Mean	0.23	0.89	8.10
S.D.	0.06	0.20	0.70

<sup>a</sup>The letters (a, b, and c) represent the statistical differences between the mean concentration of metals in atmospheric dry deposition that computed by One-way ANOVA and Duncan multiple range test ( $p = 0.05$ ).

#### 3.2. Statistical Analysis Results

The independent one-sample t-test comparing the analyzed heavy metal contents in the atmospheric dry deposition samples with the MPC ( $\text{mg kg}^{-1}$ ) (30.0, 100.0, and 1500.0 for Co, Cr, and Mn, respectively) established by WHO (34) shows that the mean contents of elements in all the samples were lower than the MPC.

In the current study, Pearson's test was used to compare the heavy metal concentrations in the atmospheric dry deposition. A positive relationship was found between Co and Mn ( $r = 0.735$ ,  $P = 0.024$ ) and also Cr and Mn ( $r = 0.857$ ,  $P = 0.003$ ). In this regard, when the Co and Cr contents increased, the Mn content also increased.

#### 3.3. Potential Ecological Risk Assessment Results

The results of the evaluation of the potential ecological risk factor and RI are presented in Table 3. Based on the results, the order of the potential ecological risk coefficient of heavy metals in the atmospheric dry deposition in Hamedan city was  $\text{Co} > \text{Cr} > \text{Mn}$ . Also, the  $E_r^i$  coefficient values with an average of 0.06, 0.06, and 0.007 for Co, Cr, and Mn, respectively, indicated a low ecological risk. Therefore, the computed  $E_r^i$  coefficient value represents

the low ecological risk of heavy metals in the atmospheric dry deposition in the study area. On the other hand, since the RI values were 0.16 for sampling station A, 0.13 for sampling station B, and 0.10 for sampling station C, the risk level of heavy metals in the atmospheric dry deposition in Hamedan city was low in all the stations.

#### 4. Discussion

Atmospheric dry deposition is a natural global process of cycling PM that is now dominated by anthropogenic-origin pollution in most urban settlements. Therefore, this study was conducted to assess the ecological risk of Co, Cr, and Mn in the atmospheric dry deposition in Hamedan city.

##### 4.1. Cobalt

Natural and anthropogenic sources, including erosion, weathering of soil and rocks, sea water spray, forest fires, volcanoes, continental and marine biogenic emissions, and also traffic, are the main sources of Co in the atmospheric dry deposition or street dust (35). In the current study, Co values in the atmospheric dry deposition samples were found to be within the range of 0.17 to 0.34 mg kg<sup>-1</sup>. The highest mean level of Co was found in the station with heavy traffic intensity (0.29 ± 0.04 mg kg<sup>-1</sup>), coming from the wear of the brake lining and corrosion of the metallic parts of vehicles (2, 36). In this regard, it should be noted that the level of Co in the dry deposition samples was found to be lower than the mean values in Baotou, Nanjing, Oslo, Honolulu, Kayseri, and Hangzhou (24, 37-42). Also, the level of Co in the present study is much varied from that in the investigated area in Madrid (3.00 mg kg<sup>-1</sup>) and Luanda (2.90 mg kg<sup>-1</sup>) (37, 43). Based on the results of the related literature, the Co content in the resuspended particles of urban street dust collected from Baotou City reveals moderate to considerable ecological risk (42). The computed potential ecological risk factor of Co in the atmospheric dry deposition in the study area indicated that the ecological risk of dust was low. A comparison of metal content in the atmospheric dry deposition/street dust from Hamedan city with some other cities reported in the literature is presented in Table 4.

##### 4.2. Chromium

Chromium is used in many alloys, particularly stainless steel. In this regard, welding, grinding, and polishing of stainless steel can lead to the release of Cr into the environment. The consequences of chronic exposure to Cr are skin irritation, damage to the kidneys or liver, and circulatory and neurological disorders (20, 52). In this study, the

Cr contents in atmospheric dry deposition samples were found to be within the range of 0.61 mg kg<sup>-1</sup> to 1.21 mg kg<sup>-1</sup>. The highest mean level of Cr was found in the station with moderate traffic intensity (0.89 ± 0.20 mg kg<sup>-1</sup>). However, no significant difference was found between the heavy and moderate traffic stations. The presence of Cr in the samples can be related to combustion of fossil fuels and waste incineration (20, 53). The obtained results are contrary to the findings of Li et al. (24) and Kartal et al. (39) who concluded that the values of Cr in urban street dust collected from Nanjing, China, and the street sediment samples from Kayseri, Turkey, were 67.13 mg kg<sup>-1</sup> and 27.91 mg kg<sup>-1</sup>, respectively. Also, Xu et al. (2015) reported that the Cr content in the resuspended particles of urban street dust collected from Baotou city reveals low to moderate ecological risk levels (42). In the current study, the computed potential ecological risk factor of Cr indicated that the ecological risk of atmospheric dry deposition collected from Hamedan city was low. A comparison of our findings with that of other studies is shown in Table 4.

##### 4.3. Manganese

It has been proven that geological material (lithogenic source), traffic, and tire wear are the main sources of Mn in the street dust or atmospheric dry deposition (44). The Mn content in the atmospheric dry deposition samples was found to be within the range of 7.19 - 8.95 mg kg<sup>-1</sup>. Also, the highest mean level of Mn was found in the station with heavy traffic intensity (8.82 ± 0.11 mg kg<sup>-1</sup>). The average concentration of Mn reported in the literature is 687 mg kg<sup>-1</sup> in the street dust collected from Xian (54). On the other hand, the computed values of the potential ecological risk confirmed the result of the other study which showed that the ecological risk of Mn content in the resuspended particles of urban street dust collected from Baotou city was low (42). A comparison of the Mn contents in the atmospheric dry deposition in Hamedan city and that in other selected cities are presented in Table 4.

##### 4.4. Conclusion

Based on the results of the present study, the potential ecological risk of Co, Cr, and Mn was at low levels. Also, the results showed that the Co and Mn contents in the atmospheric dry deposition collected from a station with heavy traffic intensity were significantly higher than that of the other stations. Therefore, based on the results as well as the research constraints, including lack of financial support and lack of time, control of the anthropogenic sources which cause discharge of hazardous pollutants, particularly toxic heavy metals, into the atmosphere, including industrial activities, power generation, construction activi-

**Table 3.** Evaluation of Potential Risk of Heavy Metal Pollution in Atmospheric dry Deposition in Hamedan City

Sampling Station	Potential Ecological Risk Factor Ei			RI	Risk Grade
	Co	Cr	Mn		
A	0.08	0.07	0.01	0.16	Low
B	0.06	0.07	0.001	0.13	Low
C	0.05	0.04	0.009	0.10	Low
Mean	0.06	0.06	0.007	0.13	Low

**Table 4.** Comparison of the Heavy Metal Contents (mg kg<sup>-1</sup>) in Atmospheric Dry Deposition in Hamedan City and Other Selected Cities

Location	Metal			Reference
	Co	Cr	Mn	
Iran (Hamedan)	0.23	0.89	8.10	Present study
Poland (Mazowieckie)	-	29.50	392.30	(25)
Kosovo	10.77	26.03	92.75	(36)
Turkey (Yazgat)	26.10	72.80	274.00	(44)
Angola (Luanda)	-	25.65	258.00	(43)
China (Guangzhou)	13.00	78.80	481.00	(45)
Turkey (Kayseri)	16.50	29.00	-	(40)
Iran (Tehran)	-	33.30	1212.00	(46)
Jordan (Aqaba)	14.85	22.34	64.67	(2)
China (Xi'an)	-	52.61	-	(47)
China (Hangzhou)	19.96	51.29	-	(41)
China (Baoji)	15.90	126.70	804.20	(48)
China (Shanghai)	-	110.75	-	(49)
Iran (Kermanshah)	-	37.45	-	(50)
Iran (Bushehr)	5.14	-	-	(51)
China (Baotou)	56.20	247.80	566.30	(42)

ties, corrosion of automobile parts, and fossil fuel combustion, assessment of other hazardous chemical compounds in the atmospheric dust, and also, health risk assessment of the toxic heavy metals in atmospheric dust is recommended.

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