Research Paper
The Effect of Land-Use Changes on the Amount of Heavy Metal Pollution in Urban Runoff in Tehran

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ABSTRACT

Background & Aims of the Study: Urban development trends and land-use changes harm the quality of urban runoff. Heavy metals are one of the most important pollutants in urban runoff. This study aimed to investigate the amount of heavy metal pollutants (Zn, Pb, Cu, As, Hg, and Cd) in different land uses in a densely populated urban area of Tehran.

Materials and Methods: Six stations were selected for urban runoff sampling in five land uses. Land uses were residential, commercial, industrial, traffic, and outdoor. A station (sixth station) with mixed land use was selected, which included the runoff of all uses. The event mean concentration (EMC) model was used to estimate this study's heavy metal pollution load.

Results: The amount of all heavy metals except Arsenic in fields with industrial use was higher than other land uses (Cu=0.292 mg/l), (Pb=0.6166 mg/l), (Zn=1.36 mg/l), (Cd=0.0114 mg/l), and (Hg=0.1332 mg/l). While the amount of Arsenic metal in the station with outdoor land use (AS=0.111 mg/l) was the highest.

Conclusion: The results of this study indicate that the risk of metals on long dry days without precipitation is very high. Uncertainties related to the accumulation of pollution and various human activities can be attributed to the high amount of heavy metals in the mixed land use compared to land use alone.

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1. Introduction

The trend of urban development and land-use changes harm the quality of urban runoff [1]. The type of human activities in the use of different urban lands is one of the reasons for the decrease in the quality of urban runoff [2]. Urban growth increases the amount of urban runoff pollutants by at least twice the ratio of natural conditions in the watershed [3]. Land-use diversity and catchment characteristics, such as intensity and duration of precipitation, soil type, catchment slope, and vegetation affect urban runoff pollution [1]. Heavy metals are one of the most important pollutants in urban runoff [4]. Widespread distribution of heavy metals due to their interaction in different parts of the biosphere, including the atmosphere, hydrosphere, and lithosphere, and its toxic impacts on the environment, is one of the issues considered very important [5].

Heavy metals in urban runoff are mainly caused by vehicle exhaust, industrial smoke, burning fossil fuels, dust storm sand, and corrosion of various metal facilities [6]. Heavy metals, such as Copper, Zinc, and Lead are common compounds in runoff [7]. High concentrations of heavy metals are problematic in the environment and can easily accumulate in the human body and plants through the food chain and other ways after entering the downstream catchment's waters and imposing a high pressure on the biogeochemical cycle [8]. Also, the heavy metals in urban runoff can affect the physicochemical properties of the riverbed and can even lead to the release of heavy metals into the water, such as lakes and water sources, and cause significant environmental damage [9]. Due to the presence of relatively high fine particles, wet sediments can increase runoff more than dry sediments of heavy metals and cause a reduction of heavy metals in sediments of water bodies [10]. Understanding the relationship between the amount of heavy metals in water bodies and precipitation properties is essential for their distribution in water resources and effective pollution control [11]. Increasing the toxicity of heavy metals in the ecosystem also causes significant changes in vegetation and contaminates surface soils. This issue leads to a slow process in the ecological restoration of barren lands [12].

In urban catchments, the roads' surface makes up approximately 10 to 15% of the total area. In commercial and industrial areas, parking lots can occupy up to 46% of the total area of urban areas. Different urban land uses have a different share in the production of metal pollutants in urban runoff. For example, in most cases, highway runoff contains higher amounts of heavy metals

than residential and commercial land runoff [13]. Metals in a runoff on rooftops and roads account for up to 80% of the total pollution load in combined drainage systems [14]. Various researchers have investigated the toxicity of runoff in traffic areas. Kayhanian et al. [15] identified Cu and Zn solutions as the leading causes of toxicity in highway runoff. Tiffander et al. [16] found high levels of Lead and Copper in industrial uses.

Mean event concentration (EMC) is a method that is widely used to calculate the concentration of heavy metal pollutants in various land uses and runoff collection systems. Although data collection is very costly for calculating site-specific EMCs, researchers prefer the EMC because of its greater accuracy and simplicity of method [17]. Heavy metals in urban runoff have been considered in many previous studies. However, few studies have examined the characteristics of heavy metal changes in urban runoff in different land uses. Also, the amount of metals, such as Hg and AS in the urban runoff of various land uses, which is necessary to reduce the risk of these metals on human health and ecosystem safety, has not been predicted in studies. This study investigated the amount of heavy metal pollutants, such as Zn, Pb, Cu, As, Hg, and Cd in different land uses in Tehran's densely populated urban area.

2. Materials and Methods

Area of study

One of the 22 districts of Greater Tehran is District 17, which is bounded on the north by Districts 9 and 10, on the south by District 19, on the east by Districts 11 and 16, and on the west by District 18. This area is 7 square kilometers and has 360 thousand people and 80 thousand families. District 17 consists of 3 areas and 21 neighborhoods (Figure 1). The geographical area of the 17th district, from the southern areas of Tehran, is about 822.09 hectares with an occupancy level of 1.1% of the total lands of the legal area of Tehran adjacent to the 9th, 10th, 11th, 16th, 18th, and 19th districts. This region is located at latitude "11 "38 ° 35 and longitude "10 '21 ° 51 to latitude "14 "40 ° 35 and longitude 58 '22 ° 51.

Sampling method as event mean concentration

This study uses the EMC model to estimate user pollution load. EMC is a fast, simple, and practical method for assessing nonpoint pollution in small urban basins and is used as a unit index in milligrams per liter to determine the concentration [18]. Considering that the amount of pollutants in urban runoff depends on various factors,
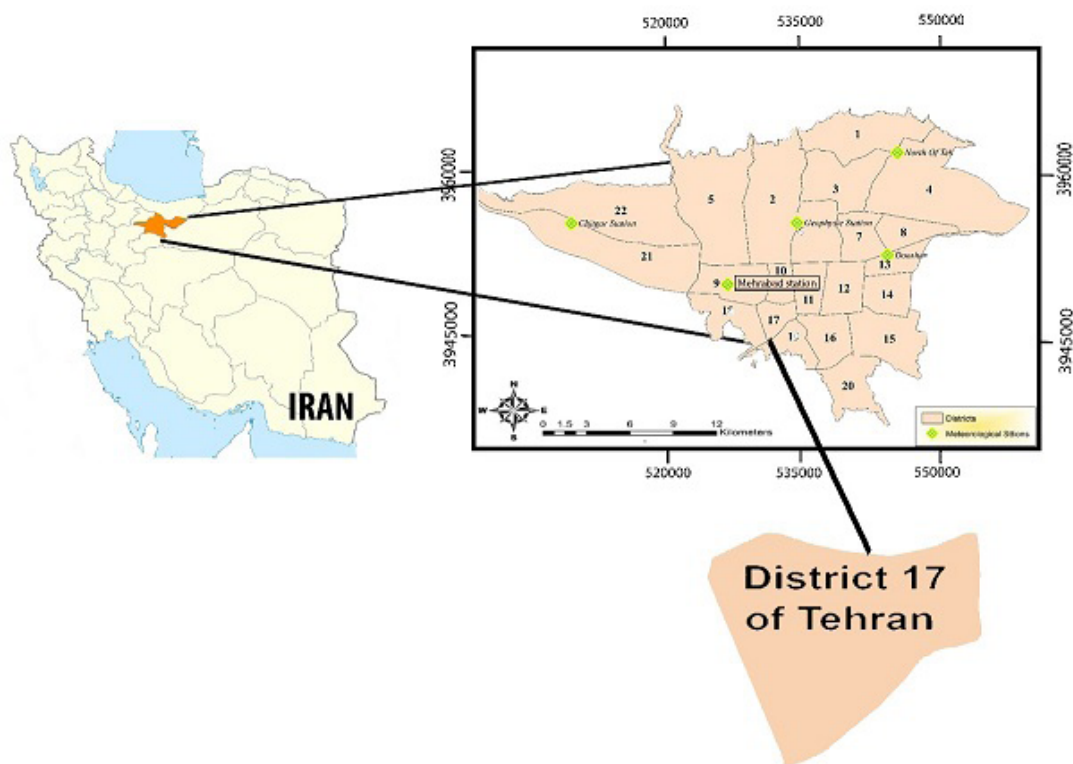
Figure 1. Location of District 17 Municipality in Tehran

a- Residential
b- Commercial
c- Industrial
d-Open Space
e- Road and transportation
f- mixed land use

Figure 2. Sampling stations in District 17 of Tehran

Soltaninia S, et al. Effect of Land-Use Change on the Heavy Metal Runoff Pollution. Arch Hyg Sci. 2022; 11(2):137-146

139

such as intensity and duration of precipitation and land use type, EMC calculates the mean amount of pollutants in urban runoff at specified intervals of a precipitation event, according to the runoff flow obtained at a specific land use [19]. Therefore, urban runoff flow rate and time are requirements for the EMC method [20]. A simple method for calculating EMC is to divide the total mass of pollutant (M) discharged during an event by the total volume (V) of municipal runoff discharge [21]; however, due to the fact that in this method, the runoff flow rate is ignored at time intervals, the EMC calculation method according to Equation 1 has evolved as the mean multiplication of the pollutant concentration in the urban runoff flow rate at time intervals [22].

1. $EMC(mg/l) = \dfrac{Event\ per\ loading\ pollutant\ total\ (M)}{Event\ per\ volume\ runoff\ total\ (V)} = $

$\dfrac{\sum C_i Q_i \Delta t}{\sum Q_i \Delta t}$

$C_i (mg/L)$: Concentration of municipal runoff pollutant at time intervals Δt

$Q_i (m^3/min)$: Runoff flow in the time interval Δt

$\Delta t(min)$: Sampling interval M_i

According to Figure 2, six stations were selected for urban runoff sampling in five land uses. Land uses included residential, commercial, industrial, traffic, and outdoor. A station (sixth station) with mixed land use was selected, which included the runoff of all uses. The percentage of mixed land use in the sixth station included 41% of residential land, 26% of the road, 18% of commercial land, 11% of industrial land, and 4% outdoor.

Sampling was performed in five events in a rainy year from 2019 to 2020, twice in autumn, twice in winter, and once in spring. A station was equipped with a rain gauge and speedometer (model WS-9004-IT) to estimate the runoff flow rate in each event. Sampling was started immediately after precipitation and observation of runoff flow at the outflow points. In general, sampling was done in the first hour, one sample every 15-20 minutes and after one hour, every thirty minutes, once for three hours. Samples were collected in plastic sealed containers and transferred to a water quality laboratory to measure the amount of heavy metals.

In order to analyze runoff samples for measuring metals, all containers were soaked in 5% nitric acid solution for 12 hours before acidic digestion of the samples to remove pollutants from the containers used. Then, to determine the amount of elements, 40 ml of runoff samples were poured into PTFE (polytetrafluoroethylene) pipes, and then, 5 ml of nitric acid/hydrochloric acid mixture was slowly added to the samples in a ratio of 1: 3. The samples were then placed in a thermoreactor for one hour at 50°C and then one hour at 120°C for complete digestion [23]. After complete acidic digestion, the samples were passed through a 42 micron Whatman filter paper for purification, and finally, the samples were made up to 25 ml with deionized water. Heavy metals were measured in digested runoff samples using the ICP-MS model HP-4500 (USA).

3. Results

The runoff quality data collected in the catchment basin of District 17 varied according to the characteristics of the event, including rain depth, intensity, duration of precipitation, and dry days without precipitation. Figure 3 shows the concentration of pollutants in each land use in each precipitation event.

Table 1. EMC method to calculate mean concentrations of pollutants for five precipitation events in the rainy year 2019-2020

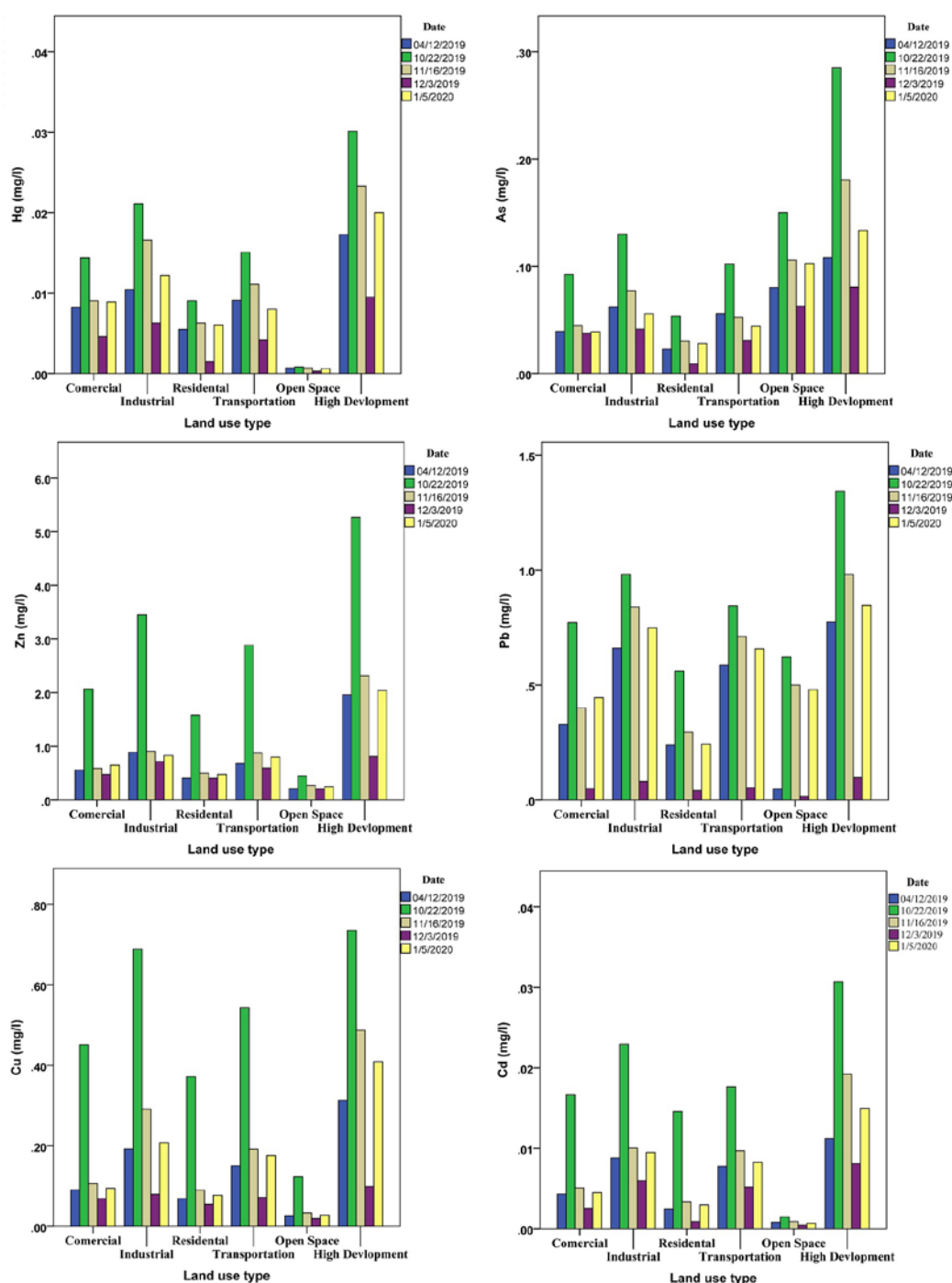| Land use	Cu	Pb	Zn	Cd	As	Hg
Residential	0.13268	0.2758	0.6762	0.00484	0.02876	0.00566
Commercial	0.16236	0.3992	0.8694	0.00662	0.05054	0.009026
Industrial	0.29202	0.6616	1.3596	0.01146	0.07326	0.01332
Transportation	0.22662	0.5704	1.1664	0.00972	0.0571	0.0095
Outdoor	0.0462	0.333	0.2766	0.00088	0.11104	0.00062
Mixed	0.409	0.8084	2.4794	0.01684	0.15758	0.02004

Figure 3. The concentration of heavy metal pollutants in each event in each sampling station

The results showed that the highest amount of EMC was calculated so that the highest and lowest amount of heavy metal measured in runoff in all land uses were related to Zn and Cd (EMC Zn>EMC Pb>EMC Cu>EM As>EMC Hg>EMC Cd) (Figure 4 and Table 1). The mean concentration in all measured events for Zn was 2.47 mg/l and for Cd was 0.016 mg/l in integrated land use. The amount of all heavy metals except As in lands with industrial use was higher than other land uses (Cu=0.292 mg/l), (Pb=0.6616 mg/l), (Zn=1.36 mg/l), (Cd=0.0114 mg/l), and (Hg=0.01332 mg/l). Then, transportation, commercial, residential, and outdoor land uses had the largest share in the amount of these heavy metals, respectively. However, the amount of As metal in the station with outdoor land use (As=0.111 mg/l) was the highest, followed by industrial, transpor-

Soltaninia S, et al. Effect of Land-Use Change on the Heavy Metal Runoff Pollution. Arch Hyg Sci. 2022; 11(2):137-146

141

Table 2. The effects of heavy metals in the food cycle on human health [26, 25]

| Heavy metals	Dangers of Heavy Metals on Human Health
Hg	Autoimmune diseases, depression, drowsiness, fatigue, hair loss, insomnia, attention deficit disorder, restlessness, impaired vision, tremor and anxiety, cerebral damage, renal, and lung failure, carcinogenesis
As	Effect on essential cellular processes, such as oxidative effect, phosphorylation, and synthesis of ATP, arsenicosis, carcinogenicity
Zn	Dizziness, fatigue, vomiting, renal failure, and spasm
Pb	Neurological and cardiovascular diseases
Cu	Brain and renal failure, cirrhosis of the liver and bile, chronic anemia, and heartburn
Cd	Carcinogenicity, mutagenicity, endocrine disruptors, renal failure, lung failure, and bone fragility affecting calcium regulation in biological systems

tation, commercial, and residential land uses had the largest share in As metal.

4. Discussion

In this study, cluster analysis was used to group burial sites. The purpose of grouping data in cluster analysis is to divide the observations into homogeneous groups so that the observations of each group have the most similarity and the observations of different groups have the least similarity [24]. A hierarchical analysis test was used to investigate the grouping and categorization of different sampling stations based on the amount of pollutants measured in the sampling. The dendrogram of the hierarchical analysis results is shown in Figure 5. As the hierarchical clustering diagram (dendrogram) shows, the studied stations were divided into three groups based on similar and dissimilar measured parameters, with residential, commercial, and traffic stations in group 1, outdoor station in group 2, and station with industrial use and mixed land use in group 3.

Identifying sources of heavy metal pollutants in urban runoff is of particular importance in controlling and reducing pollutants related to trace elements [25]. Industrial and traffic areas introduce more heavy metals into urban runoff than other land uses. The existence of industrial land use in cities will increase urban traffic and
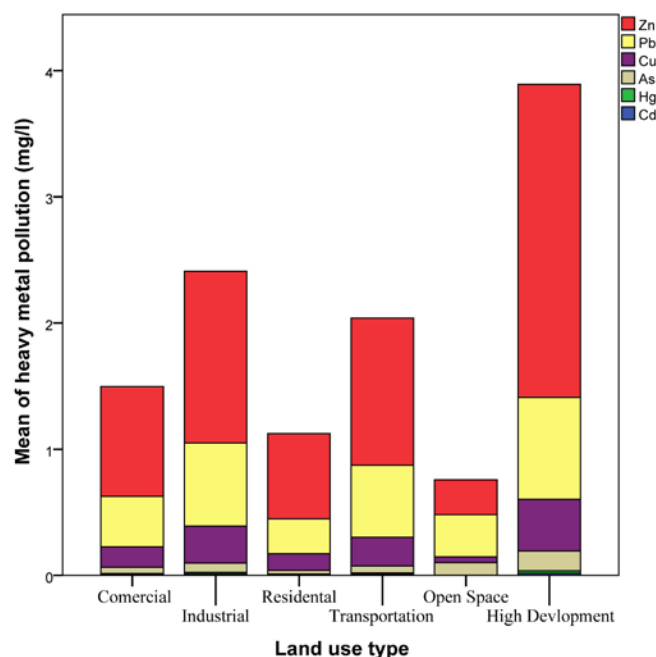
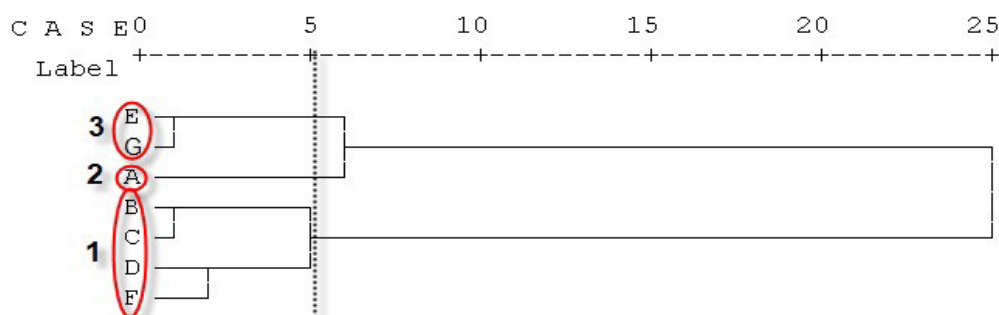**Figure 4.** Mean concentrations of heavy metals in five events in five land uses

Figure 5. Dendrogram of hierarchical clusters analysis for the studied stations

Archives of Hygiene Sciences
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transportation of heavy vehicles, which is one of the important sources of heavy metal pollutants in runoff [25]. In this study, Zn and Cu had the largest share of heavy metal pollution in urban runoff, whose primary sources in densely populated urban areas are the consumption of diesel in heavy vehicles and industries [26]. In addition, Zn can enter urban runoff through precipitation on galvanized sheets, such as guardrails, traffic signs, and city signs [27]. Cu in the urban runoff of Tehran can be caused by car brake pads [28]. Electrical industries and electrical waste in the city are also sources that introduce Cu into the urban runoff during precipitation [26]. The primary source of Pb in urban runoff is gasoline and diesel combustion in cars and industries. Also, car batteries are an important source of urban runoff Pb [27]. The color of sidewalk tables and industrial activities contains Pb and Cd metals, which can penetrate the urban runoff [25]. Cd from engine oils and car breakdowns, construction facades, roofs, and shaved car tires can also enter the urban runoff [27]. Local fossil fuel combustion, metal production, cement production, medical and industrial waste disposal, and incineration are sources of Hg [29]. The high level of As in the 17th urban district of Tehran may be due to the furniture industry in the district and spraying in green spaces [30]. Also, the results showed that in the sixth station with mixed land use, the amount of heavy metal pollutants was much higher than each of the land uses separately (Table 1).

The amount of heavy metals concentration measured in each land uses, separately and in combination, including all land uses, compared to the measured amount of metal pollutants measured in other countries, showed that their amount was significantly higher in Tehran's urban runoff. The amount of EMC calculated in other countries for Pb metal is 0.016-0.493, for Zn is 0.8-1.33, for Cu metal is 0.003-0.0061, and for Cd is 0.001-0.00001 mg/l. [31]. This can result from intra-city industrial activities, heavy vehicle traffic to transport industrial goods, railway crossings through the district, car repair shops, and industrial particulate matter resulting from the activities of industrial workshops in the district. As and Hg, which are not studied and calculated in urban runoff due to their low levels, are abundant in Tehran's urban runoff. Directing urban runoff through canals to agricultural lands in the downstream basins of Tehran causes soil pollution and bioaccumulation in agricultural products. The entry of heavy metals calculated through the food cycle can cause various diseases. Table 2 lists some of the hazards of the impacts of heavy metals in the food cycle on human health [32-34].

5. Conclusion

Low impact developments (LIDs), including permeable concrete in urban environments, can effectively remove heavy metals. Also, removing industrial land use from urban environments and moving it out of the urban area significantly reduces the risk of heavy metals. Also, this study showed that the risk of metals on long dry days without rain is very high. Uncertainties related to the accumulation of pollutants and various human activities can be attributed to the high amount of heavy metals in the mixed land use compared to land use alone. On the other hand, due to air pollution in the metropolis of Tehran, which is evident most of the time of the year, this pollution settles in the form of dry sediment on the streets, alleys, roofs, etc. In the form of dry sediments, these pollutants contain many pollutants, including metals, which can negatively impact the environment. Based on the results of the present study, when it rains, these pollutants mix with the rainwater to form runoff contaminated with various pollutants; the amount of runoff pollutants collected from the surface of the studied stations in the 17th district of Tehran in all studied stations was found. These metals can have adverse effects on the environment and human health due to their high durability, non-degradability, and bioaccumulation capacity. Therefore, based on the results of this study, it is necessary to study and implement projects to decrease air pollution to reduce metal and other pollutants in the air of Tehran.

Soltaninia S, et al. Effect of Land-Use Change on the Heavy Metal Runoff Pollution. Arch Hyg Sci. 2022; 11(2):137-146

143

Due to the lack of statistics, in order to calibrate urban runoff models, it is suggested that in relatively large cities, an area be selected as a representative basin, and all statistics related to precipitation, hydrology and hydraulic flow, and other items that are common for major cities to be recorded and used for calibration.

Ethical Considerations

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144

Soltaninia S, et al. Effect of Land-Use Change on the Heavy Metal Runoff Pollution. Arch Hyg Sci. 2022; 11(2):137-146

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Soltaninia S, et al. Effect of Land-Use Change on the Heavy Metal Runoff Pollution. Arch Hyg Sci. 2022; 11(2):137-146

145

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