original article

Effect of contaminated soils with lead, zinc, and cadmium and their related dust effect on air pollution in Isfahan (Iran)

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ABSTRACT

Aims: The purpose of this research was to determine the effects of soils contaminated with lead, zinc and cadmium on the high concentration of these metals in the urban air.
Materials and Methods: In this regard 63 samples of soil and 18 air samples were taken at sampling grids from various regions of the city. After digestion of samples, the extracted liquids were analyzed by atomic absorption spectroscopy.
Results: The concentration of lead, zinc, and cadmium in the soil samples were not higher than international standards, but was two to three times as high in the air as that found in European countries and U.S. Results also showed a correlation between concentration of these metals in the city soils and their increased level in the city air through dust and wind, particularly in the northern parts of the city, whilst no such correlation is found in the southern parts, which could be due to wind blowing dust polluted with these metals from heavy industries located at south-west of Isfahan.
Conclusion: As, at present time, there is a ban on consumption of leaded petrol throughout the city, two main probable sources of lead pollution in the air of the city of Isfahan are dust from contaminated soil and also, presence of a large steelworks industry in the south-west of Isfahan which is in the direction of south-west to north-westerly winds.

Key words: Air, cadmium, dust, Isfahan, lead, zinc

INTRODUCTION

Rapid development of Isfahan city coupled with the accelerated growth of industry and population, has turned this city into one of the most polluted regions in Iran. Preliminary studies on the presence of heavy metals in the city air showed high concentration,[1] whence making it imperative to determine how these pollutants enter the city air. A number of studies have been carried out as regards sources of metal pollutants in various parts of the world.[2,3] Natural concentration of heavy metals in soils is due to erosion and weathering of rocks and minerals.[4] Although the presence of some of these elements, such as copper and zinc at low concentrations is necessary for living things, but these may become highly toxic at high concentrations.[5]

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In the last few decades, several studies regarding soil contamination from industrial activities and automobile exhausts were carried out and compared with concentration of metal in the soils from rural areas and virgin woodlands.[6,7] Therefore, distinguishing between soil contaminations sources in the cities due to natural geological processes and that caused by industrial activities and city traffic is of utmost importance. Isfahan soils are located on the lead and zinc mineralized belt. Also around Isfahan city there are many rich mines, such as Irankooh and Tiran mines that have naturally contaminated the soils, the shales in Isfahan region are also contaminated with these metals.[8]

Taking into account the existence of a considerable amount of metals such as lead, zinc, and cadmium in the soil and the air of Isfahan city, by conducting research for correlation between concentration of these metals in the soil and in the air, the level of effects of the soil on air pollution in the city can be determined.

Presence of heavy metals in high concentrations with their detrimental effects on the environment is caused either through natural processes or human activities. Natural sources of metallic pollutants in soils are a result of presence of different elements comprising earths' crust such as rocks and minerals which due to physical weathering, chemical and biological processes. These materials are turned into dust and via transfer factors such as wind and water enter the environment. Level of contamination of these metals in the soil depends on the type of rocks and minerals, type of soil, age of soil, drainage, vegetation coverage, and proximity to mineral veins.[9] In all, heaviest elements in the earth's crust have mean concentration, less than 100 mg/kg.[10,11] Generally, clay and shale have higher concentration of metals than grains of sand, as they are better able to uptake metallic ions.[12] Table 1 shows concentration of some of the metals in the earth's crust, stones, and soils.[2,13-15] Natural sources of metallic pollutants in the air are mainly from fire in forests and vegetations, volcanoes, dust containing metals getting blown into the atmosphere, which is intensified in dry regions without vegetation coverage.[4]

Human sources for distribution of heavy metals into the atmosphere could be from various industrial processes, particularly, metal smelting industries such as iron and steel, copper and zinc smelting, ferro-magnisium industries, power stations, refineries, petrochemicals, cement factories, and brick kilns,[4] of which mostly are present around Isfahan city. Research carried out on surface soils near a zinc concentration plants indicates concentration of lead as 200-1100 mg/kg, zinc as 5000-8000 mg/kg, and cadmium as 900-1500 mg/kg.[11,16] Other human sources include burning of fossil fuels, used not only in the industry, but also, high percentage of these fuels are burnt in transportation, automobiles, household appliances, and smoke resulting from these contains large amounts of heavy metals. Driving automobiles on the streets and roads which surfaces contain contaminated dust, could also cause spread the dust into the air.[4] During mining operations such as explosion and extraction of minerals, concentration processes, and transportation of concentrate powder, heavy metals can also get into the atmosphere.[17]

Therefore, the purpose of this study is to determine the concentration of lead, zinc, and cadmium in the soil and the air of Isfahan and also to correlate between the level of contamination of soil and air of these metals in the city.

MATERIALS AND METHODS

Geographical location of study area

Isfahan city is located on the edges of central west of Iran, and is on the geographical longitudes between 51°_38' to 51°_42' and latitudes between 32°_36' to 32°_42'. Isfahan city is 1680 to 1730 m above sea level from north to south, respectively.

Geology and climatology of study area

The most important geological environmental feature near the studied region is the Irankooh Mountain which is located on a fault and contains lead and zinc rich veins. In this mountain, mineralized carbonated units with Cretaceous age contain rich veins of lead and zinc.[8] Other than southern parts of Isfahan which are mostly Jurassic shales contaminated with lead and zinc metals, northern, eastern, and western parts of the city are also covered by sediments resulting from weathering and erosion of Cretaceous and Jurassic rocks.[8] The climate is mild with snow in the winter and rain in the spring. As Isfahan is located in a dry region, desert winds blow considerable amount of dust to the city.[17]

Sampling, preparation and analysis of soil samples

From the existing maps of the city of Isfahan, a map with the scale of 1:25000 was prepared. A four sided sampling grid of 7 by 5 kilometer was drawn on this map, and about 63 intersections were taken as soil sampling points. The distance between these points was 750 meters approximately [Figure 1]. Sixty-three samples of soil in this area were taken to the depth 15 centimeter from the surface. Attempts were made for the samples not to be contaminated. At each sampling station, a

Table 1: Variation of concentration of metals in earth's crust, rock and soils (dry weight mg/kg)

Heavy metals	Mean crust		(9) Rocks				Soils	
	(8)	(21)	Igneous	Shale	Sandstone	limestone	Variation range (8)	Permitted values (6)
Pb	16	20	16	20	10-40	5-10	20-300	100
Cd	0.18	0.098	0.13	0.3	-	-	0.01-2.4	3
Zn	80	71	80	50-300	5-20	4-20	10-300	300

point was selected as the center, around which, 10 samples of soil on a 5 meter radius were taken. These 10 samples were then thoroughly mixed and a sample was taken from the mixture for testing purposes.[5,18] It is noteworthy that wherever sampling point proved impracticable or inaccessible (middle of streets, houses, etc), sampling radius was extended to 100 meters approximately, and then samples were taken around the main point. After transfer to the laboratory, samples of soil were dried at 20°C and then crushed and passed through a 2mm stainless steel sieve. These samples were used for extraction separation of metals. To extract separate metals from small grain soils, particularly clay, that has the ability to adsorb attract metals and easily turn into dust, at first, 5 grams of the soil sample in a duplicate form were dried at 110°C and to eliminate any organic matter, were placed at 400°C and then put on an 80°C hot plate with a 3:1 mixture of hydrochloric and nitric acids to digest. After these stages, samples were diluted to 100 ml and passed through a Whatman 42 paper filter. Finally, concentration of metals in the solutions was obtained using atomic absorption (Philips PU 9100) at Geology Department, University of Isfahan.[19]

Sampling, preparation and analysis of air samples

For the purpose of determining concentration level of lead, zinc, and cadmium in the air of the Isfahan a high-volume air sampler with Quartz-fiber filter (Whatman QM-A) model was used and suspended particles in the air in 18 stations around the city were collected.[20] The reason for 18 stations was due to equipment limitations. Samples of air were taken at 1.5 meter above ground level at the rate of 1 m^3/min. To collect adequate air samples and precise values, each stage of sampling was carried out over a 12 hour period from 7 AM to 7 PM, with two persons taking samples simultaneously. Sampling work was done during spring season.

To separate heavy metals and dust on the filter papers used for sampling, filter papers were placed in a solution of nitric and hydrofluoric acids in a PTFE (polytetrafluoroethylene) beaker for one hour at 90°C, so that metals dissolve in the solution. Then by adding HNO3 and applying heat, the remainder of HF was extracted from the solution. The final solution was then transferred into a 25ml flask and de-ionized water was added to reach the volume.[20] Like soil samples, atomic absorption was used to determine level of heavy metals in the solution. The wavelength used for measurement of the level of absorption was 217.0 nm for lead, 213.6 nm for zinc, and 288.8 nm for cadmium.[20]

For better presentation of results of soil and air analysis in the Isfahan city, Surfer software was used. The software was able to analyze statistical information and draw concentration lines. In order to prove the hypothesis in this study, the total

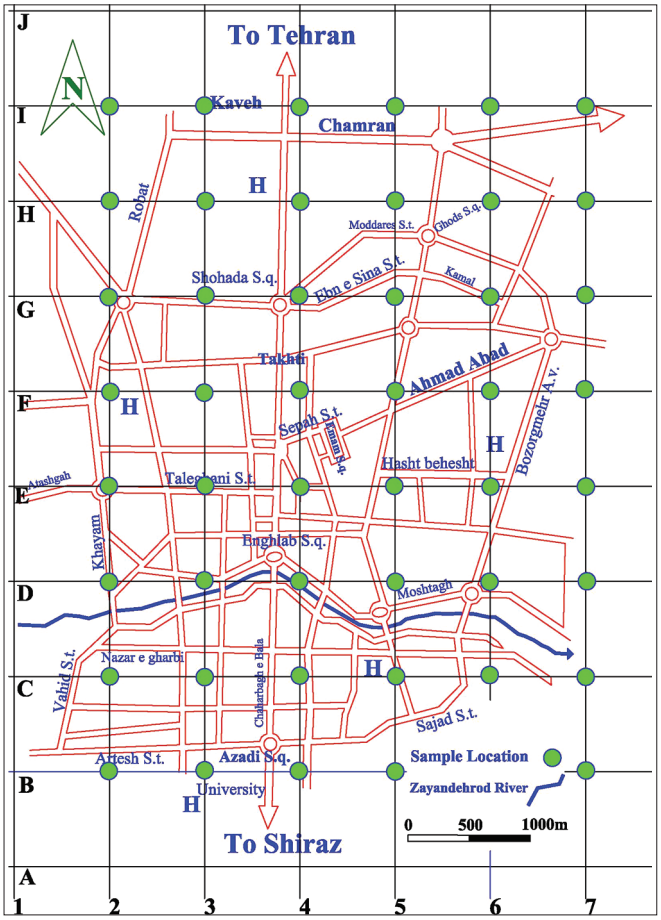

Figure 1: Location of sampling points within the study area (scale 1:25000)

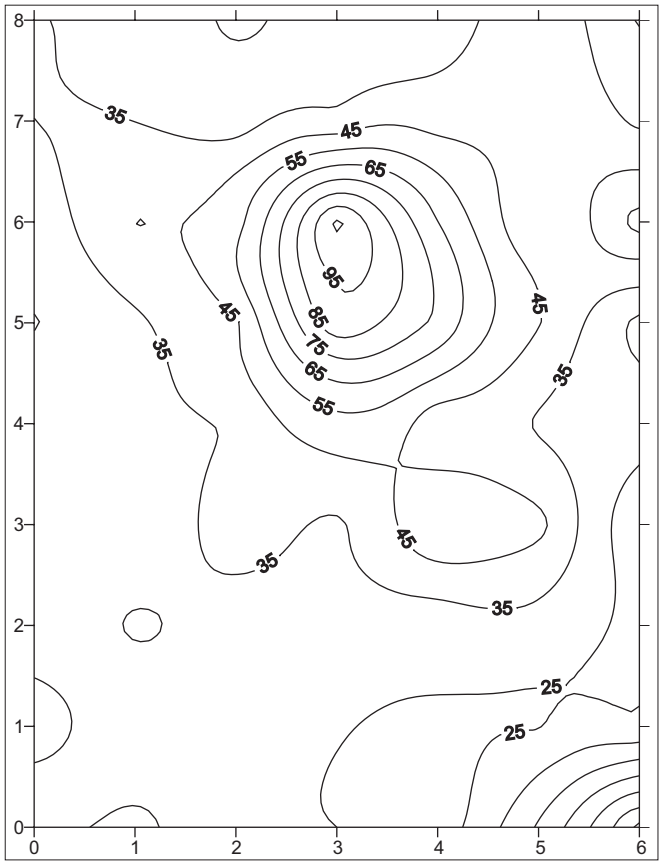

Figure 2: Concentration map of lead in the soils of Isfahan in mg/kg dry weight (scale 1:25000)

suspended particles (TSP) in the air was also measured, enabling determination of whether or not there is a correlation between increased dust level and increased concentration of these metals.

RESULTS

The results of soil analysis

Figures 2-4 show concentration maps of lead, zinc, and cadmium contaminated soils of Isfahan, respectively. As shown in Figure 2, the highest level of lead concentration is found in the north part of the city with over 100 mg/kg dry weight. Figure 3 shows level of zinc in the soil of the city, with the highest concentration in the northern parts of Isfahan, with over 160 mg/kg dry weight. Figure 4 shows concentration of cadmium in the eastern and western parts with 1.7 mg/kg dry weight.

Results showed concentration of lead, zinc, and cadmium to be 20.75 mg/kg, 48.5 mg/kg, and 1.0 mg/kg dry weight, respectively. These results represent lower concentration of these metals compared to that found in the Isfahan city. Values were 37.4 mg/kg, 94.3 mg/kg, and 1.05 mg/kg, respectively. Based on the studies, mean concentration of lead, zinc, and cadmium in the Lenjan plain located at 15km west of Isfahan next to Irankooh lead and zinc mines, were 41.9 mg/kg, 145.5 mg/kg, and 1.6 mg/kg, respectively. Also, in Sepahan Shahr town at east of Irankooh mines at about 10km south of Isfahan those figures were 67.0 mg/kg, 147.7 mg/kg, and 4.4 mg/kg, respectively, indicating increased concentration of these metals in the soils at south-west of Isfahan.[1,21] Table 2 presents ranges and mean values of the concentration of lead, zinc, and cadmium in the soils of the city, as compared with normal ranges in the soils around the world and their permitted limits. As it is evident, concentration of these metals in the soils of Isfahan is within the normal range of the world; therefore, it is not classified as contaminated soils.[22,23] It is noteworthy that the permitted amount of the metals in the above table is mainly for the agricultural purposes and water contamination, and transfer of these contaminations by wind has not been considered.

Table 2: Range and mean values of lead, zinc, cadmium concentration in the soils of Isfahan compared with normal ranges and permitted limits of soils around the world in mg/kg dry weight[22,23]

Element	Soils in Isfahan		Soils around the world	
	Range	Mean	Normal range	Permitted values
Pb	17-107	37.4	2-300	100
Zn	56-242	94.3	10-300	300
Cd	0.3-1.7	1.05	0.01-2.4	3

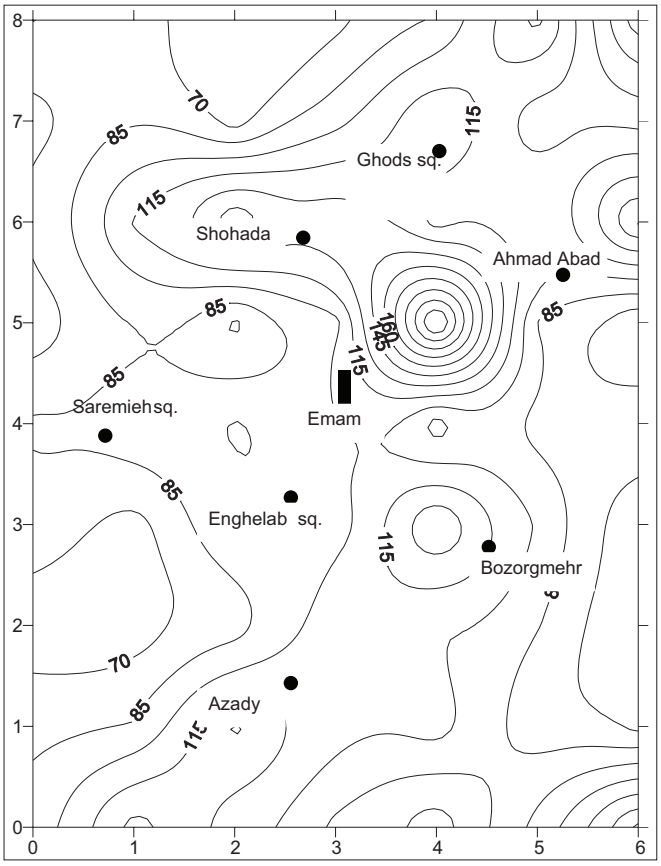

Figure 3: Concentration map of zinc in the soils of Isfahan in mg/kg dry weight (scale 1:25000)

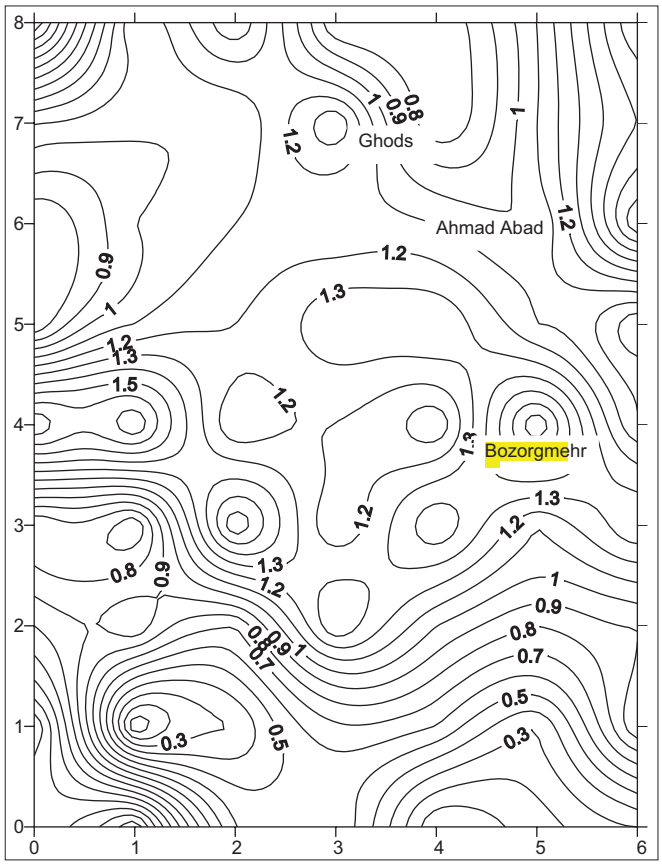

Figure 4: Concentration map of cadmium in the soils of Isfahan in mg/kg dry weight (scale 1:25000)

The results of air analysis

Results of analysis for air samples around the Isfahan city are shown by concentration maps for lead, zinc, and cadmium in Figures 5-7, respectively. As shown in Figure 5, concentration of lead in Isfahan varies from 200 ng/m^3 to 400 ng/m^3, averaging 297.5 ng/m^3 approximately. Results indicate that the highest level of lead concentration is in southern and northern parts of the city. Figure 6 shows concentration map of zinc in the air of Isfahan. It is evident that the highest levels of concentrations are in the southern and northern parts of the city with approximately about 590 ng/m^3 and the least concentration in the eastern parts with approximately 380 ng/m^3 with mean concentration of zinc around the city being approximately 488 ng/m^3. Figure 7 shows concentration map of cadmium in the air of Isfahan and indicating concentration of this metal in the eastern, western, and central parts of the city. Mean concentration of cadmium in the air of Isfahan was 6 ng/m^3, with its highest level at 7.1 ng/m^3 approximately and its lowest level at 3.9 ng/m^3 approximately. Table 3 presents mean concentration of lead, zinc, and cadmium in the air of Isfahan city compared with other countries and standards of world health organization. It can be seen that mean concentration of lead in the air of Isfahan is less than the permitted value of the world health organization, but, compared with other countries, it is 2-3 times as much. Concentration of zinc metal in the air of Isfahan is higher than its mean value in England 232 ng/m^3, Finland 170 ng/m^3, and Canada 85 ng/m^3, but lower than that in the U.S.A.[5,19]

DISCUSSION

It is evident from the results that there is no direct correlation between concentrations of these metals in the soils of the city and rich veins of the Irankooh lead and zinc mines located in the south-west of Isfahan, as the highest concentration of these metals were found in the northern parts of the city. Therefore, sources of these pollutants must be other than mineralization processes in the Irankooh mines. As Isfahan soil is not residual it has probably been transported from upper part of Zayandehrood River and presence of relatively high concentration of lead and zinc in sediments in upstream of the river around Zaman khan area at about 100km west of Isfahan,[24] could be the source of these contaminated soils that were carried by river during flooding periods.

Results obtained from concentration maps in the soil and air of the Isfahan city [Figures 2 and 7] indicate that concentration of lead, zinc, cadmium in the soil of the city is higher in the central to north-eastern parts whereas concentration of these metals in the air of the city is higher in the southern and northern parts. These results confirm the correlation between increased concentration of these metals in the air and increased concentration of these metals in the soil in central and northern parts of the city. But, in southern parts, an increase in concentration of these metals in the air and in the soil is not really in agreement. It is probable that concentration of these metals in the

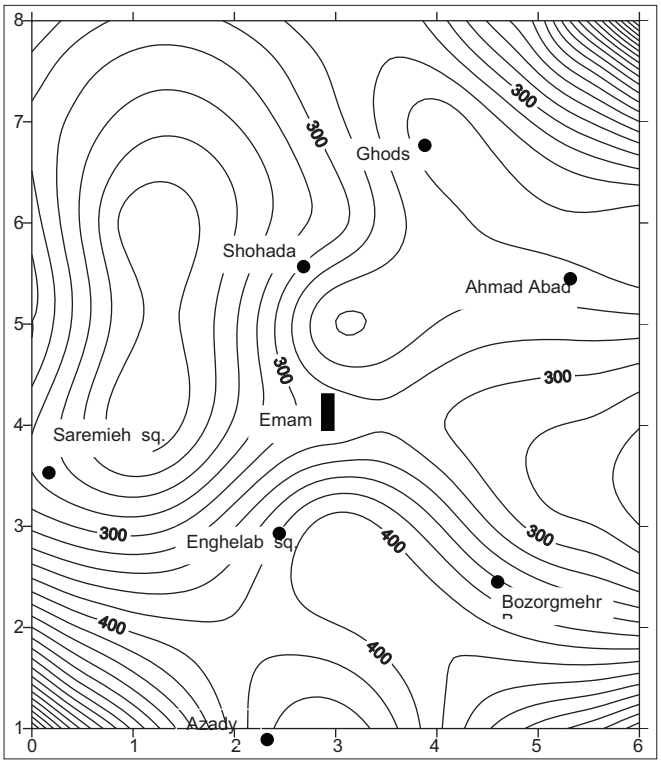

Figure 5: Concentration map of lead in the air of Isfahan in ng/m^3 (scale 1:25000)

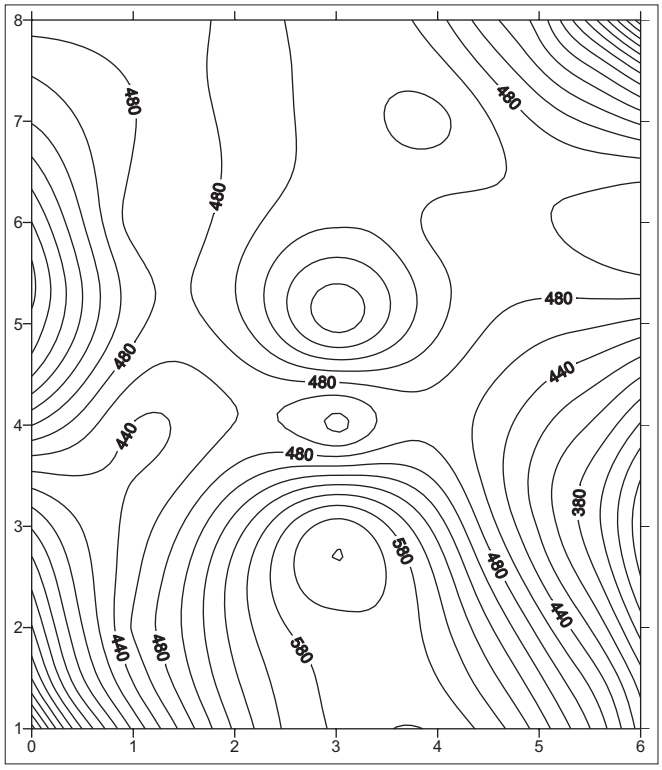

Figure 6: Concentration map of zinc in the air of Isfahan in ng/m^3 (scale 1:25000)

Table 3: Range of mean concentration of lead, zinc, and cadmium in the air of Isfahan compared with other countries and international standards in ng/m^3[5,19]

Metal	Isfahan	Norway	England	Finland	Canada	U.S.A	International standards
Lead	297.5	97	196	-	-	110	500
Zinc	498.1	-	232	170	85	1000	-
Cadmium	6.0	2.8	5.4	-	-	5-40	5

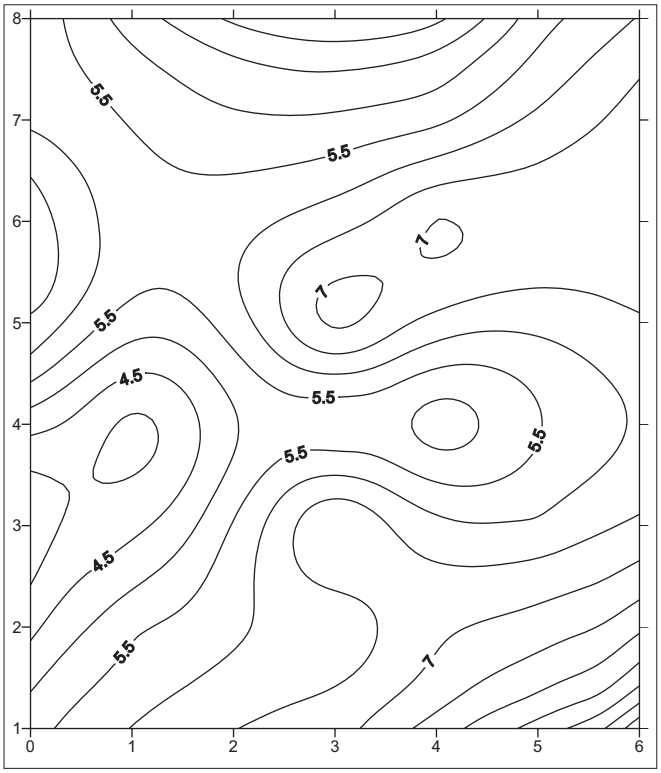

Figure 7: Concentration map of cadmium in the air of Isfahan in ng/m^3 (scale 1:25000)

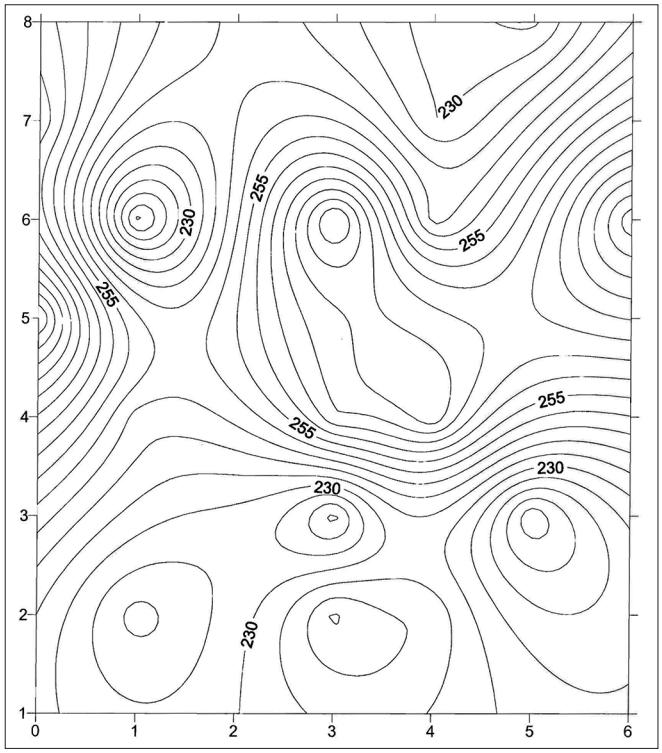

Figure 8: Concentration map of dust in the air of Isfahan in ug/m^3 (scale 1:25000)

northern parts of the city could be due to transfer of river sediments, contaminated with these metals, as well as, industrial activities, or cars.

The reason for higher concentration of metals in the air of Isfahan, apart from wind blowing dust contaminated with zinc, could be the presence of steel industries, lead and zinc mines, cement factory and automobile tire abrasion on the city roads, particularly in the congested areas. Mean concentration of cadmium in the city air being 6 ng/m^3, is slightly higher than the international standard of 5 ng/m^3.[5,19]

Figure 8 shows level of TSP in ug/m^3 in the air of the Isfahan city. It indicates that the highest level of dust in the city is in the northern parts, which is in complete agreement with increase in the concentration of these metals in the air of the city. One of the reasons for disagreement in concentration of these metals in the southern parts of the city which goes with their increase in the air could be due to the pollutants getting into the air from south-west of Isfahan where heavy industries, especially steel and iron smelting industries and others are located.

Based on the studies, approximately 85% of natural sources of lead present in the atmosphere are due to dust getting blown into the air which indicates its effect on increased concentration of lead and other metals.[4] Based on these same results, primary human sources of lead in the atmosphere include 61% due to combustion of leaded petrol, 23% due to iron and steel productions, 8% due to extraction and melting of lead, and other 5% due to burning coal.[4] It must be mentioned that values of lead getting into the atmosphere from human sources varies from place to place. These findings were presented at a time when in most places in the world leaded petrol were used, but today that consumption of leaded petrol has virtually stopped, and level of lead in the air has dropped dramatically. To this end, some researchers presented concentration of lead in large cities of the world between 1964 and 1972 as follows Berlin 3800 ng/m^3, Rome 4800 ng/m^3, Paris 4600 ng/m^3, London 5100 ng/m^3, and New York 4100 ng/m^3.[4] As is shown in Table 3, concentration of this metal in recent years has dropped below the standard limit of 500 ng/m^3 in England and Norway. Furthermore, in Denmark in the 70's, concentration of lead in the air was approximately 600 ng/m^3 and in the late 90's dropped to

values lees than 20 ng/m^3 which correlates with the amount of lead in the automobile fuels.[25]

In Isfahan also, before this study began leaded petrol was used and concentration of lead, zinc, and cadmium in the city air were higher than what was measured during this study, so that mean values were 620 ng/m^3 for lead, 500 ng/m^3 for zinc, and 30 ng/m^3 for cadmium.[1] These figures dropped to 297.5 ng/m^3, 498.1 ng/m^3, and 6.0 ng/m^3, respectively.

CONCLUSION

In sum, it can be concluded that although not using leaded petrol can cause a reduction in the level of lead in the air, this reduction, compared with other countries has not been substantial, while reduction in level of cadmium has been quite considerable, which shows probably that, because cadmium as an impurity is added to leaded petrol, and since usage of leaded petrol has been reduced to one fifth, thereby a reduction in cadmium was observed.

Possible reasons for the presence of lead and zinc in the air of the city after leaded petrol usage stopped, based on the given information,[4] could be both natural sources contamination due to dust and human source due to iron and steel production in the south-west of Isfahan, are the main factors of these metals getting into the air of Isfahan. Although level of lead, zinc, and cadmium in soils in Isfahan is not higher than international standards, these standards were prepared in western countries where it mostly rains throughout the year, making the soil moist, thereby eliminating the dust problem. As a result, immediately after leaded petrol ban in humid countries, level of lead in the air dropped drastically. In Isfahan, however, as rainfall is limited and soil is predominantly dry only slightest wind, or movement of automobiles over contaminated roads, can cause wind blown dust into the air. Studies conducted by Wang and Lu (2011) revealed that higher content of Cd, Cu, Pb and Zn in the soils of Lishui city in China with respect to the background values are highly related to human activities especially in old urban areas with high-density population and commercial activities. Also, since iron smelting and steelworks industries located at south-west of Isfahan which are in the direction of winds blowing toward the city, it can cause the metals to being blown into the air from industrial stacks and move toward Isfahan, especially at southern parts of the city.

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