Investigation of heavy metals accumulation in the soil and pine trees

Javad Kharkan, Mohammad Hossein Sayadi*, Mohammad Reza Rezaei

Department of Environmental Sciences, School of Natural Resources and Environment, University of Birjand, Birjand, Iran

Abstract

Background: Human activities related to workshops in the cities contribute to the release of heavy metals into the environment, which pose serious risks to the environment and to human health. The aim of the present study was to evaluate the concentration of lead (Pb), iron (Fe), and manganese (Mn) in the pine trees and soil in various land uses of Birjand city, Iran.

Methods: The sampling stations were randomly selected from different land uses including parks, streets, carwashes, car repair shops, and car smooth shops in Birjand city. The pine trees (skin and leaves) and soil samples were collected from 15 stations located at different and uses in 2017. To determine the concentration of heavy metals, atomic absorption spectrometer (Contr AA 700) was used.

Results: It was revealed that the mean concentration of Pb, Fe and Mn in residential soil was 1.79, 419.39, and 30.76 mg/kg, respectively. Moreover, the Pb, Fe, and Mn concentration in pine skin and leaves was 0.63 – 0.18, 23.05–9.84, and 10.05–3.13 mg/kg, respectively. The geo-accumulation index (Igeo) mean of the study areas demonstrated a descending trend for Fe (16.31 mg/kg) <Mn (8.86 mg/kg) <Pb (0.41 mg/kg). Pb showed the highest transfer factor in the parks and streets followed by Mn and Fe. In the car repair and smooth shops, the highest transfer factor pertained to Pb and the lowest one pertained to Fe. The statistical analysis indicated that there was a significant difference in the Fe and Mn concentrations among various land uses (P < 0.05).

Conclusion: According to the results, the soils of car repair and smooth shops as well as carwashes in Birjand are becoming polluted by Pb, Fe, and Mn. Although, it does not threaten the city ecosystem, but with passage of time, these measures will be accumulated due to the soil alkalinity and will reach critical levels.

Keywords: Lead, Iron, Manganese, Soil, Cities


*Correspondence to: Mohammad Hossein Sayadi
Email: Mb_sayadi@birjand.ac.ir

Introduction

Environmental pollution by heavy metals has become a matter of attention on local, regional, and global scales due to their toxicity effects (1-3). Essential metals such as iron (Fe) and manganese (Mn) play a role in metabolic activity and are required for growth, development, and maintenance of body, but high concentrations of these metals have adverse health effects on different organs such as liver, heart, endocrine glands, and neurotoxic effect on the brain (4,5). In contrast, the non-essential metals such as lead (Pb) has no role in metabolic activities of organisms but at low concentrations, it has the potential to affect toxicity on different tissues of living organisms (6,7). Pb exposure can cause different health problems such as anemia, bone, renal, reproductive, nervous system disorders, neurohematological damages, and cancers (8).

The urban soil is the most important part of an urban environment. Various studies have been conducted in many countries to investigate the soil contamination by heavy metals (Pb, Fe, and Mn) in urban soils, and it was revealed that heavy metals concentrations were affected by several factors such as traffic activities, parks, and various workshops (9,10). Human activities related to workshops in the cities contribute to the release of heavy metals into the environment, which pose serious risks to the environment and human health. Brake wear, and exhaust gas are the most important sources for releasing of Pb from vehicles (11). The levels of soil contamination and plant species are two main factors that affect the dynamics of heavy metals in plant-soil interactions (12). The roadside plants’ leaves or stems may also absorb heavy metals through atmospheric deposit or road runoff (13,14).
Different parts of the plant contain different amounts of heavy metals, so that the highest concentrations of metals are found in roots, stems, and leaves (15). Some trees such as pine have been used as biological indicators for monitoring heavy metals in the environmental pollution, because these trees are extensively dispersed in most cities as the main plant species with long lifetime (16). It is interesting to note that the dominant trees in the city of Birjand is the pine trees. The vehicles, carwashes, car smooth units, and car repair shops release heavy metals in the urban environment. Since, there has not been a study on the concentration of heavy metals in pine trees (skin and leaves) in the climatic conditions of the region and different land uses, therefore, this study aimed to determine the concentration of Pb, Fe, and Mn in the soil and pine trees at different land uses in Birjand city such as different parks, streets, carwashes, car repair shops, and car smooth shops.

Materials and Methods

Study area

Birjand city is the capital of South Khorasan province in the eastern part of Iran. Birjand city lies on the border with Afghanistan and it is about 1491 m from the sea level. At 2016 census, its population was 221,756 consisting 60,240 families. This city is located at a latitude of 32°87ʹ N and longitude of 59°21ʹ E with cold semi-arid climates (Figure 1). Moreover, Birjand city from the middle of April to December has a dry season with 171 mm rainfall and 255 sunny days in the year (17).

Sampling and laboratory analysis

The total of 15 soil and pine trees (skin and leaf) samples were randomly collected from different land uses in Birjand city such as car repair and smooth shops, carwashes, streets, and parks with three replicates and transferred to the Central Laboratory of Environmental Pollutants of Birjand University. The pH of soil saturation extract was analyzed using a pH meter. Electrical conductivity (EC) of soil and soil texture was determined by an EC meter and hydrometer method, respectively (18). To measure pH, 5 g of each soil sample was placed into a 50 cc Erlenmeyer flask. Distilled water was added to the sample (1:25 dilution) and kept for 12 hours at ambient temperature. Then, pH was measured by the pH meter. Moreover, to determine the EC, 150 g of the screened soil (2 mm) was poured into a container and saturated with 150 mL distilled water (1:1). After saturation, its extract was obtained by Bacchini funnel. A filter paper was placed into the funnel and an extraction glass was kept under the funnel. The extracted soil was collected in the extraction glass. The physiochemical characteristics of the extracted soil samples were reported in Table 1.

Determination of the heavy metals concentration

To determine the concentration of heavy metals, 1 g of soaked and sieved soil was placed in an Erlenmeyer flask, then 16 cc acid [a mixture of 4 cc nitric acid (65%) and 12 cc hydrochloric acid (37%)] was added to the flask. For acid digestion, the flask was placed on the sand bath at 100°C for 6 to 7 hours. At the specified time period, 4 cc per chloric acid was added to the flask placed on the sand bath. After evaporation of 3 cc acid, the sample was flattened by a plastic funnel on the filter paper (18,19).

Determination of heavy metals concentration in pine trees

To determine heavy metals concentration in the plant texture, the samples were dried in an oven at 70°C for 48 hours, then, the samples were ground by a Chinese oven for better dissolving in the acid, finally, 1 g of the sample was placed into an Erlenmeyer flask for sample digestion. For chemical digestion of the samples, nitric acid (HNO₃)
Geo-accumulation index
Geo-accumulation index (Igeo) was used to evaluate soil pollution by comparing the current heavy metals concentration in the soil with their pre-industrial/background concentration. This index is used to determine the pollution degree and the amount of human factors affecting the soil and sediment (21) and is evaluated through Eq. (1):

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right)$$

(1)

where $C_n$ is the measured concentration of element in the sample and $B_n$ is the concentration of the same element in the sample. To correct the effects of soil material through human activities, the correction coefficient of 1.5 was used. According to this index, the soils are categorized into 7 different groups as below (22).

- $I_{geo} \leq 0$ (non-contaminated),
- $1 < I_{geo} < 0$ (non-contaminated to slightly infected),
- $2 < I_{geo} < 1$ (slightly infected),
- $3 < I_{geo} < 2$ (slightly infected to very polluted),
- $4 < I_{geo} < 3$ (very polluted),
- $5 < I_{geo} < 4$ (very polluted to severely infected),
- $5 \leq I_{geo}$ (severely infected).

Contamination factor index
According to contamination factor (CF) index, the enrichment of metals in relation to the background concentrations can be evaluated and the degree of soil pollution can be determined (23). The contamination factor is determined using Eq. (2):

$$CF = \frac{[C]_{sample}}{[C]_{background}}$$

(2)

Where $CF$ is contamination factor, $[C]_{sample}$ is the concentration of considered element, and $[C]_{background}$ is the concentration of basic element in the sample. In terms of contamination by heavy metals, soils are divided into 4 groups based on the contamination factor.

- $1 > CF$ (lowly polluted),
- $3 < CF < 1$ (moderately polluted),
- $6 < CF < 3$ (highly polluted),
- $6 \leq CF$ (polluted) (24,25).

In this study, the sample was collected from the control soil (i.e., an area without any human activity) and from the depth of one and a half meters. The background concentration of Pb, Fe, and Mn was 0.26, 305.4, and 23.94, respectively.

Pollution load index
To evaluate the severity of contamination, the pollution load index (PLI) was used. Using PLI, the effects of total contamination by different metals is evaluated. The advantage of PLI over other indicators is that the pollution risk index of all the studied metals is determined in the area. According to this index, the standardized quality of soil is divided into 5 levels (26).

- Highly polluted ($P > 0.7$),
- clean contaminated ($0.7 < P \leq 1$),
- slightly polluted ($1 < P \leq 2$),
- moderately polluted ($2 < P \leq 3$),
- and highly polluted ($P > 3$).

The pollution coefficient of Pb is evaluated based on the Eq. (3):

$$PLI = \sqrt{CF_1 \times CF_2 \times CF_3 \times \cdots \times CF_n}$$

(3)

Enrichment factor
The evaluation of the soils pollution was made by using enrichment factor to overcome the difficulties in making an overall assessment of the degree of metal contamination in soils. This factor is evaluated based on the Eq. (4)(27).

$$EF = \sqrt[\text{Sample}]{\frac{C_x}{C_{ref}}} \times \sqrt[\text{Background}]{\frac{C_x}{C_{ref}}}$$

(4)

Where $EF$ is enrichment factor, $C_x$ is the concentration of measured element in the sample, and $C_{ref}$ is the concentration of the reference element (Fe). The reference element is an element that has the geological origin. In the environmental studies, Sr, Al, Fe, Ti, and Zr are usually used as the reference elements (28). The degree of heavy metals pollution can be divided into 5 groups (29): $EF < 2$ (low pollution level), $2 \leq EF < 5$ (moderate pollution level), $5 \leq EF < 20$ (high pollution level), $20 \leq EF < 40$ (very high pollution level), and $40 \leq EF$ (severe pollution level).

Potential ecological risk
The index of potential ecological risk (Er) is used to evaluate the environmental potential risks of metals in the soil (30). In this study, the potential Er of heavy metals was determined using the following equations:

Table 1. Physiochemical characteristics of the studied soil samples

<table>
<thead>
<tr>
<th>Land Use</th>
<th>pH Soil</th>
<th>Soil EC (MSCM-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Park</td>
<td>7.73</td>
<td>2.165</td>
</tr>
<tr>
<td>Street</td>
<td>7.43</td>
<td>6.67</td>
</tr>
<tr>
<td>Carwash</td>
<td>7.5</td>
<td>5.38</td>
</tr>
<tr>
<td>Car repair shop</td>
<td>8.5</td>
<td>4.98</td>
</tr>
<tr>
<td>Car smooth shop</td>
<td>8.2</td>
<td>6.76</td>
</tr>
</tbody>
</table>
The mean (±SD) of heavy metals (Mn, Fe, and Pb) in the soil and pine tree (skin and leaf) in different land uses (mg/kg)

<table>
<thead>
<tr>
<th>Land use</th>
<th>Mn</th>
<th>Fe</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Leaf</td>
<td>Skin</td>
<td>Soil</td>
</tr>
<tr>
<td>Park</td>
<td>2.44 ± 1.66</td>
<td>23.81 ± 3.91</td>
<td>42.77 ± 3.14</td>
</tr>
<tr>
<td>Street</td>
<td>2.03 ± 0.31</td>
<td>11.86 ± 1.25</td>
<td>22.8 ± 3.24</td>
</tr>
<tr>
<td>Carwash</td>
<td>2.81 ± 0.54</td>
<td>4.26 ± 0.30</td>
<td>27.21 ± 1.28</td>
</tr>
<tr>
<td>Car repair shop</td>
<td>4.62 ± 0.40</td>
<td>6.07 ± 2.72</td>
<td>24.21 ± 4.02</td>
</tr>
<tr>
<td>Car smooth shop</td>
<td>3.82 ± 0.60</td>
<td>4.28 ± 1.06</td>
<td>36.8 ± 10.29</td>
</tr>
<tr>
<td>F value</td>
<td>4.57</td>
<td>7.80</td>
<td>40.43</td>
</tr>
<tr>
<td>P value</td>
<td>0.23</td>
<td>0.004</td>
<td>0.001</td>
</tr>
</tbody>
</table>

The average concentration of heavy metals Pb, Fe, and Mn was measured by atomic absorption spectrophotometer (AAS) in soil and pine trees (skin and leaf) in different land uses (Table 2). The average concentration of Pb, Fe, and Mn was 0.87, 150.79, and 14.65 mg/kg, respectively. The statistical analysis indicated that there are significant differences in Pb concentration in the soil and pine's skin among various land uses \( (P<0.05) \). Also, there was a significant difference in the Fe concentration in pine's skin and leaf \( (P<0.01) \). There were significant differences in Mn concentration in the soil and pine's skin \( (P<0.01) \). The average concentration of Pb, Fe, and Mn in the soil was 1.79, 419.39, and 30.75 mg/kg, respectively. The average concentration of Pb, Fe, and Mn in the pine's skin and leaf was 0.63, 23.04, and 10.06 mg/kg and 0.17, 9.84, and 3.14 mg/kg, respectively. It is clear that, the concentration of these metals in different parts of pine exhibited a descending order of leaf < skin < soil.

The highest concentration of Pb belonged to car repair shop and the amount of Pb in different land uses was in a descending order of Park < Street < Car smooth shop < Carwash < Car repair shop. So, carwash and car repair shop significantly increased Pb in the urban environment. Pb had the highest concentration (4.56 mg/kg) in car repair shop and the lowest one in park (0.28). Fe and Mn in park demonstrated the highest concentration. Pb, Fe, and Mn showed the highest concentration in the soil and their concentration in pine's skin was more than the leaf. The statistical analysis showed that there are significant differences in Pb and Mn concentration in the soil and pine's skin among different land uses \( (P<0.01) \). Also, there was a significant difference in the Fe concentration in pine's leaf among different land uses \( (P<0.01) \). The results of Pearson correlation coefficient showed that there was a strong correlation between the studied elements (Table 3). Strong correlation was observed between the elements that were contaminated from the common sources like wastes from car wash and repair or through soil materials. In a similar study, Bhuiyan et al evaluated the correlation of heavy metals by Pearson correlation coefficient and concluded that the metals that showed high correlation, probably had the same pollution.
sources (26).

### Geo-accumulation index

According to Table 4, the mean of Igeo of the study areas exhibited an increasing order of Igeo Pb (0.41) < Igeo Mn (8.86) < Igeo Fe (16.31). As shown in this table, the Igeo value of both elements Fe and Mn was over 5, therefore, the area is very heavily polluted.

### Contamination factor

The CF of Pb showed low (12.5%), moderate (31.25%), high (62.6%), and severe pollution (50%). Furthermore, Fe and Mn exhibited low (18.75%) and moderate pollution (81.25%), respectively (Table 5). As shown in Table 4, the CF mean in the study areas showed an increasing order of Mn (1.27) < Fe (1.35) < Pb (6.50).

### Enrichment factor

The enrichment factor (EF) average for the studied heavy metals in the soil samples showed a descending order of Mn (1.27) < Fe (1.35) < Pb (6.51), therefore, the enrichment factor average for Pb was more than 1.5 (Table 6).

### Potential ecological risk

In this study, the potential ecological risk (Er) for Pb was evaluated. The values of potential Er are presented in Table 7. The results showed that the average potential Er for Pb was 34.36 and its low and significant values were 60% and 13.3%, respectively (Table 8). Thus, Pb is an effective factor in increasing the potential Er in the aforementioned and uses soil. This metal, which is found as a colored material and petroleum product and used in the car smooth and repair shop, is very dangerous.

### Transfer factor

Transfer factor of the studied heavy metals in the soil and pine's skin and leaf is shown in Table 9. Pb showed the highest transfer factor in the parks and streets followed by Mn and Fe. In carwash, the transfer factor demonstrated a descending order of Fe < Pb < Mn. In the car repair and smooth shops, the highest transfer factor pertained to Pb and the lowest one to Fe. High value of transfer factor of Pb signifies high ability of pine to absorb Pb from the soil. In several plants, the concentration of Pb was hundred times more than the permissible limits of its accumulation in the plant.

### Discussion

Different human activities like car workshops can cause soil pollution that leads to major environmental problems. After a long time, heavy metals can accumulate in the human body. The bivalent Pb is replaced in the body, instead of calcium ion, and this replacement permits Pb to remain in the body for a long time. Pb accumulation can disrupt the human circulatory system as well as kidneys. It also has serious negative effects on the physical development of children. The reasons for the use of Pb in car smooth, repair shop, and carwash is that it is one of the petroleum products and its derivatives are used not only in producing various colors, but also for disposal of motor oil from battery water (34). In a study in Kerman city, the most important factors that increase the heavy metals in the soil, especially Pb, Zn, and Cu, were traffic and its related activities such as gas stations, battery packs, oil changes, and car painting and smooth (35). The results of a study by Saboohi et al showed that the floor dust of Yazd battery factory workshops has high level of heavy metals concentration so that it has the potential environmental and health risks (36). The most dangerous
The results of statistical analysis of ecological risk (Er) for Pb in the studied stations

<table>
<thead>
<tr>
<th>Ecological risk</th>
<th>Very high ecological risk</th>
<th>High ecological risk</th>
<th>Significant ecological risk</th>
<th>Moderate ecological risk</th>
<th>Low ecological risk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of stations</td>
<td>2 (13.3%)</td>
<td>4 (26.6%)</td>
<td>9 (60%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Table 9. Transfer factor of heavy metals (mean ±SD) in different land uses

<table>
<thead>
<tr>
<th>Land use</th>
<th>(\text{TF}_{\text{Fe}})</th>
<th>(\text{TF}_{\text{Pb}})</th>
<th>(\text{TF}_{\text{Mn}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Leaf</td>
<td>Skin</td>
<td>Leaf</td>
</tr>
<tr>
<td>Park</td>
<td>0.6 ± 0.4</td>
<td>0.56 ± 0.6</td>
<td>0.33 ± 0.05</td>
</tr>
<tr>
<td>Street</td>
<td>0.93 ± 0.2</td>
<td>0.52 ± 0.3</td>
<td>0.2 ± 0.01</td>
</tr>
<tr>
<td>Carwash</td>
<td>0.10 ± 0.2</td>
<td>0.16 ± 0.05</td>
<td>0.2 ± 0.01</td>
</tr>
<tr>
<td>Car repair shop</td>
<td>0.17 ± 0.2</td>
<td>0.24 ± 0.07</td>
<td>0.2 ± 0.01</td>
</tr>
<tr>
<td>Car smooth shop</td>
<td>0.7 ± 0.9</td>
<td>0.1 ± 0.1</td>
<td>0.02 ± 0.01</td>
</tr>
</tbody>
</table>

The results of Igeo index showed that Pb had the highest pollution level, whereas Fe and Mn had the lowest one. In addition, the results showed that Pb enters the environment through human activities and it does not have a natural origin. Yang et al in their study on urban soils of Chung Chun found that Pb, Cu, Ca, and Hg have significant correlation and identified industrial activities and traffic as the sources of metals pollution (30). Taghipour et al reported that Pb, Zn, and Cu, respectively had the highest concentration in urban soil due to industrial activities (44). Therefore, the results are consistent with the results of this study wherein high level of Pb contamination was found in the soil of carwashes and repair workshops, so it is quite essential to decrease heavy metals levels to inhibit the potential hazards of these metals in the environment. Various studies of ecological risk assessment showed that Pb caused various diseases in humans like kidney problems, liver diseases, and cancer (45,46). Thus, Pb can affect the local ecological function in the long run and currently, it does not have the ability to create health and environmental problems (47-49). So, it is important to consider the levels of heavy metals to inhibit the potential hazards of these metals in the environment. The transfer factor shows that pine can be used to refine the polluted areas. Lebeau et al reported that the transfer factor of elements from terrestrial to aerial organs can be used to identify the over accumulated organs (50). Some researchers used the ratio of heavy metals concentration in the aerial part/root to describe the plant resistance and reaction against high levels of metals in the soil wherein this ratio is greater than one in plants containing more than one reagent, and less than one in plants having less than one reagent (51).

Conclusion

According to the results, the soils of car repair and smooth shops as well as carwashes in Birjand are becoming polluted by Pb, Fe, and Mn. Although, it does not threaten the city ecosystem, but with passage of time, these measures will be accumulated due to the soil alkalinity and will reach critical levels. The soil and plant surrounding the...
streets and parks are contaminated by Pb from vehicles gases. Effectually, Pb concentration in the soil and plant increases with traffic volume and decreases with the distance from the main roads and streets. However, in this study, the contamination factors like accumulation land index and contamination factor were evaluated. The contamination load and enrichment factor showed that Pb showed moderate to high pollution, whereas Fe and Mn represented low to moderate pollution in the car repair and smooth shops. According to the ecological risk index, Pb, Fe, and Mn in the aforementioned land uses doesn’t have the ability to create the health and environmental problems. However, to prevent these problems, the potential hazards of these metals in the environment should be considered. In parks and streets, the transfer factor more than 1 signifies the high ability of pine to absorb Pb from the soil. So, it can be safely concluded that pine can be used to refine the contaminated areas in parks and streets.

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Ethical issues
The authors certify that all data collected during the study as stated in the manuscript, and no data from the study has been or will be published separately elsewhere.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
All authors participated in the data collection, analysis, and interpretation. All authors critically reviewed, refined, and approved the manuscript.

References
18. Sayadi MH, Rezaei MR, Rezaei A. Sediment toxicity and


33. Erfanmanesh M, Afsuny M. Environmental Pollution Water, Soil and Air. Esfahan: Arkan; 2005. [In Persian].


