Soil assessment for heavy metal contamination and potential ecological risks

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Abstract

Pollution in soil (particularly heavy metal contamination) is a result of industrialization, urbanization, intensified use of fertilisers, insecticides and irrigation water. The quality of agricultural soil in the vicinity of the industry is of wide concern due to associated health risks caused by presence of heavy metals in it. Heavy metals pollution in the soil leads to its poor health, groundwater and food contamination which is hazardous to human health.

In the present study, wavelength dispersive X-ray fluorescence (WDXRF) technique has been used for soil assessment in one of the industrial areas of Himachal Pradesh, India. The XRF results show a larger concentration of some of the heavy metals in different soil samples as compared to the permissible values. The high values of contamination factor especially for titanium (Ti), vanadium (V), chromium (Cr), cobalt (Co) and barium (Ba) show that the contamination in the agricultural soils in the vicinity of the industries is due to their shear negligence. The investigated contamination factor lies in the range; 3.79<CF<14, 3.29<CF<17.86, 1.64<CF<18.96, 2.78<CF<6.22 and 2.38<CF<6.30 for Ti, V, Cr, Co and Ba respectively. Moreover, the results indicate that the risk index ranges from moderate potential risk to considerable potential risk.

Keywords: X-ray fluorescence, soil contamination, WDXRF, risk factor and heavy metals.

Introduction

Ecological well being is firmly associated with the soil condition mainly due to the amount of soil contamination; therefore, soil pollution has drawn enormous concern all over the globe. Soil acts as a dip as well as origin of contamination, having the capability to commute contaminants to groundwater and hence to ecological system. Many agricultural products can accumulate contents of heavy metals, resulting in the increase of metals proportionate in agricultural products and thus are closely related to human health.

Around 40 percent of global causalities are induced by water, air and soil pollution due to anthropogenic activities. In developing countries, industrial sectors pose significant environmental and occupational health risks to its populations. As industries are booming, large quantities of industrial waste are being dumped illegally either in open or in the nearby riverbeds. Urban societies are increasing rapidly all over the globe especially in the developing countries. Urban growth has created crucial alteration to the ecological system by broadening waste inflation through human activities. Urban and industrial extensions are compelling the farmers to grow crops in polluted soil.

In urban areas, populations use sewerage treated water for enhancing crop production and this has become a major source of soil pollution. A considerable accumulation of toxic metals exists in industrial discharge/ sludge and therefore, it is a primary contributor for the soil irrigated with industrial effluent. Different kinds of industry waste, sewerage and sludge irrigation have all become the source of heavy metals. These pollutants amend the soil profile, which results in diminishing the fertility of the land and makes it unfit for crop production. A study of heavy metals in environmental sample is of immense importance because of their toxic nature.

Heavy metals exist in the surroundings, as a result of human and natural pursuits and are responsible for disturbing the ecological system through many pathways. Irrigation of agricultural lands with sewerage/industrial effluent leads to considerable pollution with heavy metals and hence, trace metal accumulation in cultivated crops. Tran et al. evaluated the existence of eleven trace elements in a hard clam and explained the bioaccumulation of heavy metals from the environment to living organisms.

Solid hazardous waste and its dumping are of prime concern in the chosen study area. Industrial units also indulge in illegal and adhoc dumping of waste all over in the nearby residential areas, riverbeds, forests, roadsides and any open space available. Such dumping has become a serious hazard as well as nuisance for the ecosystem. Soil and water in the region are becoming increasingly unfit for irrigation of vegetables and crops due to the presence of metals in it. Without exact information about the quality and quantity of pollution sources present in soil, it is impossible to eliminate or reduce these pollutants. For a comprehensive path to study environmental pollution, a variety of specimens are required to be adequately assessed over an extensive range of parameters.

Several lab experiments can detect the contaminants in the form of heavy metals in soil. X-ray fluorescence (XRF) spectroscopy is the simplest and utmost preferred technique for non-destructive, multi-elemental assessment of soil,

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water and plants etc. XRF technique is immensely applied for the evaluation of heavy metal in environmental samples. Over the past several years, this technique has seen a remarkable progress and proved its applicability to a variety of fields such as environment, geology and material science.

Recent developments in XRF spectroscopy along with advancements in sample analysis enhanced the analytical competences and applications of this approach to the analysis of solid and liquid specimens. Elements from Sodium to Uranium are frequently studied using energy-dispersive X-ray fluorescence (EDXRF).

In contrast, utilization of wavelength-dispersive X-ray fluorescence (WDXRF) allows adequate determination of low-Z elements. Bamford et al\textsuperscript{2} applied XRF technique for trace elemental analysis of environmental samples like soil, water and plants and recommended XRF for determination of elements in the range Na to U. Melquiades et al\textsuperscript{12} used XRF technique for heavy metal contamination in soil and found it reliable for simultaneous elemental analysis. Wu et al\textsuperscript{13} evaluated the reliability of portable XRF for heavy metal contaminated soil samples and found XRF technique highly reliable in comparison to other methods (i.e. AAS and ICP-MS).

Wo\l\c{e}jko et al\textsuperscript{23} studied the effect of sewerage sludge on the accumulation of heavy metals in soil and their mobility to plants grown in it using XRF and concluded that plants absorb Cd, Zn, Cu easier than Pb and Ni from the polluted land. Margui et al\textsuperscript{11} measured the elemental analysis of liquid sample using XRF and suggested XRF as a reliable technique for elemental analysis. Ali et al\textsuperscript{1} measured the soil pollutants near industrial sites in Sudan using XRF and found contamination of about 10 elements above pollution threshold limits.

Neiva et al\textsuperscript{14} applied wavelength dispersive X-ray fluorescence for assessment of leather samples and reported alarming quantity of Cr. Koleleni et al\textsuperscript{8} used wavelength dispersive X-ray fluorescence (WDXRF) spectroscopy to analyse heavy metal concentration in soils and vegetables. Their findings indicated a high level of contamination in both soil and vegetables to pose detrimental health risks to consumers. Petelka et al\textsuperscript{16} evaluated the soil pollution levels and phytoremediation potential of native plants to mitigate heavy metal concentration in soil.

Heavy metals are most determined contaminants in the ecosystem such as water, soil, plants and animals because of their defiance to disintegrate in ordinary circumstances. The indigestion of heavy metals in the body leads to toxicity, its accumulation in soft tissues might create harm to living organisms. It has, therefore become imperative to monitor the level of heavy metals in soil in order to assess the pollution risks. The present study aimed to assess the heavy metal concentration in agricultural soil located near Industrial areas and also to assess the associated potential ecological risk levels so that the remedial measures can be suggested accordingly.

**Material and Methods**

Eight sampling sites were selected in the target area (with approximately 318 square kilometers of land) located near the industries. Soil samples were collected from the outer surface i.e. 10–40 cm depth to quantify the contamination sources, as effluents primarily contaminate the upper layer of the soil\textsuperscript{7}. Figure 1(a and b) showed the location of sample collection sites close to industry.

In order to obtain uniformity in the soil samples, the bare soil samples were dried, sieved and pulverized by passing over a 150 micron mesh sieve. 9 g soil sample was mixed with 2.7 g of the binder for obtaining an experimental target of 11.7 g, having a diameter of 34 mm and a thickness of 4 mm. The pellet was made in a hydraulic press under a pressure of 15 tons. The sample was analysed for 37 minutes. The main advantage of XRF techniques is that it is multi-elemental, non-destructive in nature and can be directly applied to solid samples for ultra-trace elemental analysis\textsuperscript{19}.

The present measurements have been performed by using WDXRF Model: S8 TIGER (Bruker), Germany. [Figure 2 (a, b)]. The instrument works according to Bragg diffraction law. The apparatus is furnished with a rhodium X-ray tube. Scintillation and proportional detectors were used for elements detection.

**Results and Discussion**

The XRF results for the collected soil samples prove the existence of 27 elements from Calcium to Uranium. The percentage concentrations of all the elements for each of the soil samples are given in table 1.

From the experimental results presented in table 1, it can be concluded that in general, the concentrations of some of the heavy elements vary from site to site depending upon the type of the industry in the vicinity of that agricultural land. The concentration of some of the heavy metals (Table 2) was found higher as compared to the baseline/background concentration\textsuperscript{4} in most of the sites.

There is a variation in the concentration of heavy metals determined at different sites. The measured concentration of Ti, V and Cr in almost all sites is more than the background values for unpolluted soil. Ti concentration is greater than the standard value\textsuperscript{8} for all sites; V concentration is also more than the threshold value for all sites. V has an extensive and diverse application in dyeing, textile, metallurgy and electronics industry. Large number of industries in respective sites are textile, pharmaceutical and dyeing raising the concern for industrial pollution.

Krishna et al\textsuperscript{9} reported similar findings for the toxic metal pollution created by industries in Surat, India. The
percentage of Cr was found greater than the permissible limits prescribed by WHO\textsuperscript{9,24} for almost all the sites. However, Mn dominates mainly at sites A5-1, A7-1 and A12-3.

The probable reason for the presence of Cr in the soil samples could be from the direct discharge of waste from electro-plating, paint and dye, fabric manufacturing and pharmaceutical industries in the vicinity. Cobalt concentration exceeds for all the sites and battery; dying industries in the region were responsible for this soil pollution. Iron showed alert levels for the majority of the sites. Fe level also increased moderately at some sites.

The analysis of the heavy metals in studied soil showed that the concentrations of Ni, Cu, As and Zn are within the guideline value prescribed by WHO\textsuperscript{9,24} for unpolluted land. Barium levels are again higher at almost all the sites with a maximum value at A7-1 site. Since barium is a toxic metal and is considered critically hazardous, therefore, the industrial effluent in the surrounding areas needs regular and rigorous monitoring.

Fig. 1(a): Location of the target area in the map

Fig. 1(b): Map of sampling sites in target industrial area of Himachal Pradesh-India (Source Google Earth)

Fig. 2(a): Schematic diagram of WDXRF set-up

Fig. 2(b): Actual photograph of the experimental set-up
The small increase in the lead concentration at A3-1 might be due to the textile and cement industry in the vicinity. The recent XRF results show that there is significant increase in heavy metal concentration in the soil samples indicating the presence of toxicity. Furthermore, the increased proportionate of heavy metals in agricultural areas close to industry indicates that the trace metals in soil commenced primarily from industrial activities. The high content of Ti, V, Cr, Co and Ba etc. depicts the influence of industrial pollution in the agricultural areas9.

**Assessment of environmental risks:** Soil pollution by heavy metals can create deliberate and irreversible ecological hazards by inflating the food chain. Enormous aggregation of undesired metals in land can alter the aggregation of undesired metals in land can alter the
consequential disorder, as well as affects ecosystems. The assessment of the potential risk of heavy metals is suggested as a diagnostic mechanism for regulating soil pollution.

Hakanson\textsuperscript{5} derived a method to evaluate the heavy metal contamination from the perspective of ecological risk. In addition to assessment of heavy metal pollution, this method also links with ecological effects in terms of indices\textsuperscript{18}. According to this method, the contamination factor (C\textsubscript{fi}) of each metal and potential ecological risk factor (E\textsubscript{ri}) of each metal along with multi-elemental cumulative risk index (RI) are computable.

**Contamination factor:** Soliman et al\textsuperscript{21} defined the contamination factor of a particular metal as the rate of heavy metal proportionate in the soil to its baseline value as;

\[
\text{Contamination Factor (C}_f\text{)} = \frac{\text{C}_{\text{heavy metal}}}{\text{C}_{\text{baseline}}}
\]

The different ranges of contamination factor are illustrated as:

- C\textsubscript{fi} < 1 no contamination,
- 1 < C\textsubscript{fi} < 3 moderate,
- 3 < C\textsubscript{fi} < 6 considerable,
- 6 < C\textsubscript{fi} very high.

The calculated contamination factor for each individual metal at all the sites is listed in table 3. It is clear from table 3, figures 3 and 4 that some of the heavy metals show considerable and high contamination at most of sites especially at A5-1, A7-1 and A12-3. As the bulk of the industrial units in respective sites are textile, pharmaceutical and dying, this clearly hints the origin of the pollutants to be these industries in the region.

![Site specific contamination factor of each element](image1)

**Fig. 3:** Contamination factor of heavy metals in soil vs. site.

![Site specific contamination factor of each element](image2)

**Fig. 4:** Contamination factor for the heavy metals in soil samples collected from different sites

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Erdicant threat to ecological dated multi-elemental risk index (RI) along with the site-specific cumulative ecological risk. The calculated ecological risk indices are categorized by Hakanson.

The different ranges of the cumulative multi-elemental risk index (RI) are categorized by Hakanson:

- \( 80 \leq \text{RI} < 160 \) considerable,
- \( 160 \leq \text{RI} < 320 \) high,
- \( \text{RI} \geq 320 \) very high ecological risk.

The potential risk index (RI) of the multi-element is calculated as follows:

\[
\text{RI} = \sum_{i=1}^{n} \text{Eri}
\]

where ‘Eri’ is the toxicity coefficient of individual element. The reference range of ‘Tir’ for different metals varies from 1 to 40, with Zn=1 being the least and Hg=40 the maximum one. The potential ecological risk index (RI) of the multi-element can be calculated as:

\[
\text{E}_{\text{ri}} = \text{T}_{\text{ir}} \times C_{\text{ir}}
\]

where ‘Tri’ is the toxicity coefficient of individual element.

Table 3

<table>
<thead>
<tr>
<th>Element/site</th>
<th>A2-1</th>
<th>A3-1</th>
<th>A4-1</th>
<th>A5-1</th>
<th>A6-1</th>
<th>A7-1</th>
<th>A12-3</th>
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<td>8.04</td>
<td>4.25</td>
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<td>3.29</td>
<td>16.29</td>
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<td>17.86</td>
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<td>6.20</td>
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<td>1.15</td>
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<td>0.67</td>
<td>0.94</td>
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<td>0.51</td>
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<td>0.49</td>
<td>0.56</td>
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<td>0.66</td>
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<td>4.87</td>
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<td>0.18</td>
<td>0.24</td>
<td>0.33</td>
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Table 4

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<th>Element/site</th>
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<th>A4-1</th>
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<th>A6-1</th>
<th>A7-1</th>
<th>A12-3</th>
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<td>0.88</td>
<td>1.18</td>
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Potential Risk Index: The toxicity of the trace elements is assessed by the ecological risk factor \( (E_{ri}) \). \( E_{ri} \) for individual metal is calculated as follows:

\[
E_{\text{ri}} = \text{T}_{\text{ir}} \times C_{\text{ir}}
\]

where ‘Tri’ is the toxicity coefficient of individual element. The reference range of ‘Tr’ for different metals varies from 1 to 40, with Zn=1 being the least and Hg=40 the maximum one. The potential ecological risk index (RI) of the multi-element can be calculated as:

\[
\text{RI} = \sum_{i=1}^{n} \text{Eri}
\]

The results show that the risk index ranged from moderate potential risk to considerable potential risk for almost all the sites. As categorized by Hakanson, the target sites A2-1, A4-1, A6-1 and A13-1 show moderate potential risk where as A3-1, A5-1, A7-1 and A12-3 show considerable potential risk. Since these sites are highly contaminated with Ti, V, Cr, Co and Ba as compared to others, therefore they are indicating a considerable ecological risk.

Conclusion

The soils in targeted study area are indeed polluted with heavy metals (Ti, V, Cr, Co and Ba) as all the contamination indices considered, indicate low to a considerable degree of contamination. This contamination has anthropogenic origins. These elevated amounts of toxic metals can infiltrate the food cycle and present a significant threat to ecological system. It is therefore concluded that industries have an adverse (pollution) impact on the surrounding environment, which calls for its remediation at all costs.
It is also suggested that heavy metal pollution by industries should be strictly proctored and remediation measures like phytoremediation which needs to be undertaken on priority. The results attained and knowledge acquired in the present study are useful for suggesting appropriate remedial measures to safeguard the quality of soil.

Acknowledgement
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