Impact of Heavy Materials Accumulation in Soil Using Inductively Coupled Plasma Mass Spectrometry

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Abstract:
The formation of heavy metals in the soil greatly damaged the crops and caused many health issues near the region of Shikarapara. The issue of heavy metal accumulation in soil has become a significant concern with wide-reaching implications for the environment, agriculture, and public health. Heavy metals, including lead, cadmium, mercury, and arsenic, find their way into soil primarily through human activities such as industrial processes, mining, agricultural practices, and waste disposal. Once introduced, these metals can severely disrupt soil quality, potentially leading to decreased fertility, hindered plant growth, and alterations in microbial ecosystems. Furthermore, heavy metals can leach into groundwater, posing risks to water quality and aquatic life. The soil from shikarapara is taken along with few other places near to the shikarapara to find heavy metals accumulation using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Result has shown that heavy metals like lead, zinc, manganese, mercury, iron, cadmium, copper and arsenic are present in the soil samples. Particular measures must be considered to regulate this pollution.

1. Introduction
Heavy metals build up in the soil; it can harm the quality and quantity of crops, which is bad for both the environment and human health. These harmful metals can find their way into the food and drinks we consume, posing risks to our health [1]. Heavy metals are harmful pollutants and their contamination of agricultural soils and crops poses a serious environmental issue. Certain heavy metals like Cadmium (Cd) and Lead (Pb) have been found to cause cancer. On the other hand, metals like Copper (Cu) and Zinc (Zn) are actually essential for our health, but having too much of them can be harmful [2].

2. Materials and Methods

2.1. Study Area:
The study took place in Shikaripara, Jharkhand, known for its mineral wealth. Shikaripara is a rural community block in the Dumka district, characterized by hilly terrain and substantial rainfall. Agriculture is the primary income source, with rice, maize, and wheat as major crops. Nearby regions are engaged in copper mining, particularly in the copper belt. The Santals played a role in land reclamation. About 41% of Shikaripara’s land is cultivable, with limited irrigation (6.42%). The region faces forest degradation due to past exploitation and receives a significant monsoon season from June to September [3].

2.2. Sampling Materials:
Samples were collected from the regions impacted by mining activities within the Shikaripara stone mines in Dumka District. The sample were gathered from Shikarapara, Mohulpahari, Paltabari, Chitragaria Khadan 1, Chitragaria Village, Chitragaria Khadan 2, Patpahari village and Nagalbhanga village. From a homogenous
part of land, it is ploughed to a depth of 15cm the samples are collected. From that only the required amount of soil is packed carefully [4].

The dust from the soil is removed and then it is dried at room temperature and powdered to fine particles. Next it is packed and sent to laboratory for further process.

3. Testing

For the testing process a well suited equipment of ICP-MS is used to test the soil and find the materials with their weights.

- A particular amount of 0.25 ± 0.001 g soil is taken and placed in a microwave-safe polymeric container. To it 0.5 ml of water is added to enhance solubility and prevent temperature fluctuations. Then 4.5ml mixture of HCl and HF is added to soil and heated over microwave [5].
- Whatman filter paper No. 1 with 11 nm pores is used to filter after the cooling process. Later the filtrations is increased to 50ml to refine the samples to perfect condition [6].
- The sample solution is passed into an argon plasma torch, which generates an extremely hot and ionized argon gas. This high-temperature plasma vaporizes and ionizes the elements present in the sample.
- After ionized, the ions are then extracted and sent into the mass spectrometer. In ICP-MS, a mass spectrometer is used to separate ions based on their mass-to-charge ratio (m/z).
- As the ions pass through the mass spectrometer, they are detected and counted based on their mass and charge. The instrument can distinguish between different forms of the same element with varying masses and measure their abundance.
- The ICP-MS machine gives us numbers about how much of different elements are in our sample by counting ions. To make sure it's right, it is compare to standards of elements. We use special spaces and calibration standards from outside to check if the machine is set up correctly.
- The procedure also mentions that double analyses are performed on the samples, and the condition of the ICP-MS is checked regularly. This is done to ensure the accuracy and reliability of the results [7].

3.1. Analysis:

Heavy metals are accumulated in the soil and its impact depend on the area involved and type of materials found in the soil. In the study of shikarapara region the founded elements were detailed below.

- **Lead (Pb):** The actual concentration of lead is 4.579, which is below the specified limit of 5. This suggests that the lead concentration in the sample is within acceptable limits.
- **Arsenic (As):** The actual concentration of arsenic is 0.620, which is below the specified limit of 4.5. Similar to lead, the arsenic concentration in the sample is within acceptable limits.
- **Mercury (Hg):** The actual concentration of mercury is 0.12, which is below the specified limit of 0.05. This also falls within acceptable limits.
- **Cadmium (Cd):** The actual concentration of cadmium is 0.17, which is below the specified limit of 0.1. Like the other elements, cadmium is within acceptable limits.
- **Iron (Fe):** The actual concentration of iron is 11.067.46, which is significantly higher than the specified limit of 1.200. This suggests that the iron concentration in the sample is much higher than the acceptable limit, which could indicate a potential issue.
- **Manganese (Mn):** The actual concentration of manganese is 436.18, which is also significantly higher than the specified limit of 500. This indicates that the manganese concentration in the sample exceeds the acceptable limit.
- **Zinc (Zn):** The actual concentration of zinc is 10.945, which is below the specified limit of 60. Zinc is within acceptable limits.
- **Copper (Cu):** The actual concentration of copper is 2.430, which is below the specified limit of 50. Copper is within acceptable limits.
The metals present in the agriculture area are checked to know how deep the plants are affected by the accumulation of metals near the mining regions. This is shown in below table 1.

Table 1: Heavy Metals In The Soil Sample

<table>
<thead>
<tr>
<th>Metals</th>
<th>Lead (Pb)</th>
<th>Arsenic (As)</th>
<th>Mercury (Hg)</th>
<th>Cadmium (Cd)</th>
<th>Iron (Fe)</th>
<th>Manganese (Mn)</th>
<th>Zinc (Zn)</th>
<th>Copper (Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>level</td>
<td>0.145</td>
<td>0.125</td>
<td>0.15</td>
<td>0.13</td>
<td>0.7</td>
<td>0.62</td>
<td>0.15</td>
<td>1.12</td>
</tr>
</tbody>
</table>

High levels of certain metals in plants can signal that the environment might be polluted or that the plants could be harmful to eat. So, it’s really important for agricultural and environmental experts to keep an eye on these metal levels to make sure that plant-based foods are safe to eat and that the environment stays clean and healthy.

3.2. Geo-accumulation index:

In 1969, Muller developed a method called the geo-accumulation index to assess the presence of heavy metals and similar elements in sediment. This index helps us understand the pollution levels in the soil by comparing current levels with those from before industrialization [8]. This is formulated as given in equation 1.

\[
X_{\text{geo}} = \log_2 \left( \frac{T_m}{1.5G_f} \right)
\]  

(1)

Here, \( T_m \) represents the amount of the heavy metal found in the soil, and \( G_f \) is the reference value for the background level of that metal.

![Figure 1: Comparison on geo-accumulation index](image)

Geo-accumulation index for the heavy metals are shown in figure 1. Arsenic has average shale of 0.6 with control soil of 0.5. Cd has -0.4 of average shale with 1.6 of control soil. Copper has 1.8 average shale with 1.3 of control soil. Fe has -1 of average shale with 0.2 of control in soil. Mn has -1.3 of average shale with 1.9 of control soil. Lead has 0.7 of average shale with 0.4 of soil control. Zn has 0.5 of average shale with 1.7 of soil control. Hg has -1.2 of average shale with 1.5 of control soil.

3.3. Pollution Load Index:

The Pollution Load Index (PLI) is a measure of soil sediment contamination caused by specific heavy metals. It was developed by Tomlison to assess the cumulative effects of metals in soils. PLI is determined by calculating the geometric mean of the concentration factor \( C_f \) values of the metals being studied. Equation 2 is used to calculate the PLI.
Pollution index is shown in figure 2 for the regions of Shikarapara, Mohulpahari, Paltbari, Chitragaria Khadan 1, Chitragaria village, Chitragaria Khadan 2, Patpahari and Nagalbhanga.

It is seen that pollution index is 0.6 for the region of Shikarapara.

### 3.4. Nemerow comprehensive index:

Nemerow’s Pollution Index (NPI) by Nemerow is a simple tool to assess pollution and identify primary water quality pollutants. The Nemerow Comprehensive Index evaluates the environmental condition of agriculture lands near copper mining sites, indicating their environmental health. This is calculated using equation 4, 5 and equation 6.

\[
P_{index} = \left( C_{f1} \times C_{f2} \times C_{f3} \times \ldots \times C_{fn} \right)^{1/n}
\]

Where,

\[
C_f = \frac{c(metal)}{c(background)}
\]

![Pollution load index](image)

**Figure 2:** Pollution Index on comparison

Where, 

\[
M_f^i = \frac{M_f^i}{M_n^i}
\]

\[
N_{index} = \sqrt{\frac{(rM_d)^2 + (M_{f, max}^i)^2}{2}}
\]

Where,

\[
rM_d = \left( \sum_{i=1}^{n} M_f^i \right) / n
\]

\[M_f^i\] represents the amount of a metal measured in the soil (mg/kg).
$M_i^\text{n}$ represents the natural background level of that metal (mg/kg), usually found in shale.

$M_i^\text{f}$ represents the pollution index for that metal.

$M_i^\text{f}_{\text{max}}$ represents the highest possible pollution index for any metal.

$rM_i$ represents the Hakanson's modified degree of contamination index.

$n$ represents the total number of metals measured in the soil, which is 5 in this study.

**Figure 3**: Comparison of Nemerow Index

Nemerow's Pollution in shikarapara is noted as 8 and it is compared with other regions and shown in figure 3.

### 3.5. Enrichment factor:

The Enrichment Factor (EF) is a measure used to determine how much of a specific element or compound is present in a sample compared to its concentration in a reference or background sample. This is given by below equation 3.

$$k = \frac{\left( \frac{N_n}{N_f} \right)}{\left( \frac{R_n}{R_f} \right)}$$

(3)

Here $N_n$ is the Concentration of element by the $N_f$, which is the concentration of the reference element ratio to the $R_n$, background element by the $R_f$, that represent background reference element which gives the enrichment factor $k$. The comparison of enrichment factor is shown in figure 4.
4. Results and Discussion

4.1. Experimental Values of Heavy Metals:

Heavy metals obtained during analysis were Arsenic, mercury, Zinc, Copper, Cadmium, Manganese, Iron and Lead. Its comparison values with other region are shown in figure 5.

![Figure 4: Comparison of enrichment factor](image)

![Sample Location](image)

**Concentration of Iron (Fe)**

**Concentration of Cadmium (Cd)**

**Concentration of Arsenic (As)**

**Concentration of Mercury (Mg)**
5. Conclusion

Heavy metals present in the soil causes various health issues and indirectly effect plants and animals a lot making the environment polluted. It is noted that a small portion of soil is polluted and it is less compared to other places. Even though it is small, in future it may increase rapidly if particular measures are not considered properly. So, in order to save the environment and lives of various specious government should take few policies regarding this heavy metal pollution.

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Conflict of interest:

The authors declare no conflict of interest.
Reference


