Heavy Metal Ions Levels and Related Physicochemical Parameters in Soils in The Vicinity of a Paper Industry Location in Nahan Area of Himachal Pradesh

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Abstract

Background concentrations of heavy metal ions concentration in soils are important due to their pollution potential and toxic effect of these elements on human health and the environment. These metals in soils in the vicinity of paper manufacturing industry were studied. Concentrations of these heavy metal ions (e.g., Pb, Zn, Cd, Cr) were analyzed using Atomic Absorption Spectrophotometer (A.A.S). The findings revealed that the average concentrations of these metals in soil samples were three to ten times higher than the permissible limits. Levels of these trace metals in the industrial environment were generally high, indicating that the activities of paper industry and associated processes contributed to the observed higher levels of trace metals in the industry environment. The aim of this study was to determine the levels of these heavy metals in the soil and to ascertain the pollution status.

Keywords: Heavy metals; Soils; Environment; Paper manufacturing industry; Pollution

Introduction

Industrialization is on the increase and so is the environmental pollution due to emissions and waste generated from these industries. The industrial pollution due to its nature has potential to cause irreversible reactions in the environment and hence is posing a major threat to sustainable development. Since the carrying capacity of the environment is not unlimited and some areas or ecosystems are more susceptible to adverse environmental impacts than others, the unplanned and haphazard location of industries might substantially increase the risk to the environment. Shiwalik belt in Himachal Pradesh has come up in a big way in industrial development. Different types of industries have been established in the recent past. Shiwalik region is very fragile ecologically and environmentally. This zone is transition with Middle Himalayas in the north and fertile plains of Haryana and Punjab. Many industrialists from Punjab and Haryana are attracted to establish industries in this zone due to dust free environment. Water quality is has been good and many streams pass through this zone. Forest cover is adequate. Although the availability of minerals is low, therefore most of the raw material for the industries come from outside in heavy truck. Industrial pollution range from chemical, air and water. Industries are located at Baddi, Barotiwala, Parwanoo, Kala Amb, Paonta Sahib, Mehatpur, Tahiwal, Amb, Sansarpur Terrace and Golthai. Soils differ across the landscape, as each site is characterized by unique trace element concentrations based on parent material of soil and other soil-forming factors that may have supplemented or removed these elements from the soil. High background concentrations of heavy metal ions, whether natural or anthropogenic, could result in mobility and release into surface and subsurface waters and subsequently their incorporation into the food chain. Soil factors such as pH and conductivity are influenced and also influence the quantity of these heavy metals available for mobilization and release or sorption in a soil. Several studies document gradual increases in the trace element contents of agricultural and forested soils due to waste discharge and effluents from industries [1-3]. While essential in small quantities for plant growth, micronutrients like zinc (Zn) can be poisonous at high concentrations in the soil. Some elements not known to be essential to plant growth, such as arsenic (As), cadmium (Cd), chromium (Cr), and lead (Pb) are also toxic at high concentrations or under certain environmental conditions in the soil. The extent of soil pollution by heavy metals and base metal ions some of which are soil micronutrients is very alarming in the vicinity of a paper mill in Nahan Tehsil of Himachal Pradesh. It has been observed that with industrialization of this fragile ecosystem the quality of the environment has lowered down [4,5].

Concentration of these heavy metals in soils is associated with geometrical cycles and biological processes and could be greatly influenced by such industrial activities. In the food chain primary producers i.e., plants are capable of absorbing these metals from the soil [6,7]. These metals each into the soil when they undergo chemical reactions and could come in direct contact with roots of plants [8]. When these plants in the form of vegetables, are consumed by man, trace metals become bioaccumulated and eventually result in several ailments which may subsequently cause death [9]. In some cases plants accumulate some of these metals which are not injurious to them, but may be poisonous to animals grazing on the plants [10]. The paper mill was of concern because of its location close to where rural populace settlement. The distance of the paper industry to the water source of the community is a cause of worry [11].

Some of the wastes emanating from paper production unit are spread over some parts of the environment particularly on water-logged soil. Heavy metals present in the waste may therefore accumulate in the soil environment. Hence, the soils in this environment are assumed to be polluted with heavy metals. This investigation is therefore to assess

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the trace metal levels in soil within the Paper industry environment. Again, heavy metals discharged into our environment including their distribution, reaction in the ecosystem and subsequent uptake and distribution in soils are of great concern for human health [12]. Specifically, the aims of the study are to determine the levels of some heavy metals in soil within the Paper industry environment, to ascertain the pollution standing and the effect of the trace metals in the environment [13].

Materials and Methods

Study area

Paper Mill was one of the major Paper producing industries in the Nahan Tehsil of Sirmaur district of Himachal Pradesh. (The name of the mill has not been disclosed due to publishing ethics). Our study was divided in three zones. This mill was situated in the first zone (Figure 1).

Soil sample collection

Soil sampling was carried out by collecting portions of soil using a soil auger of length 15 cm at each location. The samples were put into polyethylene bags, labeled and taken to the laboratory for pre-treatment and analysis. Sampling was carried out within this environment from three different locations for summers and winters (June and January). Soils samples were collected in triplicate from each location. Control samples were also collected about 10 km away from the industry.

Preparation of soil samples, treatment and chemical analysis

Samples were air-dried at normal laboratory temperature. Soil samples were ground using pestle mortar and sieved to pass through 2 mm sieve and stored safely for chemical analysis.

Heavy metal ions concentrations

The samples were then digested using the microwave digestion procedure [14] for total Pb concentration using Scientific microwave Anton Paar Multiwave 3000. The clean soil sample was collected from region 10 km away from industry. Concentrations of heavy metal ions, in the extracts were analyzed with AAS (acetylene air flame) (Perking Elmer A Analyst -100) with addition calibration. Data presented in the investigations is an average of twelve replicates with a standard deviation.

Electrochemical properties

Electric conductivity (EC) and pH were measured in water suspensions and in 0.01 M CaCl$_2$, (Elico CM 180 and Elico LI 127), pH of the soil is one of the main parameter for determining the extent of pollution. So we prepared the standard solution of soil by weighing 20 g in 100 mL of the water as described in methods approved by NPDES. Solution prepared was kept on the magnetic stirrer for about 2 hours prior to each reading. pH meter was used for this parameter. Set of three readings were obtained. Conductance was calculated by preparing standard solutions of the samples by the methods approved by NPDES. Conductometer was used for this purpose. Set of three reading was obtained and samples were kept for constant stirring on the magnetic stirrer for almost 2 hour prior to each reading [15].

Analysis of water samples

• Water samples were treated by the pH meter to get the set of three reading for pH of the samples
• Water samples were treated by the conductometer to get the set of three reading for conductance of the samples
• Then the DO was calculated by using the apparatus Dissolved Oxygen calculator meter

Methodology for primary survey

Looking at the side effect of the industrial pollution on environment and human health a questionnaire was framed which helped in taking inputs from the local villagers about their assessment of the environmental degradation. Primary field survey concerning geographical aspects was carried out to evolve critical interaction areas, specific area needs, ecosystem needs.

Results and Discussion

Areas near Rapur Jattan, Patti Nath villages, having paper industries, indicate higher levels of lead Pb(II), chromium Cr(II) and cadmium Cd(II). For good plant growth pH between 5.5 and 7.0 is suitable. However, in these polluted terrains, pH is well above 8 i.e., the soil is alkaline [16]. The analysis results of samples collected in different time are shown in Tables 1-4 during summer and winter. Tables show the mean values of the concentration of metals.

The concentrations of metals in soils at the site and the control site indicate that there is an evidence of relative increase in the concentrations of heavy metals in soils at the site compared to the control site. The metals considered in this study include the metals which are micronutrients such as zinc, and the non-essential/toxic trace metals which are toxic to plant when present in the soil at concentrations above tolerance level. The latter class of trace metals includes lead and cadmium. Based on the results (Tables 1-4), there was a significant difference between the concentrations of all the metals at the Paper manufacturing industrial site and the control site in all the samples [17].

The natural range for the concentration of zinc in soil is 5 ppm. The mean level of Zn in soil samples of the study area five times higher...
than the permissible level of Zn in drinking water. Zinc although being an essential trace element in low concentration, is toxic in high concentration [18]. Assimilation of Zinc in excess of 12 mg per day may be a source of lung disturbance [19].

The mean concentrations of lead in the soil samples are six to seven times higher than the permissible concentration is between 0.05-0.1 ppm. Presence of lead in this environment may have been due to automobile emission and industrial emission [20]. Chronic exposure to lead can lead to chronic lead poisoning, which will result in memory loss and restlessness. Lead has been found to inhibit enzymatic activity [21]. The pollution of soil by lead is a serious problem that has been given much attention by environmental chemists. This is due to the fact lead is a accumulative pollutant [22] and the unceasing dumping of lead containing waste into the environment should be discouraged.

The natural permissible limit of cadmium in soil is 0.005 ppm. The mean concentration of cadmium in the soil samples of the study area is ten times higher than the permissible limit of cadmium in soil. The soil is therefore considered to be polluted by cadmium. Exposure to high cadmium levels may result in ailments known as osteoporosis [23]. Cadmium is regarded as the most hazardous trace element and its poisoning may cause damage to kidney and heart and prolonged exposure results in loss of calcium from the bone [24]. Toxicological

Table 1: Permissible limits of heavy metals by different agencies (ppm) in drinking water.

<table>
<thead>
<tr>
<th>Agencies</th>
<th>Lead</th>
<th>Cadmium</th>
<th>Chromium</th>
<th>Arsenic</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>WHO</td>
<td>0.05</td>
<td>0.005</td>
<td>-</td>
<td>0.05</td>
<td>5.0</td>
</tr>
<tr>
<td>USEPA</td>
<td>0</td>
<td>0.005</td>
<td>0.1</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>CPCB</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>15</td>
</tr>
</tbody>
</table>

*: No Relaxation

Table 2: Concentration of metal ions in water samples from different zones during winter season.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Pb</th>
<th>As</th>
<th>Mg</th>
<th>Na</th>
<th>Zn</th>
<th>Cd</th>
<th>K</th>
<th>Pb</th>
<th>As</th>
<th>Ca</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2012HP1009S</td>
<td>0.171</td>
<td>0.474</td>
<td>464.444</td>
<td>2.5</td>
<td>2.3995</td>
<td>0.855</td>
<td>8.3075</td>
<td>6.3915</td>
<td>3.063</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2012HP2005S</td>
<td>0</td>
<td>0.33</td>
<td>452.9685</td>
<td>15.638</td>
<td>2.047</td>
<td>0.0885</td>
<td>15.784</td>
<td>36.0595</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2012HP2006S</td>
<td>2.643</td>
<td>2.3485</td>
<td>483.6025</td>
<td>4.587</td>
<td>3.935</td>
<td>0.2435</td>
<td>15.0705</td>
<td>37.716</td>
<td>2.3825</td>
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</tr>
<tr>
<td>S2012HP2013S</td>
<td>0.512</td>
<td>0.903</td>
<td>409.3025</td>
<td>2.89</td>
<td>2.0795</td>
<td>0.2465</td>
<td>15.0705</td>
<td>37.716</td>
<td>2.3825</td>
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<td></td>
</tr>
<tr>
<td>S2012HP2016S</td>
<td>3.154</td>
<td>0.493</td>
<td>491.188</td>
<td>4.516</td>
<td>3.609</td>
<td>0.2266</td>
<td>15.784</td>
<td>36.0595</td>
<td>0.3405</td>
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<tr>
<td>S2012HP2024S</td>
<td>0</td>
<td>0.641</td>
<td>458.2685</td>
<td>4.425</td>
<td>3.745</td>
<td>0.2465</td>
<td>15.0705</td>
<td>37.716</td>
<td>2.3825</td>
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<tr>
<td>S2012HP3005S</td>
<td>0.844</td>
<td>33.0065</td>
<td>473.7685</td>
<td>9.6015</td>
<td>2.047</td>
<td>0.0885</td>
<td>15.784</td>
<td>36.0595</td>
<td>0</td>
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<tr>
<td>S2012HP3011S</td>
<td>8.184</td>
<td>0.5655</td>
<td>484.2585</td>
<td>6.278</td>
<td>2.181</td>
<td>0.2525</td>
<td>32.7841</td>
<td>0.0119</td>
<td>0.0893</td>
<td>2.8054</td>
<td>0.8246</td>
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<td>S2012HP3012S</td>
<td>0</td>
<td>1.0775</td>
<td>479.2265</td>
<td>5.8756</td>
<td>6.1965</td>
<td>0.1255</td>
<td>2.0545</td>
<td>14.1955</td>
<td>17.436</td>
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<tr>
<td>S2012HP3013S</td>
<td>0</td>
<td>0.1405</td>
<td>475.895</td>
<td>5.4505</td>
<td>2.691</td>
<td>0.0465</td>
<td>10.9845</td>
<td>42.3555</td>
<td>217.141</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Concentration of metal ions in soil samples from different sampling points during summer season.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Pb</th>
<th>As</th>
<th>Mg</th>
<th>Na</th>
<th>Zn</th>
<th>Cd</th>
<th>K</th>
<th>Pb</th>
<th>As</th>
<th>Ca</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2013HP2001W</td>
<td>0.938</td>
<td>0.085</td>
<td>479.3075</td>
<td>10.021</td>
<td>17.436</td>
<td>0.226</td>
<td>7.5305</td>
<td>36.8475</td>
<td>37.438</td>
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<td>S2013HP2002W</td>
<td>1.876</td>
<td>1.5095</td>
<td>481.2685</td>
<td>3.965</td>
<td>2.478</td>
<td>0.0045</td>
<td>7.317</td>
<td>4.278</td>
<td>3.063</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2013HP2003W</td>
<td>0</td>
<td>0.1815</td>
<td>490.118</td>
<td>3.7715</td>
<td>0.9815</td>
<td>0.0885</td>
<td>5.3045</td>
<td>75.587</td>
<td>108.5705</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2013HP2004W</td>
<td>1.194</td>
<td>3.111</td>
<td>466.486</td>
<td>3.156</td>
<td>1.6335</td>
<td>0.009</td>
<td>4.3535</td>
<td>73.8785</td>
<td>43.224</td>
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<tr>
<td>S2013HP2005W</td>
<td>0</td>
<td>0.7775</td>
<td>435.6335</td>
<td>4.2645</td>
<td>1.0025</td>
<td>0.022</td>
<td>2.9365</td>
<td>72.9585</td>
<td>2.723</td>
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<tr>
<td>S2013HP2012W</td>
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<td>449.37</td>
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<td>0.0795</td>
<td>6.278</td>
<td>0.9055</td>
<td>110.6125</td>
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</tr>
</tbody>
</table>

Table 4: Concentration of metal ions in soil samples from different areas during winter season.
properties of cadmium come from its chemical similarity to zinc, an essential micronutrient for plants, animals and humans.

The mean concentrations of chromium in the soil samples are six times than the permissible 0.05 ppm [25]. Exposure to chromium has been found to cause dermatitis [26], perforation of nasal septa and kidney damage among other diseases [21].

In Rapur Jattan village of Nahan Tehsil, due to chronic exposures of pollutants, slowly the air and water pollution is manifesting itself in various layers and dimensions. Survey studies have indicated a definite correlation in pollution levels and the type of diseases occurring in this area. New skin ailments have come up in that area. No such skin diseases were existing before 2000 and now nearly 60% of the respondents complained of the burning sensation and decolouration of skin. 30-35% of people are suffering from some or the other lung ailment be it asthma, lung problems, occasional ulceration of nasal passages, cough, or shortness of breath which were earlier non-existent. Other related problems sleeplessness, irritability, loss of appetite or chest pain are due to these polluted effluents. According to majority of respondents, due to lack of adequate health facilities, proper diagnosis and treatment is not available. Post 2000 cardiovascular diseases are also coming in higher numbers. 70% of the people interviewed are anemic. Local residents Mr Ranveer Singh and Mohammad Yami (Gram Pradhan) informed that around 8 to nine people have died of cancer in the recent past related to lungs. Life expectancy of the animals (pet and wild) has decreased considerably as majority of them directly depend on untreated effluents for drinking etc. The annual output of the mango crop of the area has reduced to much less than the average. The seasonal Rabi crop fails now to meet the basic requirement. A lot of animals and birds are at the verge of extinction as reported by respondents as we can see in 34% area a common house sparrow is difficult to be seen by villagers same as in case of vultures, eagles and many more. Plight of the villagers was reported in the print media also (Mail Today, July, 2013)

Decreasing groundwater level is due to excessive utilization in industries and contaminated surface water due to hazardous industrial waste disposal are major causes. Depth of water near industrial area is less whereas it is exceptionally much deeper in the areas considerably away from the industries. People living nearly 3 km in the radius of industries are majorly affected by the industries. Industrialization has affected almost all the parts of the environment, health, water bodies, vegetation and many other species living there.

Following points/indicators explain the effects of Industrialization in detail: The facts and Figures 2-9 in these points are based on the survey done on villagers.

- Condition of general available water is still better but surface water is worst affected.
- Water is affected in two ways, firstly ground water level is
continuously decreasing, may be due to excessive utilization in industries and secondly it is getting polluted due to the industrial waste thrown in it which can be inferred from the views of villagers about the quality of water available there.

- People living near industries has experienced many health disorders in recent years like breathing problem, blood pressure, asthma, lungs problem, chest pain etc. Breathing problem is most commonly seen. Diseases like jaundice and cancer are rarely noticed.

## Conclusion

The concentrations of heavy metal ions were observed to be higher in soils at the Rampur Jatan village. This implies that the activities that take place at the paper manufacturing industry has a major influence on the environment. The levels of these metal ions obtained in this environment may affect human health since the crops grown in this environment are continuously consumed. Thus, there is need for chemical/bioremediation of this environment and the suspension of all agricultural activities in this environment to avoid transmission of these metals to man through the food chain [27-30].

### Figure 4: Specific conductance of water samples collected from different sampling points during summers.

### Figure 5: Variation of agricultural production with distance from industry in the study area.

### Figure 6: Variation of water quality with depth in the study area.

### Figure 7: Variation of pollution in Agricultural field with distance from industry in the study area.

- Industrialization has its adverse effect on agriculture as well. Pollution in agriculture field has increased in recent years and is worst seen in the areas which is near to industries.
- As per the information provided by villagers, despite of the fact that the irrigation facilities have improved with the development of industries, agricultural productivity has not enhanced. It is same as before in Solan and Rupnagar but it has even declined in Una and Puchkula.
- Some new species have invaded after the setup of industries, mainly the birds like vulture, eagle, kite, crow etc. Pigs have also been reported in some areas.
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References


