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Heavy Metals Accumulation in Soil Irrigated with Industrial Effluents of Gadoon Industrial Estate, Pakistan and Its Comparison with Fresh Water Irrigated Soil

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Abstract

Wastewater mixed with industrial effluents is used for irrigation in Gadoon Industrial estate and thus contaminating soil. This soil was tested for heavy metal content by using atomic absorption spectrophotometer (perkin elmer 700) and compared with control soil irrigated with tube well water at seven selected spots. Accumulation of the toxic metal was significantly greater in the soil irrigated with industrial effluent than control soil ($p < 0.05$). Manganese (Mn) was the most significant pollutant, accumulated up to 9.95 ppm in the soil irrigated with industrial waste water. It was found that the samples were containing Zn in the range of 1.596 - 6.288, Cu 0.202 - 1.236, Co 0.074 - 0.115, Ni 0.0002 - 0.544, Cr 0.243 - 0.936, Mn 3.667 - 9.955 and Pb 0.488 - 1.259 ppm. No sample was containing the heavy metal above the critical level mentioned in typical and unsafe heavy metal levels in soil.

Keywords

Industrial Effluents, Soil, Tube Well Water, Heavy Metals, Pollutio

1. Introduction

Industry is the backbone of a country for its development and with the growing population, the need for establishing new industries is increasing. Industries on one side manufacture useful products but on the other side

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time generates waste products, causing various environmental problems. The waste products may be in the form of solid, liquid or gas which lead to the creation of hazards, pollution and losses of energy. The wastes containing different pollutants and heavy metals are discharged into water and soil and ultimately pose a serious threat to human and ecosystem. By-products of different industries like textile, metal, dying chemicals, fertilizers, pesticides, cement, petrochemical, energy and power, leather, sugar processing, construction, steel, engineering and food processing industries are the main contributors to the soil pollution. So the rapid industrialization is accompanied by both direct and indirect adverse effects on environment [1]. Industrial development may result in the generation of industrial effluents. It has been studied that many industries discharge untreated effluents into river and only 10% industries surveyed had primary treatment ranging from oxidation tanks, sedimentation tanks in developing countries [2] [3].

Heavy metal toxicity may results into a number of health problems including a damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in a slowly progressing physical, muscular, and neurological degenerative process, that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer [4] [5].

Heavy metals on the basis of their health importance can be classified into four major groups, as essential, like Cu, Zn, CO, Cr, Mn and Fe, which are micronutrients and are toxic when taken in excess [6] [7], non essential like Ba, Al, Li and Zr, less toxic like Sn and Al, and highly toxic like Hg and Cd. The toxicity limit and recommended or safe intake of some of heavy metals for human health is given in **Table 1**.

In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products [8]-[10].

Because of the rapid industrialization, soil pollution by heavy metals is becoming a serious problem. Being an ultimate sink for industrial wastes, almost all industrial wastes are dumped into soil. Heavy metals in wastes find specific adsorption sites in soil where they are retained relatively stronger either on inorganic or organic colloids. [11]-[13]. Research has proven that long term use of sewage effluent for irrigation contaminates soil and crops to such an extent that it becomes toxic to plants and causes deterioration of soil. This contains considerable amount of potentially harmful substances including soluble salts like Fe^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+} and Pb^{2+}. Additions of these heavy metals are Undesirable [14] [15].

The properties of the soil along with the climate change also changes due to anthropogenic impact. The influence of acid rains on soils and sorption properties of soil has been extensively studied by scientists from various disciplines. In almost all cases, they found that acid rains decrease the ability of binding heavy metals to soil particles. However, for naturally high acidic soils or very weak soils like rusty soils, the effect of acid rains on soils is shown to be much smaller [15].

The present study was conducted with an aim to study the impact of industrial effluents of different industries of Gadoon industrial estate Pakistan, carrying different heavy metals in them and absorbed in soil during irrigation. In this study only seven elements like Cu, Zn, Co, Cr, Pb, Ni and Mn were studied. The results of analysis collected from different locations have been compared and reported.

2. Experimental

Soil samples were collected from seven different sites of the Gadoon industrial estate Gadoon amazai swabi.

Table 1. Toxic limit/recommended/safe intake of heavy metals [12].

Heavy metal	Toxic limit	Recommended intake/Safe intake
Arsenic	3 mg/day for 2 - 3 weeks	15 - 25 micro g/day (adults)
Cadmium	200 micro/kg of fresh weight	15 - 50 micro g/day (adults), 2 - 25 micro g/day children
Lead	>500 micro g/L (Blood)	20 - 280 micro g/day (adults), 10 - 275 micro g/day children
Zinc	150 micro/day	15 micro g/day

The samples identification along with their location is shown in **Table 2**. From each sampling site five soil samples were collected from different location and mixed together. The samples were dried in the sun for four days, grinded and sieved. The samples were then reduced to laboratory samples by using the tabling process. The samples were named as S_1, S_2, S_3, S_4, S_5, S_6 and S_7. The samples were then dried in oven at 110˚C for about five hours to remove moisture completely. The chemicals used were Nitric acid, Per-chloric acid, distilled water.

2.1. Nitric-Perchloric Acid Digestion

Nitric-perchoric acid digestion method was performed for sample preparation [7]. One gram of a sample was placed in 250 ml digestion tube and 10 ml of concentrated HNO_3 was added. The mixture was boiled for 30 - 45 minutes to oxidize all easily oxidizable matter. After cooling, 5 ml of 70% $HClO_4$ was added and the mixture was boiled gently till the appearance of dense white fumes. The contents were cooled and 20 ml of distilled water was added, and re boiled to stop the release of any fumes. The solution was cooled again, filtered off through Whatman No. 42 filter paper and transferred to 25 ml volumetric flask. The volume was made up to the mark with distilled water. Blank solution was prepared with the same procedure except the addition of soil sample.

Standards for different elements were prepared from the stock solutions (1000 ppm) using dilution method. For each element different dilutions were made for calibration curve given in **Table 3**.

2.2. Analysis of Trace Metals

Trace metals such as Cu, Co, Fe, Pb, Cr, Mn, Zn and Ni were analyzed in all the samples using atomic absorption spectrophotometer.

2.3. Statistical Analysis

Data obtained during current study was analyzed statistically for mean, standard deviation, ANOVA and Duncan Multiple Range Test (DMRT) by using SPSS for windows, version 16.0 (SPSS Inc., Chicago, IL, USA). Probability less than 0.05 was accepted as significant.

Table 2. Locations at Gadon Amazai from where different samples were collected.

S. No	Sample ID	Sample Location
1	S_1	2 km from Sardar Chemical Industries
2	S_2	2500 m Sardar Chemical Industries and Cherat Paper Sack
3	S_3	1 km Shafi Chemical Industries and Hamza Steel Industries
4	S_4	500 m Shafi Chemical Industries Plot-2
5	S_5	500 m T.W Metal Recycling Industries and Poyal Jadoon Marble Factory
6	S_6	1 km T.W Metal Recycling Industries Plot 11/16
7	S_7	200 m Shafi Enterprises

Table 3. Standards used for different metals.

S/No	Standard Name	Standard Symbol	Concentration (ppm)		
1	Copper	Cu	2	4	8
2	Zinc	Zn	1	2	4
3	Cobalt	Co	7	14	21
4	Nickel	Ni	7	14	28
5	Manganese	Mn	2.5	5	10
6	Chromium	Cr	2	4	8
7	Lead	Pb	12.5	25	50

3. Results and Discussion

The concentration of copper in soil of the study area ranged from 0.202 to 1.236 ppm (**Figure 1**). The highest amount of this metal was present at location 5, situated on a distance of 500 m from T.W Metal Recycling Industries and Poyal Jadoon Marble Factory (**Table 2**). Accumulation of this metal in soil irrigated with industrial effluent was significantly greater than its amount in soil irrigated with tube well water ($p < 0.05$). The Typical background levels for non contaminated soil is 1 - 50 ppm, if the concentration of copper in the soil exceeds 200 ppm it become unsafe for leafy vegetable while the concentration of copper greater than 500ppm become unsafe for garden and children contact [14]. The results show that the study area contains the copper metal in a permissible range.

The concentration of zinc in the studied area varied from 1.596 to 6.288 ppm and its average concentration was 2867 ppm (**Figure 2**). At all locations, the accumulation of Zn was significantly greater in soil irrigated with wastewater than control coil ($p < 0.05$). Zinc is the second most abundant heavy metal found in the study area. The typical background levels of zinc for non contaminated soil is very broad, *i.e.* 9 - 125 ppm, while its concentration above 200 ppm is unsafe for leafy or root vegetables. If the concentration of zinc in soil exceeds 500 ppm, it is considered unsafe for gardens and children contact [15]. The results of the present study show that the study area contains zinc in permissible range.

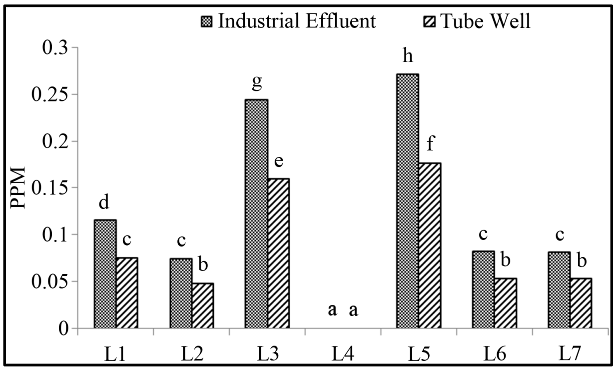

Figure 1. Accumulation of cobalt in soil irrigated with industrial effluent and tube well water at different locations in Gadoon Amazai industrial zone, Pakistan. Bars represents mean value of three replicates and bars labeled with different letters are significantly different from each other (Duncan Multiple Range test; $p < 0.05$).

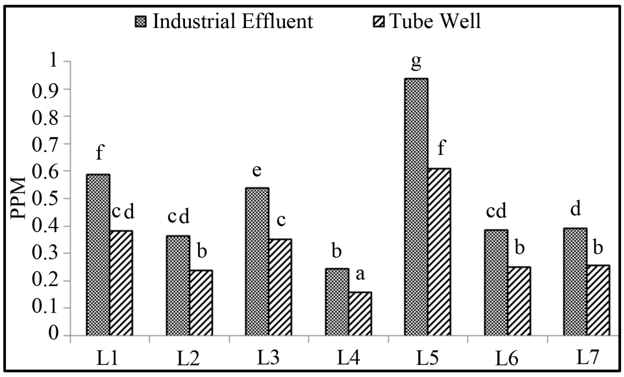

Figure 2. Accumulation of chromium in soil irrigated with industrial effluent and tube well water at different locations in Gadoon Amazai industrial zone, Pakistan. Bars represents mean value of three replicates and bars labeled with different letters are significantly different from each other (Duncan Multiple Range test; $p < 0.05$).

The concentration of cobalt was in the range of 0.001 to 0.271 ppm at different locations in the study area and its average concentration was 0.124 ppm (**Figure 3**). The highest concentration of this metal was also in the soil irrigated with contaminated water at location 5 ($p < 0.05$). Concentration of this metal was well below the toxic level in the study area and minimum among all metals detected over there.

From **Figure 4**, it is obvious, that the concentration of Nickel in the studied area was below the detection limit in soil from L1 and L2. Amount of this metal was greatest (0.38 - 0.544 ppm) in wastewater irrigated soil of location 5 and 6, which was significantly greater than the concentration of Ni in other locations ($p < 0.05$). Although the abundance of Ni was significantly greater in soil supplied with wastewater than soil irrigated with tube well water (**Figure 5**), nevertheless, it was well below the critical levels of this metal [15]. Nickle is the sixth abundant heavy metal found in the study area. The typical background levels of nickel for non contaminated soil is very broad, *i.e.* 0.5 - 50 ppm, while its concentration above 200 ppm is unsafe for leafy or root vegetables. If the concentration of nickel in soil exceeds 500 ppm, it is considered unsafe for gardens and children contact [15] [16].

Chromium was the fifth abundant heavy metal in all the locations of the study area (**Figure 6**). Its concentration varied from 0.243 in sample-4 to 0.936 ppm in sample-5 and its average concentration was found to be 0.493 ppm. Soil of location 5 had the greatest concentration of this metal ($p < 0.05$), irrespective of the water source used for irrigation.

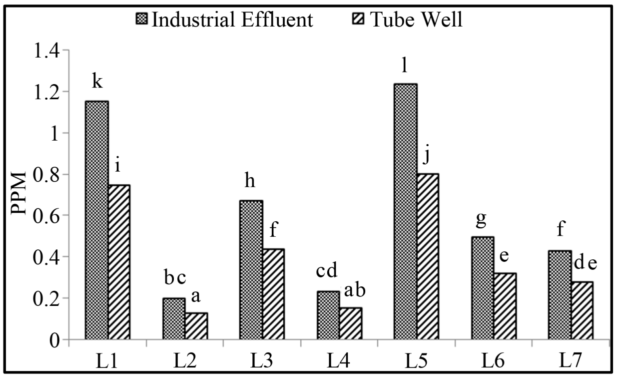

Figure 3. Accumulation of copper in soil irrigated with industrial effluent and tube well water at different locations in Gadoon Amazai industrial zone, Pakistan. Bars represents mean value of three replicates and bars labeled with different letters are significantly different from each other (Duncan Multiple Range test; $p < 0.05$).

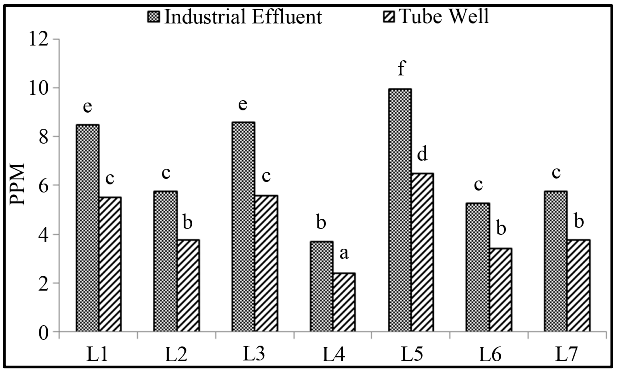

Figure 4. Accumulation of manganese in soil irrigated with industrial effluent and tube well water at different locations in Gadoon Amazai industrial zone, Pakistan. Bars represents mean value of three replicates and bars labeled with different letters are significantly different from each other (Duncan Multiple Range test; $p < 0.05$).

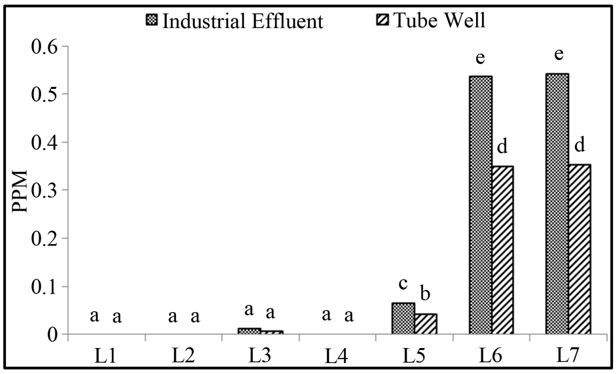

Figure 5. Accumulation of nickel in soil irrigated with industrial effluent and tube well water at different locations in Gadoon Amazai industrial zone, Pakistan. Bars represents mean value of three replicates and bars labeled with different letters are significantly different from each other (Duncan Multiple Range test; $p < 0.05$).

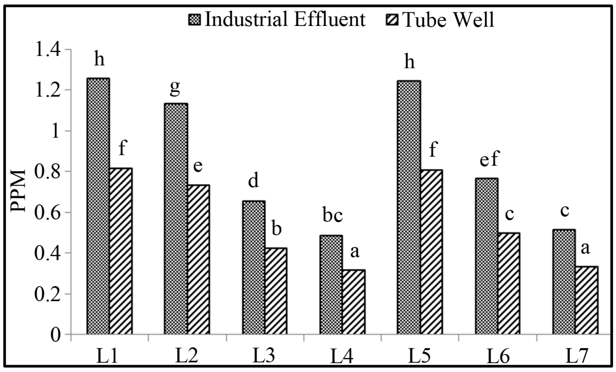

Figure 6. Accumulation of lead in soil irrigated with industrial effluent and tube well water at different locations in Gadoon Amazai industrial zone, Pakistan. Bars represents mean value of three replicates and bars labeled with different letters are significantly different from each other (Duncan Multiple Range test; $p < 0.05$).

The most abundant heavy metal found in the study area was manganese which varied from 3.667 in sample-4 to 9.955 ppm in sample-5 (**Figure 7**).

Lead in the study area varied from 0.488 in sample 4 to 1.259 ppm in sample (**Figure 8**). Lead was the third most abundant heavy metal found in our study area. The Typical background level of lead for non contaminated soil is 10 - 70 ppm. When the concentration of lead goes above 500 ppm, it become unsafe for leafy or root vegetables. If the concentration of zinc in soil exceeds 1000 ppm, it is then considered unsafe for gardens and children contact [17] [18]. The result of the present study shows that the study area contains zinc in permissible range. Overall the concentration of heavy elements in the study area are given in the order Mn > Zn > Pb > Cu > Cr > Ni > Co.

The result showed a high level of zinc and manganese and low level of cobalt and nickel in soil samples. The variations of the metal contents observed in these soil samples depends on the physical and chemical nature of the soil and absorption capacity of each metal in the soil which is altered by the innumerable environmental factors and nature of soil (Reference). Location 5 contained greater amount of heavy metals, which was elevated to even greatest by irrigation with industrial effluent. Although at all locations, the metals were well below their critical values; however, continuous monitoring of the soil may help to predict any increase in future.

Soils normally contain low background levels of heavy metals. Excessive levels of heavy metals can be hazardous to man, animals and plants. Heavy metals regulated by the EPA are arsenic, cadmium, copper, lead, nickel, selenium, and Zinc. The limits of some heavy metals for non contaminated soil and plants and garden are given in **Table 4**. Unsafe levels of heavy metals affect the soil texture, organic matter and pH.

4. Conclusion

The present study showed that heavy metals found in soil irrigated by the effluents of Gadoon industrial area are in the order of Mn > Zn > Pb > Cu > Cr > Ni > Co and their concentration is below the typical background

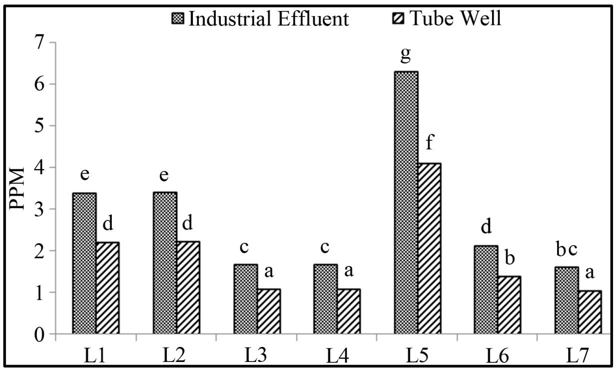

Figure 7. Accumulation of zinc in soil irrigated with industrial effluent and tube well water at different locations in Gadoon Amazai industrial zone, Pakistan. Bars represents mean value of three replicates and bars labeled with different letters are significantly different from each other (Duncan Multiple Range test; $p < 0.05$).

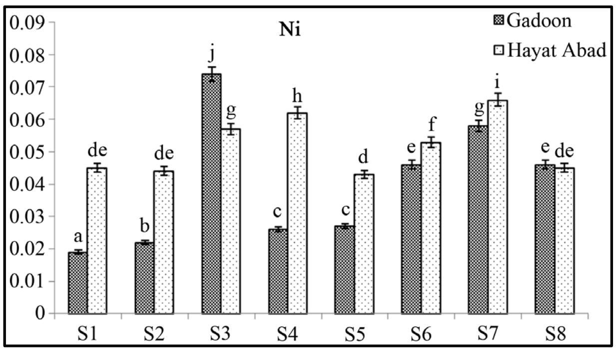

Figure 8. Mean concentration of Ni in the discharge of various industries found in the industrial area of Gadoon Amazai, Sawabi and Hayat Abad, Peshawar. Bars labeled with different alphabets are significantly different from each other (Duncan Multiple Range Test; $p < 0.05$).

Table 4. Typical and unsafe heavy metal soil levels [13].

Heavy metal	Typical background levels for non contaminated soil (ppm)	Unsafe for leafy or root vegetables (ppm)	Unsafe for gardens and children contact (ppm)
Cadmium	0.1 - 1.0	>10	50
Copper	1 - 50	>200	500
Lead	10 - 70	>500	1000
Nickel	0.5 - 50	>200	500
Zinc	9 - 125	>200	500

level for non-contaminated soil as given in **Table 4**. This shows that plants and vegetables grown in this soil should have no adverse effects on animals and human beings. However, it may be emphasized that prolong use of industrial effluent for irrigation may lead to accumulation of heavy metals to toxic level in the soil.

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