Evaluation Of Soil For Important Properties And Chromium Concentration In The Basin Of Chromite Hills In Lower Malakand

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ABSTRACT

This study was conducted to assess the concentration of chromium in soil and its association with soil EC, pH, Lime and organic matter in the basin of chromite hills of Heroshah, lower Malakand, Khyber Pakhtunkhwa Pakistan in July, 2013. Thirty five soil samples were collected from different points and analyzed for total chromium concentration and important soil chemical properties. The results showed that most of the soils in the basin of chromite rich hills were highly contaminated with chromium that ranged from $66 - 397$ mg kg^{-1} soil. These values were higher than the permissible level of $50 - 100$ mg Cr kg^{-1} soil. Among soil parameters, soil pH ranged from $7.89 - 8.24$ (mean 8.05), EC ranged from $0.47 - 1.45$ dS m^{-1} (mean 0.70 dS m^{-1}), organic matter ranged from $0.38 - 1.55$ % (mean 0.88 %), lime content ranged from $7-24.5$ % (mean 14.07 %), AB-DTPA extractable manganese ranged from $0.04 - 2.68$ mg kg^{-1}. The relationship of total soil chromium with soil properties indicated that soil chromium had strong positive correlation with manganese, organic matter and electrical conductivity and strong negative correlation with soil lime and soil pH. These results suggested that the soils of Heroshah are highly contaminated with chromium and their use for agricultural purpose is probably unsafe.

KEYWORDS: Total soil Chromium; Soil organic matter; Soil lime; Soil pH and Soil EC

INTRODUCTION

Chromite is an oxide mineral of chromium and iron. It is considered to be the only ore of chromium. In earth's mantle, it is found in peridotite. In layered ultramafic intrusive rocks, chromite is found [1]. In metamorphic rocks (like serpentine), it is also found. Chromite is commonly associated with magnetite, corundum, serpentine and olivine. In South Africa, the vast Bushveld igneous complex is a large layered mafic to ultramafic igneous body containing 90 percent of chromite which makes the rare rock type, called chromitite [2, 3].

Chromium and its compounds play useful role in common life. At room temperature, it is resistant to ordinary corrosive agents. It is used in protective coating and in electroplating. In chemicals and ferrous and non-ferrous alloys, chromium is widely used. It is mostly used in stainless steels. These steels are highly resistant to corrosion and oxidation. Cast irons contain chromium (0.5% to 30%). This provides toughness and corrosion, hardenability and wear resistant. In nonferrous alloys like iron-nickel, copper, titanium, chromium is widely used. Chromium also use in a variety of chemicals. The largest amount of chromium consumption is in paints and inks. In leather tanning, metal corrosion inhibition, textile dyes, catalysts and wood and water treatment, chromium is widely used.

Chromium content, higher than 5.0 mg kg^{-1} in edible portion of plants/crops on dry weight basis, was considered to be toxic [4]. According to different countries, in agricultural soils, the maximum allowable levels of chromium were suggested as 50-100 mg kg^{-1} soil [5]. Environmental and occupational exposure to Cr-VI is still considered a "major human health issue" today [6].

Hexavalent chromium was considered to be cancerous for human health. It is an extremely toxic, carcinogenic in large doses and highly mobile that enters the cells. It has toxic and detrimental effects on the growth and development of plants [7].

The present study was conducted to study the possible accumulation of chromium in soils and its correlation with important soil properties (pH, EC, lime, organic matter) and soil manganese (Mn) contents in the basin of chromium rich hills of Heroshah, lower Malakand, Khyber Pakhtunkhwa, Pakistan

MATERIALS AND METHODS

Study area:

The study area, for the assessment of soils for chromium concentration, was in the basin of chromite rich hills of Heroshah, Malakand, Khyber Pakhtunkhwa, Pakistan. The hills in this area are highly rich in chromite where hundreds of tons of chromite are mined every year. In the basin of these hills, crops such as berseem, beans, maize, barley and vegetables like okra, tomatoes, onions etc., are cultivated. Due to rainfall and flow of wind, chromium in dissolved or in dust form may reach to cultivated fields in the area.

Soil sampling and processing:

Thirty five soil samples 0-30 cm depth were collected from 35 fields which were under various crops including vegetables and pulses. For each sample, a composite sample was collected randomly from about six points in each field. These were stored in plastic bags and transported to the laboratory. The samples were dried in air, ground and passed through a 2 mm sieve for laboratory analysis. Data were taken for the following parameters:

Soil pH and Electrical Conductivity (EC):

Soil pH and EC were determined in the saturated soil extract by the method as described by [8]. For the determination of soil pH and EC, 50 g soil sample was transferred to a plastic beaker followed by 80 ml distilled water. The soil: water mixture in the beaker was kept overnight. The next day, the mixture was stirred with the help of spatula until a shine paste was made. The paste was transferred to the funnel attached to a vacuum pump and the extract was collected in a tube after applying the pressure. This saturated soil extract was read for pH with the help of pH meter, German type B-124 using calomel and glass electrodes and for EC with the help of EC meter type Me. 4 Electronic Switch Gear Limited.

Soil organic matter:

Soil organic matter was determined by Walkely and Black procedure as described in [9]. For the determination of organic matter, 1.0 g soil sample was taken in a conical flask and treated with 1 N $K_2Cr_2O_7$ and 20 ml H_2SO_{4conc} for about 15-30 minutes. After cooling, 200 ml distilled water was added and then filtered. Ortho-phenolpthalein indicator (2-3 drops) was added to the filtrate and then titrated against 0.5 N $FeSO_4$ until a sharp green or mehroon colour appeared. The organic matter was determined by the following formula:

Organic matter % = [(meq. $K_2Cr_2O_7$ – meq. $FeSO_4$) * 0.69] ÷ weight of soil sample (g)

Soil lime:

Lime content in soil was determined by the acid neutralization method as described by the [10]. In this method, five gram soil sample was taken in a conical flask and treated with 50 ml 0.5 N HCl. The suspension was boiled on hot plate for 5 minutes. After cooling, it was filtered through Whatman Filter Paper No. 40. The filtrate was titrated against 0.25 N NaOH in the presence of few drops of phenolphthalein as indicator, until the appearance of pink colour. Lime was determined by the following formula:

Lime % = [(meq. HCl added – meq. NaOH used) * 0.05 * 100] ÷ weight of soil sample (g)

AB-DTPA Extractable Manganese and Chromium:

The concentration of manganese and chromium in soil was determined by the AB-DTPA method of [11]. In this procedure, 10 g soil sample was shaken with 20 ml of AB-DTPA solution in an open Erlenmeyer flask for fifteen minutes. The solution was filtered and the extract was read for soil manganese and chromium on Atomic Absorption Spectrophotometer (Perkin Elmer Analyst-200, USA).

Total Chromium in soil:

The Aqua-Regia digestion method [12] was used for extracting total chromium in soil. In this method, one gram soil sample was taken in Teflone beaker and treated with 10 ml hydrofluoric acid (HF). The beaker was placed on hot plate at 200 C° to dry. After drying, 20 ml Aqua-Regia (combination of HNO_{3conc} and HCl_{conc} in 1:3) was added and placed again on a hot plate until the sample was dried. Then 20 ml 2 N HCl was added and heated for 20 min. The sample was cooled and filtered into 50 ml flask. Distilled water was added up to the mark and chromium concentration was determined by Atomic Absorption Spectrophotometer.

Correlations were determined between chromium concentrations in soils and soil important properties (like EC, pH, O.M) through MS EXCEL.

RESULTS AND DISCUSSION

Electrical Conductivity (EC):

The soil samples electrical conductivity values are given in Table 1. The electrical conductivity of the samples ranged from 0.47 to 1.45 dS m^{-1} with an average value of 0.69 dS m^{-1}. The highest value of 1.45 dS m^{-1} was observed in field number 10 followed by 1.23 and 1.10 dS m^{-1} in the fields' number 3 and 33, respectively. Similarly, the lowest value of 0.47 dS.m^{-1} was observed in field number 25 followed by 0.48 and 0.50 dS m^{-1} in the field's number 8 and 6, respectively. Similar results for electrical conductivity were observed by [13] at different orchards grown in Phando area of District Peshawar that varied from 0.1 to 0.98 dS m^{-1}. All the samples were non-saline and the agricultural crops in this area were safe from the hazardous effects of salinity.

Soil pH:

The results obtained on soil pH are presented in Table 1. The soil pH ranged from 7.89 to 8.24 with an average value of 8.09. The maximum pH value of 8.24 was observed in the field number 16 followed by 8.18 in field number 20 and 21. Similarly the minimum pH value of 7.89 was observed in field number 3 followed by 7.95 in the field's number 10. The samples analyzed for pH showed that most of the fields were alkaline in reaction. [14] Studied the physico-chemical properties of some soil series of Dir district and found that soil pH ranged from 6.64 to 8.1. In more alkaline conditions, elements availability decreases [15] and symptoms of nutrient deficiency may result, including thin plant stems, yellowing (chlorosis) or mottling of leaves and slow or stunted growth 16]. In the study area, the pH range 7.89-8.24, indicates alkaline soil, which is obvious in the presence of carbonate rocks in the area.

Organic matter:

The results obtained on soil organic matter contents are presented in Table 1. The soil organic matter content ranged from 0.38 to 1.55 % with an average value of 0.88 %. The highest values of 1.55 % and 1.41 % of organic matter were found in the fields' number 10 and 24 respectively. Similarly the lowest value of 0.38 % was observed in the field number 25 and 6. According to [17] half of the analyzed samples were low in organic matter while half of them were medium in organic matter. The low contents of organic matter may be due to the calcareousness nature of the soil.

Table 1: EC (dS m^{-1}), pH and organic matter (%) in soils of Heroshah, Malakand.

Field No.	EC (dS m^{-1})	pH	O.M%
1	0.54	8.13	0.59
2	0.51	8.09	1.08
3	1.23	7.89	1.17
4	0.88	8.03	1.38
5	0.51	8.16	0.93
6	0.5	8.13	0.38
7	0.51	8.16	0.59
8	0.48	8.13	0.52
9	0.86	7.96	1.3
10	1.45	7.95	1.55
11	0.71	8.16	0.72
12	0.71	8.13	0.52
13	0.53	8.14	0.76
14	0.6	8.04	1.07
15	1.04	8.04	1.04
16	0.74	8.24	0.69

17	0.51	8.1	0.59
18	0.97	8.14	1
19	0.51	8.09	0.41
20	0.53	8.18	0.62
21	0.51	8.18	0.59
22	0.64	8.08	1.04
23	0.6	8.14	0.93
24	0.53	8.1	1.41
25	0.47	8.04	0.38
26	0.54	8.16	0.86
27	0.62	8.14	0.97
28	0.78	8.05	1.17
29	0.68	8.09	1.1
30	0.6	8.08	0.86
31	0.83	8.15	0.59
32	0.55	8.15	0.79
33	1.1	7.97	1.24
34	0.58	8.08	0.93
35	1.04	8	1.1

Soil Property	Range	SD	Mean	
Organic matter %	0.38 - 1.55	0.31	0.88%	
pH	7.89 – 8.24	0.07	8.05	
EC (dS m^{-1})	0.47 – 1.45	0.24	0.70	

Total soil chromium:

The results obtained on Aqua-Regia extractable total soil chromium are presented in Table 2. Total chromium concentration ranged from 66 to 396 mg kg^{-1} with an average value of 203 mg kg$^-$.The highest value of 396 mg kg^{-1} was found in the field number 3 and minimum value of 66 mg kg^{-1} was observed in field number 8. The fields with high amount of chromium were near to the hills. As evident in Table 3, the chromium level in most of the soil samples were more than the permissible limits of chromium in soil. This high amount of chromium in the soils might be due to the deposition of chromium coming from the chromite rich hills above the basin during rain water and mining processes. Maximum allowable levels of chromium in agricultural soils were suggested as 50- 100 mg kg^{-1} according to different countries. The findings are consistent with those [18, 19, 20] who noted a decrease in Cr in soils with distance from the ferrochrome smelter. [21] also find out that the concentration of water soluble Cr in soil is always higher near to the source.

Table 3: Chromium concentration (mg kg^{-1}) in soils of Heroshah as influenced by distance from chromite hills.

Distance (m) from chromite hills	Ranges (mg kg^{-1})	Standard deviation	Mean
0 – 300	311 - 396	32	342
300 – 1000	122 - 265	49	193
1000 – 2000	66 - 107	15	77

Changes in chromium concentration in soil with distance from chromite hills:

The data collected for chromium concentration in soil with distance from chromite hills are presented in Table 4. It was observed that chromium concentration was greater near the hills (source), and decreased with increasing distance from the source Fig.1. It means that chromium was deposited more in the near fields from the nearby chromite hills due to weathering. The chromium also moved down to other fields at distance from the hills but its concentration diluted as one move away from the hills. The findings are consistent with those of [18, 20, 21] who noted a decrease in Cr in soils with distance from the ferrochrome smelter.
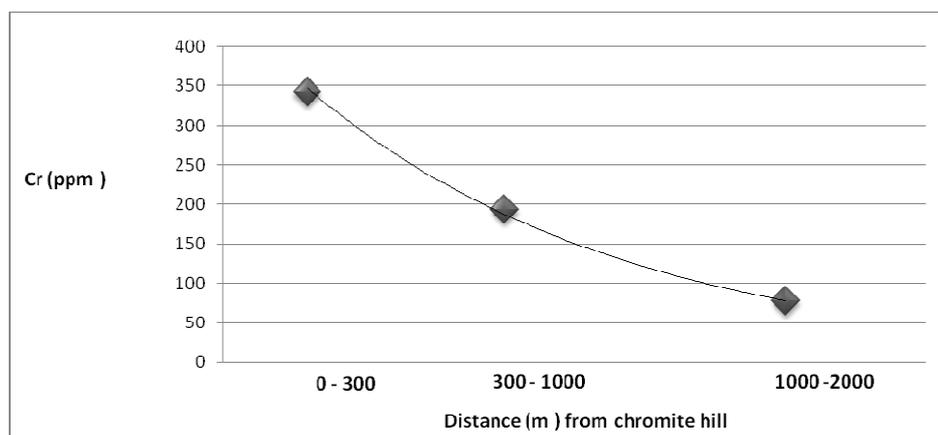
Fig. 1: Relationship between chromium concentration (ppm) in soils and distance from chromite hills.
Correlation of Chromium with the soil parameters:

Correlations were determined between total soil Cr and important soil parameters using MS Excel Software. Chromium was negatively correlated with soil pH $r = - 0.77$ Fig.2. Chromium was positively correlated with soil EC (Fig. 3), implying that chromium will be high if the soil contains more soluble salts. Chromium also showed positive correlation with organic matter Fig.4. Organic matter possesses high sorption capacity for metals [22, 23].
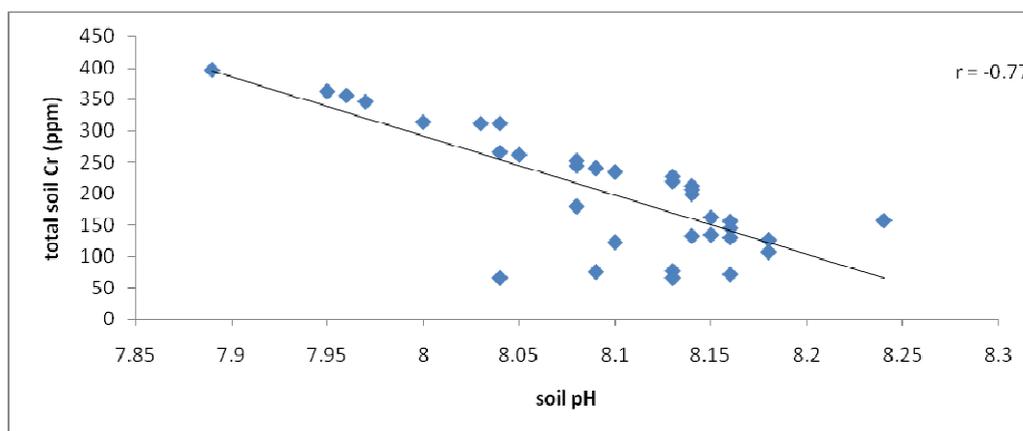
Fig. 2: Relationship between total soil chromium and soil pH.
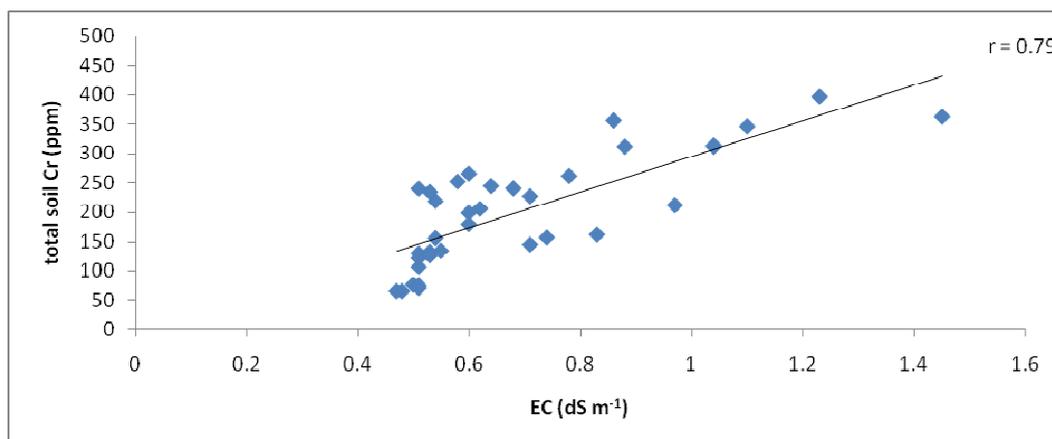
Fig. 3: Relationship between total soil chromium and soil electrical conductivity.
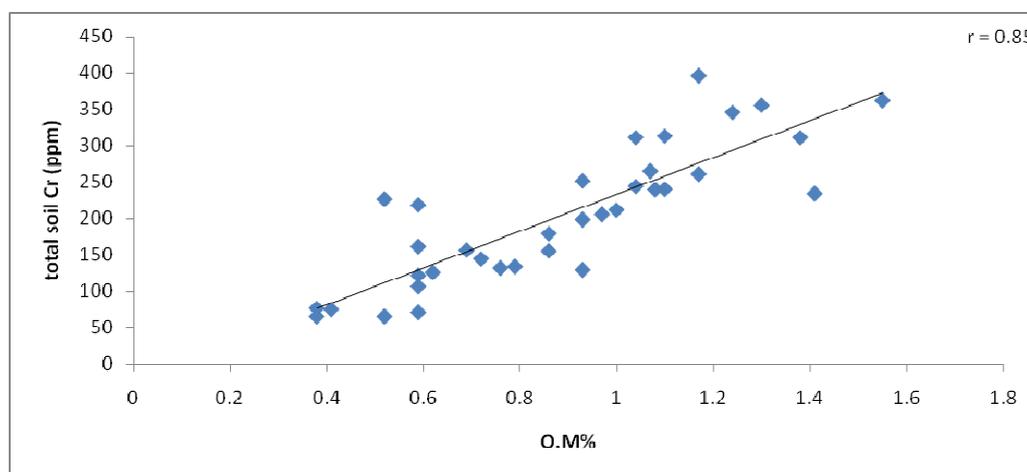
Fig. 4: Relationship between total soil chromium and soil organic matter content.

Conclusion And Recommendations:

On the basis of results, it is concluded that pH values showed that most of the fields were alkaline in reaction and all the samples were non-saline and the agricultural crops in this area were safe from the hazardous effects of salinity while half of the soils were low and half were medium in organic matter contents. Moreover, soil samples were highly contaminated with chromium. The correlation studies showed that chromium is positively correlated with soil EC, soil organic matter, and negatively correlated with soil pH. It is recommended that people living in the studied area should be careful while using the agricultural products of the land. Government and research institutions should give attention to minimize the chromium contamination of the soil.

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