# DISTRIBUTION AND SOURCE IDENTIFICATION OF HEAVY METALS IN AGRICULTURAL SOIL OF DISTRICT AMRITSAR, INDIA: A MULTIVARIATE STATISTICAL ANALYSIS

**[1]SANDIP SINGH BHATTI, [2]SARTAJ AHMAD BHAT, [3]VANEET KUMAR, [4]ADARSH PAL VIG, [5]AVINASH KAUR NAGPAL, [6]VASUDHA SAMBYAL**

[1,2,3,4,5]Department of Botanical and Environmental Sciences, Guru Nanak Dev University, Amritsar, India
[6]Department of Human Genetics, Guru Nanak Dev University, Amritsar, India
E-mail: [1]singh.sandip87@gmail.com, [6]vasudhasambyal@yahoo.com

**Abstract—** Heavy metal contamination of agricultural soils is a serious cause of concern because heavy metals get accumulated in crop plants, thus affecting animals and humans through food chain. Wheat (Triticum aestivum L.) is the main food crop of Rabi season in northern India and heavy metal contamination of wheat can pose major health risks to the population consuming contaminated crop. Therefore, a spatial study was conducted by collecting 28 soil samples to analyze the variation in contents of four heavy metals viz. chromium, cadmium, cobalt and copper in wheat cultivated agricultural soils of Amritsar district of Punjab, India. The studied soil samples were alkaline in nature with pH ranging from 7.55 – 8.55 and Soil Organic Matter (SOM) ranging from 3.37 – 9.78 %. The contents of Cr, Cd, Co and Cu ranged from 6.8 – 37.6 mg/kg, 0.25 – 1.8 mg/kg, 1.8 – 8.9 mg/kg and 8.5 – 42.4 mg/kg, respectively, which were below maximum permissible limits. Among different metals studied, maximum variation was found for Cd having highest coefficient of variation (59.84 %). Significant positive correlations were found among the heavy metals studied indicating their similar sources. Spatial distribution maps showed that comparatively higher levels of metals were observed in inner urban parts of Amritsar, which may be due to higher industrial and vehicular activity in these areas. Principal Component Analysis showed that the main source of Cr and Co was parent rock materials and Cd and Cu came from anthropogenic activities such as agriculture and industrialization.

**Keywords—** Agricultural soil; Heavy metal; Spatial variation; Wheat.

## I. INTRODUCTION

Soil is one of the most important natural resource and the rising pollution in soils (especially agricultural soils) is a rising global concern. When considering the different kinds of contaminants, heavy metals are especially dangerous because of their persistence and toxicity[**1**]. Although metals like Cr, Cu and Co are essential for regulation of human metabolism, but at concentrations higher than recommended they cause metabolic disorders [**2**]. Metals such as Cd are known to be toxic for both plants and humans. In particular, potentially toxic elements accumulated in agricultural soils can can result in a loss of soil functions concerning environmental quality protection, maintenance of human health and productivity, which are relevant aspects of soil quality [**3, 4].** Usually metals are present in soil from natural origins such as parent rock materials, but in last few decades metals contents in soil have risen to dangerous levels mainly due to anthropogenic activities such as industrialization, urbanization, dangerous agricultural practices etc. [5-7]. Considering the rising level of heavy metals in soils spatial studies are conducted to assess heavy metal contents in soils throughout the world. Spatial distribution of heavy metals in agricultural soils is correlated with their natural sources and anthropogenic inputs [8]. A combination of multivariate statistics (such as Principal component analysis) and spatial analysis using mapping techniques is an important tool for identifying pollution characteristics of heavy metals in soils and distinguishing their natural sources and anthropogenic inputs [9].

In the present study, a spatial analysis was carried out to determine the levels of four metals (Cr, Cd, Co and Co) in soils under wheat cultivation in Amritsar district of Punjab, which is one of the main agrarian states of India. The main objectives of this study were to assess the distribution of these metals in various parts of district and find out the possible sources of these metals using multivariate statistics.

## II. MATERIALS AND METHODS

### *A. Study area*

Amritsar is a district situated in northwestern part of Punjab. It is important historic place and one of the biggest tourist destinations of world due to famous Golden Temple. The soil in this area is mainly sandy loam in nature. The annual rainfall in this area is 435.6 mm and has semiarid to subhumid climate. Agriculture is the main occupation of this district with two main crop seasons Kharif (fall) and Rabi (spring). Extensive use of fertilizers, pesticides and herbicides is widespread here. Groundwater is the main source of irrigation in the district.

### *B. Sampling and preparation*

Soil sampling was done in the month of March, 2016. Twenty eight sites were selected for collecting composite soil samples throughout the Amritsar

district from fields under wheat cultivation (Fig. 1). The composite soil samples (approximately 2 kg) were prepared by pooling five subsamples collected from at least two sampling fields at each sampling site. The soil samples were airdried, ground, passed through 2-mm sieve and stored in clean polythene bags until further analysis.

### *C. Physico-chemical analysis*

The soil pH was determined in soil–water (1:5) suspension using HM digital meter-COM-100 (New Delhi, India). The soil total organic carbon was measured after igniting the sample in a muffle furnace at 550 °C for 60 min by the method of [**10]**. A factor of 1.72 was multiplied with organic carbon content to determine SOM.

### *D. Heavy metal analysis*

For heavy metal determination, 1 g of soil was digested with 15 mL of aqua regia ($HNO_3$–HCl in 3:1 ratio) at 80 °C till a transparent solution was obtained [**11]**. The digested samples were filtered and diluted with deionized water up to 50 mL and analyzed for the metals, viz chromium (Cr), cadmium (Cd), cobalt (Co) and copper (Cu) by flame atomic absorption spectrophotometer (AAS) (Agilent 240 FS AA model). Properly washed glassware, double-distilled water and analytical grade reagents were used throughout the study. The standard solutions of selected heavy metals were procured from Agilent (1000 mg/L) and were used to make solutions of varying concentrations by dilution of the standards. After every ten sample readings, the standards were run to assure the working of machine with 95 % accuracy.

### *E. Statistical and Spatial analysis*

The descriptive statistics and PCA analysis of physico- chemical parameters and hevay metals was done using PAST software. Pearson's correlation coefficients were calculated to analyze the correlation between physico-chemical properties and heavy metals in soil using Minitab version 14.0 (Pennsylvania, USA) computer software. Google maps and Paint software was used to draw maps in order to represent the distribution of metals in Amritsar district.

## III. RESULT AND DISCUSSION

### *A. Physico-chemical parameters*

Table 1 represents the physico-chemical parameters and heavy metals studied in the sampled soil samples. pH and soil organic matter (SOM) were the physic-chemical parameters studied in the soil samples. The analyzed soil samples were found to be alkaline in nature having mean pH 8.0. The SOM ranged between 3.37 – 9.78 %. The results were in conformity with the earlier studies done on agricultural soils in Amritsar and Punjab [**12-14]**. The low organic matter found in the area can be due to the sandy loam texture of the soils of Amritsar [**12]**.

Positive correlation (Table 2) was observed between pH and various heavy metals (statistically significant correlation in case of Cd) which was due to greater retention and decreased solubility of the heavy metals with higher pH [**15-16]**.

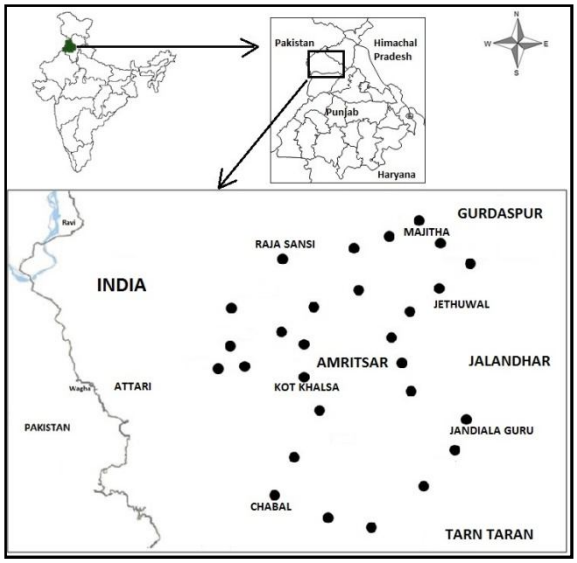



**Figure 1. Location of the sampling sites in Amritsar, Punjab**

### *B. Heavy metal contents and their distribution in sample areas*

The Cr, Cd, Co and Cu were the heavy metals analyzed in the present study (Table 1) which ranged as 6.8 – 37.6 mg/kg, 0.25 – 1.8 mg/kg, 1.2 – 8.9 mg/kg and 8.5 – 42.4 mg/kg, respectively. Fig 2 displays the distribution of heavy metals in the study area. In the present study the order of average metals contents observed in soil samples was, Cr > Cu > Co > Cd. Cr and Cu are required in trace amounts by plants and important components of parent rock materials. Therefore these are present in higher amounts than Co and Cd which are toxic and non essential for plants [**1, 9]**. Although small amounts of naturally occurring trivalent chromium ($Cr^{3+}$) are essential for nutrition, the presence of industry produced ($Cr^{6+}$), in water or the food chain is considered to be highly hazardous [**5]**. Figure 2 shows the distribution of these metals at the studied sites. Maximum samples in the present study (68 %) had Cr in 20 – 30 mg/kg range (Fig 2a). Very few chromium waste generating industries (such as steel, alloys, chrome plating and pigment production) are present in the study area therefore the main source of Cr in the studied is from parent rock material. Cadmium is a very toxic metal. All soils and rocks, including coal and mineral fertilizers, contain some cadmium. It is highly toxic and a known carcinogen for plants and animals [**7]**. The average Cd content in the present study was found to be 0.51 mg/kg (Table 1). 71 % soil samples in the present study (Fig 2b) had Cd content less than 0.5 mg/kg, which is contradictory

to the expected level as high amount of NPK fertilizers are used in wheat cultivation and NPK fertilizers are main sources of Cd in agricultural soils [**17**]. But low level of SOM, sandy loam texture of the studied soils, metal uptake by wheat plants or leaching of metal to lower layers of soil, can be the main reasons for low retention of Cd and other metals in soil. The Co contents in the studied soil samples were generally low with only one sample having Co content > 40 mg/kg (Fig 2c). Cobalt usually occurs in association with other metals, such as copper, nickel, manganese and arsenic, which was evident from significant positive correlation between Co and Cu (Table 2). The mean Cu content in the studied area was 20.70 mg/kg. Figure 2d shows marked copper contents in soils of studied area. Most of the samples have Cu contents in the range 20 – 40 mg/kg. The main sources of Cu in these soils are application of agrochemicals, especially the use of fungicidal sprays that reach the soil surface directly or indirectly as leaf litter [**1**]. Copper is also characterized by the point sources of contamination, namely uncontrolled waste dumps, blast furnaces, etc. [**6**].

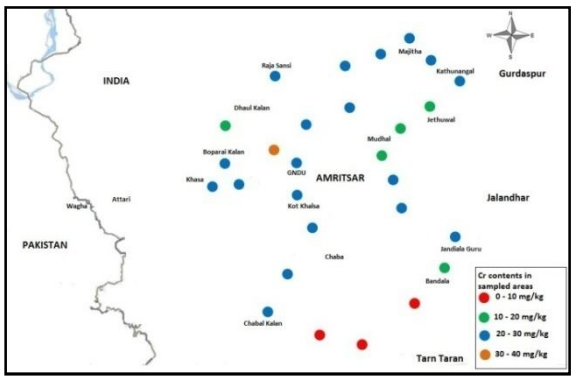
TABLE 1 DESCRIPTIVE STATISTICS OF PHYSICO-CHEMICAL PROPERTIES AND HEAVY METAL CONTENTS OF AGRICULTURAL SOILS OF AMRITSAR (N=28)

| | pH | SOM | Cr | Cd | Co | Cu |
|---|---|---|---|---|---|---|
| Min | 7.55 | 3.37 | 6.8 | 0.25 | 1.2 | 8.5 |
| Max | 8.55 | 9.78 | 37.6 | 1.8 | 8.9 | 42.4 |
| Sum | 224.18 | 130.50 | 594.9 | 14.3 | 144.85 | 579.65 |
| Mean | 8.01 | 6.52 | 21.25 | 0.51 | 5.17 | 20.70 |
| Std. Error | 0.05 | 0.34 | 1.22 | 0.06 | 0.36 | 1.28 |
| Variance | 0.07 | 2.33 | 41.42 | 0.09 | 3.57 | 46.13 |
| Stand. dev | 0.26 | 1.53 | 6.44 | 0.31 | 1.89 | 6.79 |
| Median | 8 | 6.71 | 21.68 | 0.45 | 5.18 | 20.3 |
| 25 prcntil | 7.76 | 5.45 | 17.9 | 0.36 | 3.71 | 16.78 |
| 75 prcntil | 8.2 | 7.17 | 25.25 | 0.55 | 6.13 | 24.26 |
| Skewness | 0.09 | 0.21 | - 0.28 | 3.08 | 0.07 | 0.96 |
| Kurtosis | - 0.74 | 0.61 | 1.28 | 11.76 | - 0.39 | 2.87 |
| Geom. mean | 8.00 | 6.35 | 20.06 | 0.46 | 4.78 | 19.64 |
| Coeff. var | 3.26 | 23.41 | 30.29 | 59.84 | 36.53 | 32.81 |

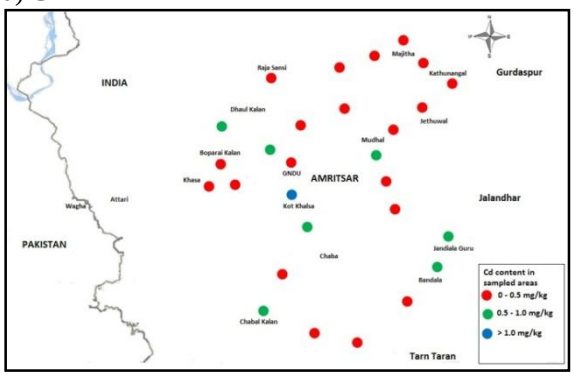
TABLE 2 PEARSON'S CORRELATION MATRIX OF PHYSICO-CHEMICAL PROPERTIES AND HEAVY METAL CONTENTS OF AGRICULTURAL SOILS OF AMRITSAR, PUNJAB

| | pH | SOM | Cr | Cd | Co |
|---|---|---|---|---|---|
| SOM | 0.212 | | | | |
| Cr | 0.144 | 0.368 | | | |
| Cd | 0.637* | 0.103 | 0.222 | | |
| Co | 0.255 | 0.187 | 0.745** | 0.201 | |
| Cu | 0.233 | 0.219 | 0.721* | 0.535* | 0.738** |

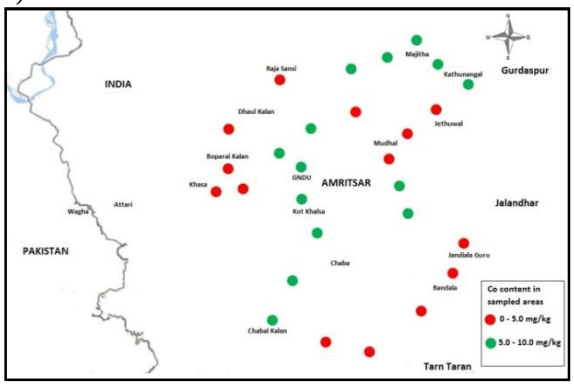
*** Correlation is significant at the 0.05 level (2-tailed).**
**** Correlation is significant at the 0.01 level (2-tailed).**



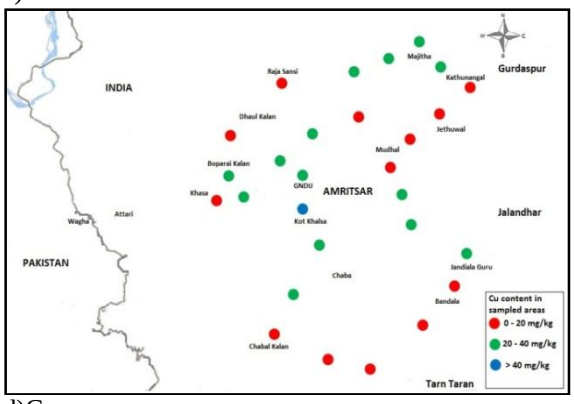

a) Cr




b) Cd




c) Co




d)Cu

**Figure 2 Distribution of metals across various sites in Amritsar, Punjab**

Among the studied metals overall maximum variability was observed for Cd having maximum Coefficient of Variation (59.84 %) and least variance was observed for Cr (30.29 %). This might be due to variation in anthropogenic input of Cd and uniformity

in natural bedrock contents of Cr. It can be observed from Fig 2 that comparatively higher levels of the studied metal were found in the soil samples collected from inner urban areas of Amritsar than the outer rural areas. It was mainly due to anthropogenic factors such as vehicle emission, industrial wastes, the sedimentation of dust and suspended substances in the atmosphere, the combustion of coals and the dry and wet precipitation of other pollutants [**3]** in these urban areas. Specifically highest amount of studied metals were found in areas near sites near Kot Khalsa and GNDU. The main reasons for it is that these areas have higher industrial activity (coal based brick kiln, textile etc.) and very high vehicular load as these sites fall in urban settlements. Also sewage water is used for irrigation in these areas which is also a source of heavy metals. It can be noted that the spatial distribution analysis represented in Fig 2 is very useful in analyzing the sources and patterns of soil contamination in addition to descriptive statistics. Thus, such spatial analysis must be accompanied in addition to the normal metal

TABLE 3 NATIONAL AND INTERNATIONAL MAXIMUM PERMISSIBLE LIMITS OF HEAVY METALS FOR SOIL

| **Maximum permissible limits for soil (mg/kg)** | **Cr** | **Cu** | **Cd** | **Co** |
|---|---|---|---|---|
| Indian [18] | - | 135-270 | 3-6 | - |
| European Union [19] | 150 | 140 | 3.0 | - |
| Ewers [20] | 100 | 100 | 3.0 | 50 |

analysis in order to analyze in depth patterns for contamination. The studied heavy metal contents were below various national and international maximum permissible limits (Table 3).

### *D. Principal component analysis (PCA)*

PCA was used to identify the origin of the heavy metals in the agricultural soils, and the results are presented in Table 4. The eigenvalues of the second extracted components were all greater than 1.0. Therefore, the heavy metals could be grouped into a two-component model that accounted for 88.29 % of all the data variation. The component matrix showed that Cr and Co were strongly associated with the first component (PC 1). The second component (PC 2) included Cd and Cu. Based on the PCA results, PC1 can be considered to be a lithogenic component, as the variability of the elements seems to be controlled by parent rocks. The parent rock factor explains 66.42 % of the total variance and is the most important component. This result suggests that the distribution of Cr and Co has a lithogenic control as the parent material present in calcareous areas (such as Punjab), determines Cr and Co contents [**1]**. PC2 includes Cd and Cu which can be defined as an anthropogenic component. As explained above, Cu and Cd can come from agrochemicals related to specific agronomic practices such as phosphate fertilizers, fungicidal sprays etc. are an important source of heavy metals entering agricultural soils, especially Cd, Cu and Zn. These conclusions are in agreement with previous works done by [**1]** and [**9]**. The observed results are further verified by the significantly

TABLE 4 TOTAL VARIANCE EXPLAINED AND COMPONENT MATRIX FOR HEAVY METALS IN THE AGRICULTURAL SOILS OF AMRITSAR.

| **Component** | **Initial eigenvalues** | | |
|---|---|---|---|
| | ***Total*** | ***% of Variance*** | ***Cumulative %*** |
| 1 | 2.6566 | 66.42 | 66.42 |
| 2 | 1.0149 | 22.87 | 88.29 |
| 3 | 0.2573 | 6.43 | 95.72 |
| 4 | 0.1712 | 4.28 | 100.00 |
| | **Extraction sums of squared loadings** | | |
| | ***Total*** | ***% of Variance*** | ***Cumulative %*** |
| 1 | 2.6566 | 66.42 | 66.42 |
| 2 | 1.0149 | 22.87 | 88.29 |
| | | | |
| | **Metal** | **Component matrix** | |
| | | ***Component*** | |
| | | ***1*** | ***2*** |
| | Cr | 0.8680 | - 0.3027 |
| | Cd | 0.5234 | 0.8391 |
| | Co | 0.8698 | - 0.3257 |
| | Cu | 0.1144 | 0.9242 |

positive correlation observed between Cr-Co and Cd-Cu (Table 2). In summary, the soils studied can be considered as unpolluted as their heavy metal contents are below various maximum permissible limits. However, because the total heavy metal content is not the ultimate indicator of the availability and mobility of heavy metals in soils [**21]**, further research is required to assess the pool of potentially available species (e.g., extractable fraction) to determine the probability of these transferring from the soil to other ecosystem components (e.g., crops, underground water).

## CONCLUSION

The results from the present study showed that the soil from the studied area were alkaline in nature with low soil organic matter. The studied heavy metals (Cr, Cd, Co and Cu) were below maximum permissible limits in soils. Maximum variability was observed for Cd (59.84 %) and minimum variability was observed for Cr (30.29 %). Spatial distribution maps showed that comparatively higher levels of metals were observed in inner urban parts of Amritsar, which were due to higher industrial and vehicular loads in these areas. Principal Component Analysis showed that the main source of Cr and Co was parent rock materials and Cd and Cu came from anthropogenic activities such as agriculture and industrialization. Further studies must be carried out to assess the speciation aspects of heavy metals in soils and their uptake mechanism by plants.

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