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Distribution and source apportionment studies of heavy metals in soil of cotton/wheat fields

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Abstract Heavy metals enriched agricultural soils have been the subject of great concern because these metals have potential to be transferred to the soil solution and afterward accumulated in food chain. To study the trace metal persistence in crop soil, 90 representative soil samples were collected and analyzed for heavy metal (As, Cd, Cu, Fe, Mn, Ni, Pb, and Zn) and anions (chloride, nitrates, phosphates and sulfates). Cluster and factor analysis techniques were used for the source identification of these excessive heavy metal levels and ecological risk was determined with potential ecological risk assessment. The degree of enrichment of eight studied heavy metals in comparison with the corresponding background levels decreased in order: Cd > Pb > Fe > Ni > Mn > As > Cu ~ Zn. Arsenic and cadmium exhibited 1.30- and 1.64-fold exceeded levels than threshold limits set by National environment quality standards, respectively. Cd in cotton field's soil may lead to higher potential risk than other heavy metals. On overall basis, the cumulative mean potential ecological risk for the district (207.75) corresponded to moderate risk level with higher contributions from As and Pb especially from Cd. Cadmium formed strong positive correlation with phosphate content of soil at $p < 0.01$. Cluster analysis indicated that Cluster 1 (extremely polluted) probably originated from anthropogenic inputs of phosphate fertilizer and past usage of arsenical pesticides.

Keyword Heavy metals · cotton/wheat soil · potential ecological risk · Phosphate fertilizer · multivariate statistical methods

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Introduction

There is an emergent public concern over the prospective accumulation of heavy metals in the soils of cotton and wheat fields owing to rapid industrial development and increasing reliance on agrochemicals during the last several decades (Wong et al. 2002; Nicholson et al. 2003). The advance agricultural activities especially excessive use of fertilizers, pesticides, liming, sewage sludge and irrigation water contain heavy metals which accumulate in agricultural soil and, hence, pose a risk to humans and wildlife (M. Jamali et al. 2007; Atafar et al. 2010; Shan et al. 2013; Jiang et al. 2014; Tariq et al. 2016). Lime and superphosphate fertilizers used frequently in agriculture contain not only the major elements necessary for plant nutrition and growth but also

the trace metals like As, Cd and Pb as impurities (Pezzarossa et al. 1990). Urea, calcium superphosphate, iron sulfate, and copper sulfate contain high levels of Cd, Co, Mn, Ni, Pb, and Zn (Gimeno-García et al. 1996). Similarly, the application of sewage sludge to agricultural land as the best practicable environmental option for its disposal, has reduced fertilizer costs, increased the organic matter content and have improved the soil "workability" and water holding capacity (Hough et al. 2003). However, sewage sludge may contain elevated concentrations of heavy metals such as As, Cd, Cu, Pb and Zn etc. that may affect the quality of soil as well as crops grown (Hough et al. 2003; Jiang et al. 2014).

Excessive accumulation of heavy metals in agricultural soils especially in cotton growing areas may not only result in environmental contamination, but elevated heavy metal uptake by crops may also affect the food quality and safety (Jamali et al. 2009). Enormous quantities of nitrogenous fertilizers (urea, calcium ammonium nitrate and ammonium sulfate) and phosphate fertilizers (single triple and superphosphate, mono and diammonium phosphate) are used in cotton-wheat cropping pattern of Punjab. The recommended dose of these fertilizer are 75–160 kg/ha for nitrogen, 60–110 kg/ha for phosphate and 60 kg/ha for potash for wheat and 120–170 kg/ha for nitrogen 60 kg/ha for phosphate 60 kg/ha for potash for cotton crop. As wheat is alternative crop in the cotton growing areas of Pakistan so, these heavy metals may also affect the quality of wheat grains (Hough et al. 2003). Nan et al. 2002, reported that an increase in the total soil contents of heavy metals (Cd, Cu, Pb, Zn) may enhance the Cd accumulation by grains, and the increased total Zn content of soil may lower the grain Pb accumulation (Nan et al. 2002).

Soil properties are the main factors that influence the bioavailability of heavy metals in the soil. pH, soil organic matter, various redox phenomena, cation exchange capacity, competition among various metal ions, and their ligation by anions affect the persistence and mobility of metals and their uptake by plants (Weggler-Beaton et al. 2000; Aiken et al. 2011; Bradham et al. 2006). The production of a good quality food demands the management of excessive metal levels in agricultural soil, so the soil from fields of food crops must be monitored regularly. Multivariate statistical tools were used to differentiate between various sources that cause variations in soil composition in terms of its metal

content (Li and Feng 2012). The aim of the present study was to evaluate the load of trace metals in the soil of cotton/wheat cropping pattern fields and to trace their sources. The determination of probable ecological risk degrees for production of good quality wheat crop was another important objective of the study.

Materials and methods

Sampling site

Okara is the district of Punjab that is famous for its fertile lands, peaceful natural environment and green fields of potato, tomato, sugarcane, cotton, wheat, rice, and maize crops. It encompasses a total area of 4377 km^2 housing 2232 thousand persons. The climate of the district is hot in summer and cold in winter. May and June are the hottest months with maximum temperature reaching up to 44 °C. January is the coldest month with minimum temperature falling to 2 °C. Average annual rainfall here is 200 mm (GOP 2006). In addition to fertile agricultural lands, a number of agriculture based industrial units are also operative in the city. These include: sugar mills, flour mills, textile spinning/weaving mills, confectionery, rice husking units, cotton ginning/pressing factories and oil expelling units. The district is also one of the best milk producing districts of Punjab (GOP 2006). It is reported that here a compost based on crushed cotton gin residues is used mostly which significantly increases the yield of wheat under dry land conditions (Tejada and Gonzalez 2003).

Sample collection and preparation

Representative soil samples were collected from cotton/wheat growing areas of Okara (Fig. 1). These samples were taken from different field plots by digging down to a depth of 20 cm by using the stainless steel soil auger in accordance with composite sampling plan of Tan 2005 (Kim 1995; Tan 2005). Nine different sampling areas were selected randomly from Okara district and 10 cotton/wheat fields were chosen from each selected sampling area. Four soil samples from four corners of the field and one from approximate center was taken on site and then thoroughly mixed to make a representative composite sample. For controls, soil samples were taken from a field, located 1 km away, where pesticides had never been applied. The samples were placed in black

polythene bags, labeled properly and transported to the laboratory at Lahore College for Women University, Lahore. From each of the well mixed composite samples (approximately 1 kg before drying), triplicate samples were made for laboratory analysis.

Quality control and analysis

Estimation of physico-chemical parameters of soil samples

Standard analytical procedures were adopted for the determination of soil physico-chemical properties. The pH and electrical conductivity were determined in 1:2, soil: water extracts by using pH meter (model WTW, Inolab-720) and conductivity meters (with conductivity meter WTW, Inolab-720). Organic matter was determined by (Walkley and Black 1934), while soil texture was determined by using hydrometer (ASTM 1524) (Ryan et al. 2007). Cation exchange capacity (CEC) and Cl^- content were determined by colorimetric method of Chapman and Pratt (1961)). Sulfate, phosphate and nitrate were determined by using Spectrophotometer and glass cells (Radojevic and Bashkin 1999; Ryan et al. 2007; Chapman et al. 1996).

Determination of total metal content in soil samples

The levels of total heavy metals such as Cd, Cu, Fe, Mn, Ni, and Zn present in the soil samples were estimated by FAAS while Pb and arsenic were determined by graphite furnace AAS. For this purpose HITACHI AAS, Z-5000 Atomic Absorption spectrophotometer with Zeeman correction was used (Pakistan 2006).

The stock standard solutions of metals at a concentration of 1000 ppm were obtained from Merck, Germany. The working standards (1–10 ppm) were prepared by appropriate dilution of stock standards with double distilled water.

Pretreatment of soil samples

Nitric acid-hydrogen peroxide digestion method (US-EPA Method 3050B) was used for the estimation of trace metals in soil samples. Briefly, a 2.0-g portion of air-dried and sieved soil sample was treated with 10 mL of 1:1 HNO_3 under continuous stirring in a Pyrex beaker. The contents of the beaker were covered with a watch glass, heated to about 90–95 °C and refluxed for about 10–15 min without boiling. Subsequently, they were cooled to room temperature, added with 5 mL concentrated HNO_3 and heated for 30 min. The volume of the contents was reduced to 5 mL and the same process was repeated again. The contents were cooled to room temperature and 2 mL of deionized water and 3 mL of 30 % H_2O_2 were added. Beaker was then covered and heated gently while avoiding vigorous effervescence. Repeatedly, 1 mL of H_2O_2 was added and heated gently until effervescence subsided. Then 10 mL of doubly distilled (DDW) water and 5 mL of concentrated HCl were added and contents were heated for 15 min (without boiling). The contents were cooled and filtered through a Whatman filter paper no. 42 into volumetric flasks of 50 mL capacity. Volume of acid extract was made up to mark with doubly distilled water (EPA. 1996). This extract was aspirated onto AAS for metal estimation.

Quantification of metals by AAS

The calibration curve method was adopted for the quantification of results during the present study. In this method a calibration curve is traced by using the reference substance (standard solution) of known concentration and the absorbance of the unknown sample is fitted to the curve to obtain the concentration. Standard solutions were prepared in appropriate range (1–10 ppm) and their absorptions were recorded on the instrument. The instrument in automatic mode plots the calibration curve itself. At least four standards were run covering the absorption range of samples. Triplicate samples were run to ensure the precision of quantitative results. In order to check the accuracy of data obtained by AAS; standard reference material SRM 2711 "Montana Soil" was run with each batch of samples. The analysis results were reliable when repeat sample analysis error was below 5 %, and the analytical precision for replicate samples was within ±10 %.

Data handling and data analysis

Potential ecological risk index (PER)

Potential ecological risk index was originally proposed by Hakanson (1980) and is widely used to screen the degree of soil contamination caused by
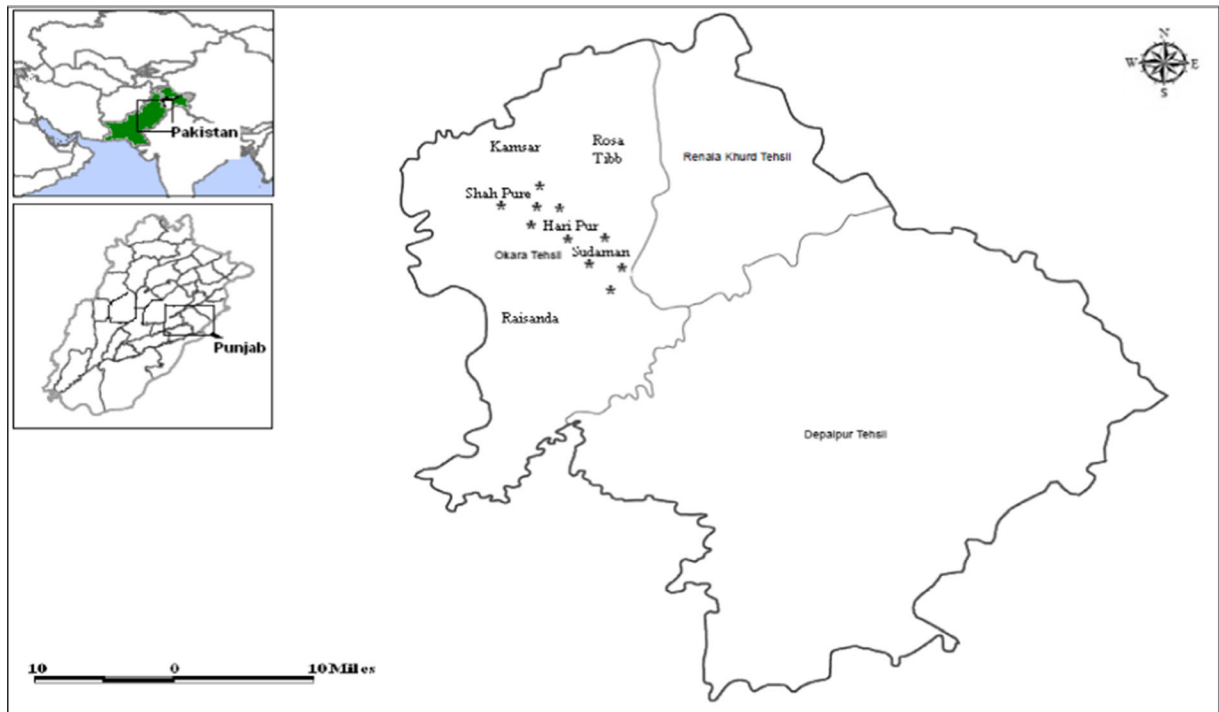
Fig. 1 Map of Okara indicating the sampling points

heavy metals (Saeedi et al. 2012; Hakanson 1980). In other words, potential ecological risk index (PER) assesses the degree of ecological risk of heavy metals present in the soil. The value of RI can be calculated by the formula:

$$C_f{}^i = C_D{}^i / C_B{}^i \qquad (1)$$

$$E_r{}^i = T_r{}^i x \ C_f{}^i \qquad (2)$$

$$RI = \sum\nolimits_{i=1}^{m} E_r{}^i \qquad (3)$$

Where RI is the sum of the potential risk of individual heavy metals, $E_r{}^i$ is the potential risk of individual heavy metal, $T_r{}^i$ is the toxic-response factor for a given heavy metal, $C_f{}^i$ is the contamination factor, CD^i is the present concentration of heavy metal in soil, and $C_B{}^i$ is the pre-background record of heavy metal concentration in soil. Based on Hakanson's approach, the toxic-response factors for Cu, Zn, Pb, As, and Cd are 5, 1, 5, 10, and 30, respectively. Hakanson defined five categories of $E_r{}^i$

and four categories of RI (supplementary materials Table 1).

Source apportionment studies of metals

The statistical analysis of trace metal data was carried out to determine the distribution of various measured parameters and correlations among them. Basic statistical parameters (minimum, maximum, median, standard deviation, standard error, skewness, and kurtosis) determined the spread of measured data. Pearson correlation coefficient matrix was evaluated to determine the correlations between different metal pairs and interrelationship between metal levels and physico-chemical parameters. Multivariate statistical techniques, such as principal components analysis (PCA) and cluster analysis (CA), are powerful tools that identify the various sources contributing to the soil metal pollution and segregate these sources on mass basis (Borůvka et al. 2005; Facchinelli et al. 2001). These analyses are widely used to predict the variability of heavy metals and their controlling factors; and also to highlight the influence of

human activities on heavy metal contents of soils (Li and Feng 2012).

Results and discussion

Statistics of soil physico-chemical parameters and heavy metal: their comparison with NEQS, degree of enrichment

The soil samples from study area of Okara district are loamy, alkaline, non-saline, and have mean cation exchange capacity (CEC) of 4.45 cmol kg^{-1}, which indicates their high crop productivity. Although these soil conditions favored the persistence of studied heavy metals in soil, hence the chances of food chain contamination is rear but a pH shift from alkaline to acidic pH may released the bulk of metals like Pb and Ni making the situation alarming (Rafique et al. 2011).

Mean soil chloride content from the study area is 1.5 times higher as suggested by Agricultural bureau of South Australia (Agricultural Bureau of South Australia 1997). These samples were also found to be rich in sulfate and nitrate (i.e., 281.9 and 153.4 mg/kg respectively). The phosphate levels of the soils were recorded to be very low as compared to the limits set for calcareous crops like wheat and non-calcareous crop of cotton (Agricultural Bureau of South Australia 1997). Phosphorus deficiency leads to impaired vegetative growth, weak root system and low yield. Therefore, there is need to replenish the P-deficiency of the agricultural soils here.

The heavy metal concentrations in cotton/wheat fields of selected study area were all higher than their corresponding background values (Table 1). This was especially true for the cases of Cd, Pb Ni, Mn, and As which were found to be 5.7, 3.68 1.54, 1.47, and 1.42 times of their background values, respectively. Sources of these enhanced metal levels were traced in agronomic activities such as the use of natural and synthetic fertilizers, herbicides, and pesticides to improve the crop yields (Tariq and Rashid 2012; Iqbal et al. 2011).

Compared with the corresponding background values, the degree of enrichment of the eight studied heavy metals decreased in the order: Cd > Pb > Fe > Ni > Mn > As > Cu. The total concentrations of Cu, Zn, and Pb on average basis were 21.45 ± 14.76, 60.84 ± 7.16 and 10.68 ± 1.38 mg kg^{-1}, respectively, which were lower than the maximum acceptable limits of Pakistan, India, Europe, and China [(Llopis et al. 2006; Nicholson et al. 2003; Rowell 1994; Ahmad and Goni 2010; Awasthi 1998) (supplementary material Fig. 1), while the mean concentrations of As and Cd exceeded the threshold limits as being 1.30 and 1.64 times, respectively. Thus it is anticipated that the high concentrations of As and Cd in cotton field soil may cast adverse biological effects. Phosphate fertilizers, fungicides, and some pesticides are known to contain Cd and thus these are an important source of these two metals in the soils (Luo et al. 2009; Gimeno-García et al. 1996). It was also estimated that about 30–50 % of Cd in the soils comes

Table. 1 Descriptive statistical analysis of trace metal concentrations in the soil of cotton/wheat fields of Okara, Pakistan (n = 90)

	Cu	Fe	Ni	Zn	As	Mn	Pb	Cd
Minimum	7.63	489.8	13.40	49.7	2.50	264.5	7.150	0.110
Maximum	65.80	845.0	94.60	75.3	10.90	322.7	14.60	2.890
Mean	21.45	605	33.80	60.84	7.68	294.5	10.68	1. 310
Range	58.15	355	81.50	25.6	8.41	58.2	7.490	2.78
Median	18.40	559	24.70	58.8	8.25	296.9	10.67	1.260
S. D.	14.76	110.8	22.87	7.16	1.89	16.54	1.380	0.670
S. Variance	217.8	12,282	522.9	51.24	3.59	273.5	1.900	0.450
S. E.	1.560	11.68	2.41	0.75	0.200	1.740	0.140	0.070
Kurtosis	3.680	−0.230	2.30	−0.56	0.070	−0.610	0.830	−0.840
Skewness	2.110	1.020	1.88	0.64	−0.86	−0.350	0.130	0.270
B.G levels MAC, Pakistan	26.0, 30–40[a]	430, 75–150[b]	21.9, 30–70[c]	86.0, 135–150[a]	5.4, 5.9[a]	200, 80–7000[c]	2.9, 85–450[a]	0.23, 0.80[a]

(Alloway 1990; Iqbal et al. 2011; Rowell 1994)

Table. 2 Basic statistics of potential ecological risk assessment (PER) of heavy metals in soil samples of Okara ($n = 90$)

| Parameters | E_r^i | | | | | | | | RI |
	Cu	Fe	Ni	Zn	As	Mn	Pb	Cd	
Min.	0.294	1.14	0.611	0.578	0.464	1.32	2.47	0.487	52.18
Max.	2.53	1.96	4.33	0.875	2.02	1.61	5.05	12.57	423.3
Mean	0.825	1.41	1.54	0.707	1.42	1.47	3.68	5.68	207.7
S. D.	0.568	0.258	1.04	0.083	0.351	0.083	0.475	2.91	89.77

from the application of phosphate fertilizers (McLaughlin and Singh 1999; Nziguheba and Smolders 2008). Sewage sludge is also capable of accumulating significant concentrations of Cd, Cu, and Zn (Holmgren et al. 1993).

Potential ecological risk assessment of heavy metals

Potential ecological risk assessment was carried out to detect the potential ecological risk levels of these heavy metals in cotton-wheat cropping pattern soil from the Okara district. Calculated single element pollution factor, potential ecological risk of individual element and comprehensive potential ecological index are presented in Table 2. The calculated mean potential ecological risk degrees decreased in the order of Cd > Pb > As > Cu > Zn. Thus Cd in cotton field's soil exhibited a high potential ecological risk degree than the other four heavy metals. From the viewpoint of the whole district, the cumulative mean RI (207.7) belonged to moderate risk level with higher contributions to RI being from Cd, Pb, and As. The heavy metal concentrations measured in this study do not pose a serious health risk due sub-alkaline environment of the soil which limits mobility of metals (Huang et al. 2007).

Heavy metals interaction in soil environment

Metal–metal correlations

The correlation among heavy metals may provide useful information on the sources and pathways of heavy metals. Pearson correlation coefficient matrixes data (with significant r values $\geq \pm 0.209$ at $p < 0.05$) for the present study is presented in Table 3. The most significant positive correlation was observed between Pb and As pair with r value of 0.66, depicting the fact that in 66 % cases Pb and As concentrations went hand in hand. The other metal pairs that exhibited strong positive correlations included Ni-Zn ($r = 0.623$), Ni-Fe ($r = 0.602$), Pb-Cd (0.553), Fe-Zn (0.472) etc. Li and Feng (2012) and Saeedi et al. (2012) reported that if the value of correlation coefficient between the heavy metals were positive, these may share a common source, exhibit mutual dependence and identical behavior during their transport (Saeedi et al. 2012; Li and Feng 2012). The results of the present study indicated that Cd-Pb-As were significantly inter-related, hence perhaps their origin in these soils was the same. Similarly strong negative correlation of Cu with Fe, Ni, and As with Cu was observed during present survey.

Table. 3 Correlation co-efficient matrix for the selected metals in soil samples of Okara ($n = 90$)

	Cu	Fe	Ni	Zn	As	Mn	Pb
Fe	**−0.526**						
Ni	**−0.260**	**0.602**					
Zn	**0.279**	**0.472**	**0.623**				
As	**−0.285**	**0.384**	0.116	**0.295**			
Mn	0.183	−0.014	**−0.277**	**0.321**	**0.480**		
Pb	**0.273**	−0.066	−0.128	0.140	**0.656**	0.164	
Cd	−0.080	0.152	0.192	0.126	**0.378**	−0.092	**0.553**

Bold values are significant

r values >0. 21 or <−0. 21 are significant at $p <$ .05000

Metal-to-soil physico-chemical properties correlation

The correlation coefficient data for heavy metals and soil physico-chemical parameters evidenced strong positive correlations as enlisted in Table 4. (pH-Cd), (E.C-Pb), (Cl$^-$-Mn) and (CEC-Zn) were observed to be correlated positively with r values >0.65 at $p = 0.05$. The zinc deficiency Zn Alkaline soils inhibit the plant's roots to absorb Zn (Agricultural Bureau of South Australia 1997) so may occur in these soil. Chloride formed significant correlation with most of the metals except Pb and Cd. Saline irrigation water containing high level of Cl might enhance the mobilization of metals due to the formation of heavy metals– chloride complexes thus aggravate heavy metal pollution problems (Ghallab and Usman 2007). Its most significant correlation was observed with Mn that depicted an increase in the concentration of soil Mn with an increase in chloride content. It in fact forms soluble complex with Mn and thus increases the mobility of this metal in the soil (Khoshgoftar et al. 2004).

Cadmium was found to be significantly, positively correlated with phosphate of soil ($r = 0.63$). The sulfate of soils was positively correlated with Fe, Ni, As, and Mn while negatively correlated with Cu. The nitrate content of soil had strong positive correlation with Cu and Zn with r values of 0.47 and 0.35, respectively. Negative correlations were observed with As ($r = -0.33$) and Mn (-0.31). Soil moisture levels and organic matter content of agricultural soils also influenced the bioavailability of trace metals. Organic matter was positively correlated with Cd, Pb and Cu which showed negative correlation with Fe, Ni, Zn, and Mn.

Soluble Cd is considered as the biologically available Cd. It forms carbonate complexes in soil at pH < 7 and these complexes get dissolved with a moderate drop in pH (Devau et al. 2011; Reddy and Patrick 1977). In case of Okara, soil is alkaline, so the chances of Cd persistence are enhanced. Cd^{2+} sorbs weakly to the organic matter, clays, and oxides at pH below 6 and may be released into the environment with a change in ionic composition of the pore waters thus Cd uptake by plants is enhanced at low pH (Järup et al. 1998). Moreover, Cd hydroxides may be oxidized to release Cd metal in soil environment which is considerably more difficult to access biologically (Reddy and Patrick 1977).

Source identification based on multivariate statistical analyses

Principle component analysis

PCA is an effective method to distinguish between anthropogenic or natural sources of various pollutants such as heavy metals (El Nemr et al. 2006). For the present study, varimax normalized PCA was conducted that identified three components for the soil samples of Okara all with cumulative total variance of 65.11 % (Fig. 2). Factor loading greater than 0.71 are typically considered excellent while those less than 0.32 are regarded very poor (El Nemr et al. 2006). The F-1 with a total variance of 25.64 % received significant loadings for Fe (0.81), As (0.78) and SO_4^{2-}(0.71) evidencing that the origin of Fe, As, and sulfate anions was the same in the agricultural soils. The major source of As in crop fields is irrigation with As contaminated water and spray

Table. 4 Metal-to-physico-chemical properties correlation coefficient matrix of selected soil samples of Okara ($n = 90$)

	Cu	Fe	Ni	Zn	AS	Mn	Pb	Cd
pH	**0.291**	−0.115	−0.127	0.166	**0.390**	0.179	**0.664**	**0.825**
E.C	**0.305**	**−0.351**	−0.173	**0.339**	0.153	**0.707**	−0.012	−0.171
Cl$^-$	**0.233**	**−0.232**	**−0.207**	**0.290**	**0.217**	**0.829**	0.026	−0.143
M.C%	−0.063	**0.586**	0.197	**0.554**	0.212	**0.312**	0.085	**0.257**
O.C%	**0.208**	**−0.691**	**−0.215**	**−0.360**	−0.149	**−0.218**	0.244	**0.448**
CEC	0.022	**0.471**	0.234	**0.673**	**0.480**	**0.526**	0.255	**0.523**
SO_4^{2-}	**−0.479**	**0.558**	**0.360**	0.135	**0.496**	**0.233**	−0.047	0.019
NO_3^-	**0.474**	−0.122	0.067	**0.347**	**−0.326**	**−0.306**	0.015	0.030
PO_4^{3-}	−0.080	0.152	−0.075	−0.033	0.178	−0.150	**0.291**	**0.631**

Bold values are significant

r values >0. 209 or <−0. 209 are significant at $p < 0.05000$
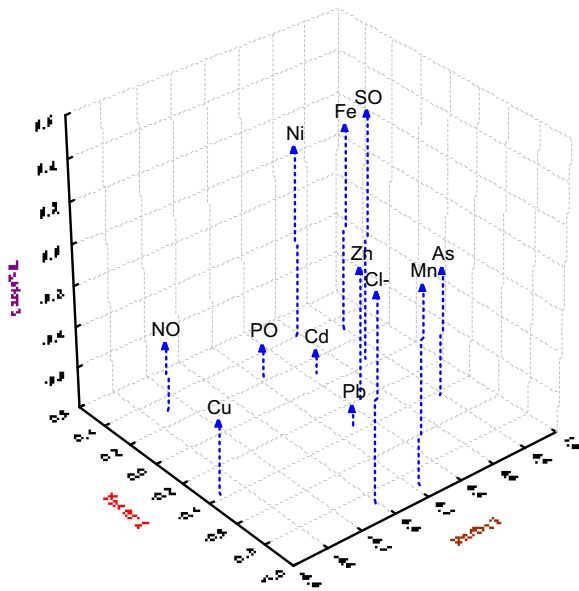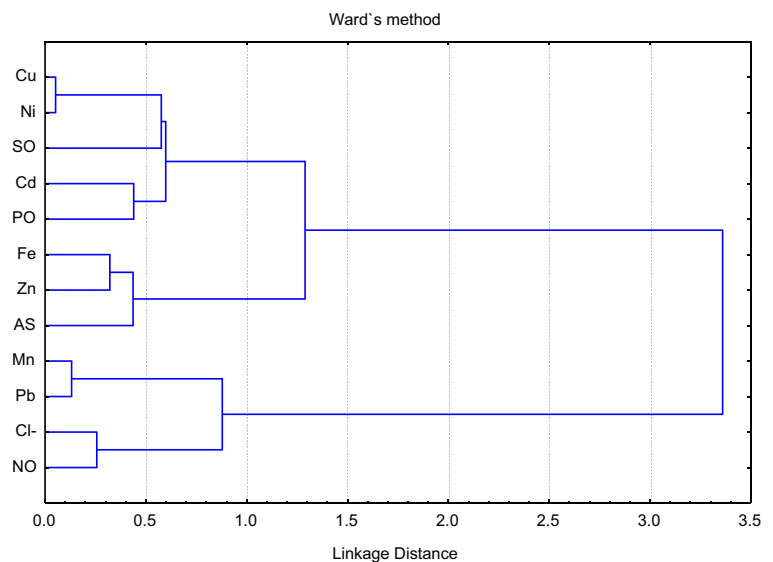
Principal components Analysis

Fig. 2 3D PCA loading of trace metals in soil of Okara

with As based pesticides (Cao et al. 2010; Hough et al. 2003). F-2, dominated by Mn (−0.91) and Cl⁻ (−0.88), accounted for 20.95 % of the total variance. Also manganese and Cl⁻ were highly associated in Factor 4 as depicted by their high factor loading values. F-3 received major contribution from Pb (−0.72) and Cd (−0.71), accounting for 18.51 % of the total variance. Pb and Cd are anthropogenic in origin, so this factor represented an anthropogenic source. Ni received comparable loadings in Factor 1 and Factor 2. Further, these

loadings were not as high as those of other parameters receiving dominant contribution. Thus it exhibited a quasi-independent behavior in these soil samples. Superphosphate is the fertilizer that contains the highest concentrations of Cd, Co, Cu, and Zn as impurities. Copper sulfate and iron sulfate have the most significant concentrations of Pb (Gimeno-García et al. 1996).

Cluster analysis

The hierarchical clustering was performed on the data set by applying the Ward's method to determine the similarities in origin and association between different trace metals and anions (Fig. 3). The strongest association was observed between Cu-Ni pair that was associated with SO_4^{2-} at later stage. In addition four distinct primary clusters Fe-Zn, Mn–Pb, and Cl⁻-NO$_3^-$ were formed within the linkage distance 0.5 that indicated the source of these metals and anions were same in this soil. Soil arsenic levels formed secondary cluster with iron and zinc within linkage distance >0.5 which implied a similar distribution pattern for these metals. The cluster analysis supported the results of correlation between metal-metal and metal-physico-chemical properties. Cd was found to be strongly associated with PO_4^{3-}. In fact phosphate fertilizers have been shown to be the major source of Cd and Pb in the soil. Thus repeated and excessive applications of fertilizer and pesticide may lead to much enhanced concentrations of heavy metals such as Cd and Pb in the soil (Gimeno-

Fig. 3 Dendrograms of selected metals in cotton/wheat soil samples of Okara using Ward's method

García et al. 1996). It is therefore necessary to educate the farmers for the wise use of pesticides and fertilizers and also avoid the soil conditioning by using the sewage sludge.

Conclusions

The cotton/wheat soil of Okara district was found to be highly contaminated with As and Cd and among the anions Cl^-, NO_3^-, SO_4^{2-} were abundantly present. The strong positive correlation of soil phosphate levels with Cd and Pb indicated that their source in Okara soil originated from excessive application of nitrogenous and phosphate fertilizers. The mean potential ecological risk of studied trace metals was low except for Cd which had the calculated RI in moderate risk range. PCA and CA confirmed the origin of Cd and As to be from excessive agrochemical usage.

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