Research Article

Multivariate Analysis of Metal Levels in Paddy Soil, Rice Plants, and Rice Grains: A Case Study from Shakargarh, Pakistan

Saadia R. Tariq and Nabila Rashid

Department of Chemistry, Lahore College for Women University, 45600 Lahore, Pakistan

Correspondence should be addressed to Saadia R. Tariq; saadiartariq@yahoo.com

Received 22 June 2012; Accepted 12 July 2012

Academic Editor: Athanasios Katsoyiannis

Copyright © 2013 S. R. Tariq and N. Rashid. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The present study aims at determining the relationship between trace metal levels in paddy soils, rice plants, and rice grains obtained from these plants. The levels of selected metals (Fe, Co, Ni, Cd, Pb, and Cr) were determined by atomic absorption spectrophotometry in the soil, rice plants, and rice grain samples collected from paddy fields. All the metals were present at enhanced levels in paddy soil. Among the selected metals, Fe, Ni, Cd, and Cr were predominantly associated with oxidizable fraction. The metals such as Cr, Ni, Co, and Fe were significantly positively correlated in soil and plants, but no such correlation was observed in soil-grain matrix evidencing that these metals have a soil-based origin in the plants, but they were not translocated to grains. The Pb content of soil was strongly positively correlated with plants as well as the grains. The principal component analysis and cluster analysis were used to depict the origin of enhanced metal levels in rice plants. Under the given field conditions, different metals possess different translocation behaviours from soil to roots to shoots to grains. There is a dire need to implement the strategies for wise and optimum use of agrochemicals.

1. Introduction

The greater urgency to obtain more and more crop yields per capita has led to the excessive use of agrochemicals which not only supply the nutrients to the soils and adjust their pH but also protect the precious crops from various pests [1]. Despite all these benefits, the excessive and continuous use of agrochemicals may lead to a substantial increase in concentrations of major elements like K, Ca, and Mg and heavy metals such as Cd and Zn in soil solutions, thereby deteriorating the soil quality with a subsequent effect on plants that show stunted growth and thus lower crop yields [2].

In developing countries, the heavy-metal-contaminated sewage sludges are also used as fertilizers, which on continuous application may lead to the accumulation of toxic metals into the soil. The subsequent uptake of metals in the edible parts of vegetative tissues may result in a direct pathway into the human food chain [3]. Moreover, these metals may leach from contaminated soils into the water bodies thereby deteriorating their quality as well [4]. Therefore, attention has been diverted towards the determination of metal levels in various agricultural soils and their extent of bioavailability to plants due to their detrimental effects on soil flora and fauna and their potential human health risks [5–10].

Rice is a favorite food for more than three billion people around the world [11]. In Pakistan, rice is grown under diverse climatic and edaphic conditions. Paddy soils are specifically of interest because for the cultivation of rice; these soils are kept submerged for longer periods of time, which may cause reduction and subsequent mobilization of various metals such as Fe and Mn [12]. Therefore, paddy soils have been of interest to the scientists for the determination of the levels and sources of heavy metals [1]. Qishlaq and Moore reported fungicides as major cause of Cu contamination of agricultural soils [7]. In rice-consuming countries like Iran, rice was suggested as one of the major sources of Cd intake due to high potential of these plants to accumulate Cd from contaminated soils into their grains [13].

In view of the hazards caused by the accumulation of heavy metals in the soil due to excessive agrochemical usage, the present study was formulated to determine the
metal contents of soil samples collected from paddy fields of Tehsil Shakargarh, Pakistan, to determine the fractionation of metals present in paddy soils to study their bioavailability and mobility, and then to study the uptake of metals by rice plants and their translocation to edible parts. The study will not only highlight the metal contamination of the paddy fields arising due to excessive and unwise use of agrochemicals but also help to identify the potential risk of elevated levels of these metals to the consumers.

2. Experimental Methodology

2.1. Description of Sampling Site. The samples were collected from paddy fields of tehsil Shakargarh of Punjab province of Pakistan. The city is located at 32°16'N 75°10'0E on the west bank of the river Ravi, encompassing an area of about 1272 km². Its rich and fertile lands are well known for wheat and top-quality rice cultivation. The main sources of irrigation in the sampling area are tube wells and electric pumps (water table 40–50 ft). The soil texture here is loamy, which is considered to be best for agricultural purposes because this can be ploughed easily and has tendency to retain good moisture content. Flour mills and rice processing units are the only industries present here.

2.2. Sample Collection and Pretreatment. A total of 35 samples each of top soil (1–5 cm), rice plants, and rice grains were collected in triplicate in 500 g capacity from different rice fields located at a distance of 1 km apart. The samples were properly labeled and immediately transferred to laboratory for analysis.

The collected soil samples were cleaned manually for twigs, roots, stones, or any other foreign matter, homogenised, and dried in an electric oven set at 80°C for 24 h. The rice plant samples were thoroughly washed with deionised water, dried in shade, chopped, homogenized, and stored in zip mouthed bags. Similarly, the rice grains after cleaning, washing, and grinding were stored in polythene bottles.

Analytical grade reagents with a certified purity of 99.9%, procured from E. Merck (Germany), were used throughout the work. The stock solutions of metals (1000 ppm) contained in strong opaque polyethylene bottles were also purchased from E-Merck Germany and stored in a cool and dry place.

2.3. Determination of Soil Physicochemical Parameters. The physicochemical parameters of the soil samples were determined by using the water extracts of these samples, prepared by shaking soil sample with deionized, distilled water in 1:1 ratio for 5 minutes. Subsequently, the contents were equilibrated for thirty minutes and filtered. The filtrate was used for the determination of physicochemical parameters in accordance with standard methods. The moisture content of the soil samples was determined gravimetrically [14].

2.4. Determination of Metal Contents of Soil Samples. In order to determine the metal contents of soil samples, air-dried and sieved soil samples, (2 g) were digested by using HNO₃ and H₂O₂ [14]. The digested samples were then diluted with distilled water and analyzed for the selected metals by using Hitachi Flame Atomic Absorption Spectrophotometer (FAAS) model Z-5000.

The speciation studies of selected metals in the soil matrix were carried out by adopting the sequential extraction procedure as recommended by Community Bureau of References [15]. The procedure comprised of extracting exchangeable, reducible, oxidizable, and residual fractions by using glacial acetic acid, hydroxyl ammonium chloride, H₂O₂-ammonium acetate, and nitric acid, respectively. After each extraction, the contents were centrifuged and subsequently filtered. All the four fractions obtained were analyzed for the estimation of selected metals, that is, Co, Fe, Cd, Ni, Pb, and Cr by FAAS.

For the determination of trace metals in the rice grains and plant samples, wet acid digestion method was used whereby one gram portion of sample was digested with HClO₄ and conc. HNO₃ in the presence of traces of H₂SO₄. The contents were cooled to room temperature and diluted with doubly distilled water. For Fe and Mn determination, the contents were boiled for few minutes before filtering [14]. All the analyses were performed in triplicate and the corresponding result matched within 0.05%.

2.5. Statistical Analysis of Data. In order to develop the better understanding of the obtained data set on various physicochemical parameters of soil and various metals present in the soil, plants, and grains samples, the univariate and multivariate statistical analyses were performed. They involved the extraction of basic statistical parameters like mean, standard deviation, skewness, and kurtosis essential to determine the spread and distribution of measured data. Correlation coefficient analysis was carried out to establish the correlation pattern of various metal pairs in the same media and also in different media like soil, plant, and grain samples. The multivariate statistical analysis in terms of principal component analysis and cluster analysis were performed by using statistic software [16] to get a better understanding of sources of various metals in the soil, plant, and grain samples [17].

The mobility index values of the soil samples were determined by using the formula provided in literature [18]. A high mobility index of a metal was indicative of its bioavailable and mobile nature [19].

3. Results and Discussion

3.1. Physicochemical Parameters. The physicochemical parameters of thirty-five soil samples collected from different paddy fields of Shakargarh, Pakistan are provided in Table 1. The pH of collected samples was found to be alkaline with small variations. This alkaline pH may decrease the metal mobility by the formation of precipitates, by increasing the number of available adsorption sites and decreasing the competition of H⁺ for adsorption, and also by increasing the metal stability with humic substances [20].
The high moisture contents were noted for these soil samples that are characteristic of loamy textured soil.

The mean conductivity of the samples was found to be 975.4 $\mu$S cm$^{-1}$. The chloride, nitrate, and sulphate levels exhibited the order NO$_3^-$ > SO$_4^{2-}$ > Cl$^-$ with their mean concentrations standing at 24.30, 14.01, and 9.828 g/kg, respectively. Sources of these enhanced levels were traced in agronomic activities such as use of natural and synthetic fertilizers, herbicides, and pesticides used to improve the crop yields. Parental soil quality is another factor that may contribute to the enhanced levels of these anions.

3.2. Metal Levels in the Soil, Plants, and Grain Samples. The total metal contents of soil, plant, and grain samples are presented in Table 2. In the soil samples, Fe was found to be present at the highest mean concentration of 4074 mg/kg ranging from 1823 to 7498 mg/kg. It was followed by Pb standing at 1065 mg/kg with an observed standard deviation of 1092. The order for mean levels of the rest of the metals was Co > Ni > Cr > Cd with their respective levels being 747.2 > 85.84 > 37.80 > 35.02 mg/kg. The large differences observed between mean and median values evidenced nonnormal distribution of the data. Moreover, all the metals exhibited the levels far more exceeding the National Environmental Quality Standards as depicted in Figure 1 [21]. The data set obtained for metals presented an order quite similar to those observed in previous studies [2, 22]. Although Fe concentration levels are high in the studied soil samples as compared to other metals, these levels are lower than the maximum values established by the European and Spanish legislation for rice-forming soils [23].
The addition of fertilizers/micronutrients to the agricultural soils may result in enhanced Fe and Mn levels [24]. These Fe rich soils, under aerobic conditions may act as As accumulators [25, 26], which is found in the form of arsenate bound to clay particles. A good correlation, therefore, has been reported between extractable Fe, Mn, and As [27, 28], which may lead to high plant exposure to these metals and thus risk of plant uptake with consequent contamination of whole food chain [29]. Rice has been found to be most efficient at accumulating As into grains than other plants but if rice is grown under aerobic conditions, the extent of bioaccumulation of As and other metals may be reduced [30]. Further, reducing conditions and presence of organic matter may promote As mobilization to groundwaters through ion exchange mechanisms with phosphorous derived from fertilizers [31–33] thereby making it unfit for any viable human use.

In order to study the influence of enhanced metal levels in the soil on the plants and human populations, the metal content of rice plants and grains raised in these soils was also determined and incorporated in Table 2 in the form of descriptive statistics. The data evidenced Fe to be present at the highest mean level of 1256 mg/kg in rice plants ranging from 639.3 to 1624 mg/kg. It was followed by Co being present at mean level of 71.58 mg/kg. Ni and Pb were found to be present at mean concentrations of 54.50 and 48.81 mg/kg, respectively. Cr was present at quite smaller levels than Co and Ni but still at appreciable levels of 9.173 mg/kg. Cd was the metal that was present at the least mean concentration of 0.849 mg/kg. Thus, the overall order of mean concentrations of metals in rice plants was found to be Fe > Co > Ni > Pb > Cr > Cd.

The corresponding data set for rice grains obtained from these rice plants also presented Fe to be present at the highest mean concentration of 536.1 mg/kg. Co was the metal that secured the second highest concentration of 62.03 mg/kg against the mean concentration of 49.89 mg/kg. Pb was present at a mean concentration of 45.75 mg/kg, far exceeding the permissible limits in rice grains in China and Australia, that is, 0.3 to 5.2 mg/kg [34–36]. Cd was found at sub-ppm levels and was well within the safety limits that were set to range from 0.02 to 1 mg/kg in China, Australia, and Japan for rice grains [26]. The order of mean metal levels for the present study was found to be Fe > Co > Ni > Pb > Cr > Cd. Thus, the studied rice grains exhibited mean Pb levels far exceeding the safe limits. The data set obtained for grains also presented mean metal order quite comparable to that found in plants.

The orders of various metals observed in three media were quite comparable with few exceptions, that is, Pb secured the second highest position in soil while in the plant and grain samples it was present at the fourth position. The highest levels of Fe in the three media depicted their similar origin. The different orders of metals in these media may be explained on the basis of differences in nature of these metals and their bioavailability in the soil.

Ni, Co, and Cr concentrations were also comparable in both soil and plant samples with small variations as the bioavailability of metals depends upon the nature of the metal and the properties of soil. It is observed that metals from anthropogenic sources tend to be more mobile than pedogenic or lithogenic ones.

High concentration of metals in the soil does not necessarily imply their availability to plants. In the solid phase, the metals are distributed among the various soil components thereby producing various physicochemical forms that determine metal mobility [19]. Thus, in order to better assess the bioavailability of metals and their chemical association with the soil components metal fractionation behavior was studied by using the fractionation scheme proposed by community bureau of references.

The results of the fractionation analysis of the metals in the soil are presented in Table 3, where the mean values for each fraction are reported. The distribution of the metals in various operationally defined fractions evidenced that Fe was mostly found to be associated with oxidizable fraction (1743 mg/kg). The reducible fraction of this metal was also present at an appreciable concentration of 1590 mg/kg. The least amount was found to be associated with acid soluble fraction, that is, 80.77 mg/kg. For Co most of the metal was found to be associated with oxidizable fraction (372.5 mg/kg). The overall order of mean levels of all the fractions was oxidizable > residual > reducible > acid soluble. Ni being present at a total concentration of 85.84 mg/kg was mostly associated with oxidizable and residual fractions with mean concentration of 24.10 and 19.61 mg/kg, respectively. Reducible fraction of this metal was present at mean level of 16.67 mg/kg, while the acid soluble fraction was found to be present at mean levels of 14.86 mg/kg. The mobility index of this metal was found to be 0.183.

Cd, another heavy metal, was present at a total mean concentration of 35.02 mg/kg. The highest concentration of this metal was found to be associated with oxidizable fraction, that is, 10.80 mg/kg. The acid soluble and reducible fractions were present at comparable levels of 9.012 and 9.011 mg/kg, respectively. Least concentration of the metal was found to be associated with residual fraction. The percent recovery of the metal was found to be 85.40 with a mobility index of 0.219.

Pb being present at a total concentration of 1065 mg/kg exhibited a total recovery of 99.60% during distribution among the four fractions. Its highest concentration was present in acid soluble fraction. Oxidizable fraction exhibited the second highest concentration of 377.4 mg/kg, while reducible fraction was present at about 216 mg/kg concentrations. The least concentration of this metal was found to be associated with residual fraction. The mobility index of the metal was found to be 0.330. Cr, one of the most hazardous metals, was found to be associated mostly with oxidizable fraction (16.06 mg/kg). The order of the rest of the fractions was found to be residual > acid soluble > reducible. The percentage recovery of this metal was found to be 96.52% with a mobility index of 0.183.

The mobility of an element is its capacity to pass into soil compartments where it is less energetically retained [37]. The extractable content of a heavy metal is an indicator of the quantity of metals available to plants. The proportion of this fraction relative to the total amount of the metal is also an indicator of its comparative mobility [4]. The comparison of
3.3. Correlation Coefficient Matrix. The deficiency or excess of micronutrients in soil is directly associated with the plant uptake, which is indirectly associated with soil physicochemical characteristics and plant species. The physicochemical characteristics of soil are known to control the fate of the metals and largely influence the plant-soil interaction through rhizospheric processes.

The correlation coefficient matrix for various metals and physicochemical parameters of soil is presented in Table 4. The pH of these soil samples was found to be significantly negatively correlated with Co, Pb, and Cr with \( r \)-values of 0.495, 0.410, and 0.483, respectively. Chloride was also found to be significantly negatively correlated with Fe and Ni. Sulphate on the other hand was found to be significantly
Table 5: Correlation coefficient matrix for metal levels in different media (n = 35).

<table>
<thead>
<tr>
<th></th>
<th>Fe(s)</th>
<th>Co(s)</th>
<th>Ni(s)</th>
<th>Cd(s)</th>
<th>Pb(s)</th>
<th>Cr(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(p)</td>
<td>0.406</td>
<td>−0.240</td>
<td>0.342</td>
<td>−0.177</td>
<td>0.358</td>
<td>0.301</td>
</tr>
<tr>
<td>Co(p)</td>
<td>−0.182</td>
<td>0.488</td>
<td>−0.597</td>
<td>−0.498</td>
<td>−0.602</td>
<td>−0.437</td>
</tr>
<tr>
<td>Ni(p)</td>
<td>0.535</td>
<td>−0.507</td>
<td>0.557</td>
<td>0.412</td>
<td>0.487</td>
<td>0.604</td>
</tr>
<tr>
<td>Cd(p)</td>
<td>−0.031</td>
<td>−0.128</td>
<td>0.063</td>
<td>0.180</td>
<td>0.080</td>
<td>−0.149</td>
</tr>
<tr>
<td>Pb(p)</td>
<td>0.672</td>
<td>−0.799</td>
<td>0.815</td>
<td>0.696</td>
<td>0.604</td>
<td>0.889</td>
</tr>
<tr>
<td>Cr(p)</td>
<td>0.783</td>
<td>−0.809</td>
<td>0.792</td>
<td>0.653</td>
<td>0.646</td>
<td>0.904</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Fe(s)</th>
<th>Co(s)</th>
<th>Ni(s)</th>
<th>Cd(s)</th>
<th>Pb(g)</th>
<th>Cr(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(g)</td>
<td>0.400</td>
<td>−0.209</td>
<td>0.048</td>
<td>0.565</td>
<td>−0.332</td>
<td>0.165</td>
</tr>
<tr>
<td>Co(g)</td>
<td>−0.535</td>
<td>0.566</td>
<td>−0.599</td>
<td>−0.195</td>
<td>−0.604</td>
<td>−0.378</td>
</tr>
<tr>
<td>Ni(g)</td>
<td>0.270</td>
<td>−0.222</td>
<td>0.348</td>
<td>0.256</td>
<td>0.596</td>
<td>0.444</td>
</tr>
<tr>
<td>Cd(g)</td>
<td>−0.457</td>
<td>0.481</td>
<td>−0.338</td>
<td>−0.429</td>
<td>−0.427</td>
<td>−0.323</td>
</tr>
<tr>
<td>Pb(g)</td>
<td>0.312</td>
<td>−0.407</td>
<td>0.631</td>
<td>0.059</td>
<td>0.672</td>
<td>0.463</td>
</tr>
<tr>
<td>Cr(g)</td>
<td>−0.259</td>
<td>0.082</td>
<td>0.166</td>
<td>0.078</td>
<td>0.130</td>
<td>0.129</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Fe(g)</th>
<th>Co(g)</th>
<th>Ni(g)</th>
<th>Cd(g)</th>
<th>Pb(g)</th>
<th>Cr(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(p)</td>
<td>−0.066</td>
<td>0.076</td>
<td>0.237</td>
<td>0.221</td>
<td>0.161</td>
<td>0.013</td>
</tr>
<tr>
<td>Co(p)</td>
<td>−0.290</td>
<td>0.072</td>
<td>−0.353</td>
<td>0.114</td>
<td>−0.318</td>
<td>−0.500</td>
</tr>
<tr>
<td>Ni(p)</td>
<td>0.033</td>
<td>−0.030</td>
<td>0.415</td>
<td>0.170</td>
<td>0.250</td>
<td>0.242</td>
</tr>
<tr>
<td>Cd(p)</td>
<td>−0.211</td>
<td>0.399</td>
<td>−0.517</td>
<td>−0.146</td>
<td>−0.346</td>
<td>−0.398</td>
</tr>
<tr>
<td>Pb(p)</td>
<td>0.294</td>
<td>0.016</td>
<td>0.212</td>
<td>0.104</td>
<td>0.325</td>
<td>0.409</td>
</tr>
<tr>
<td>Cr(p)</td>
<td>−0.252</td>
<td>0.109</td>
<td>−0.428</td>
<td>0.094</td>
<td>0.049</td>
<td>−0.303</td>
</tr>
</tbody>
</table>

$r$-values are significant at $\pm 0.282$ at $P = 0.05$ level; s: soil, p: rice plant, and g: rice grain.

positively correlated with Pb, Co, and Cr with $r$-values of 0.511, 0.696, and 0.617, respectively.

The data presented in Table 4 evidenced a number of strong correlations among various metal pairs in different media. In case of soil, a strong positive correlation was observed between Cd and Pb with an $r$-value of 0.912, and Pb and Cr with $r$-value of 0.930. Cr was also strongly positively correlated with Co ($r$-value 0.978). Similarly, Pb was strongly positively correlated with Co (0.869). The strong positive correlations evidenced the similar origin of these metal pairs. Three of the studied metal pairs in the soil were found to be significantly negatively correlated, that is, Cd–Fe, Ni–Cd, and Pb–Ni evidencing the increase in the concentration of one metal with the decrease in the concentration of another.

In plant samples, Co was found to be significantly negatively correlated with almost all the metals with the exception of Fe. Cd–Fe pair in plant samples was found to be negatively correlated, and Cd was positively correlated with Pb and Cr similar to soil. In case of grain samples, the strongest negative correlation was observed between Co–Ni pair with an $r$-value of 0.930. Fe was also found to be negatively correlated with Ni and Pb. Similarly, negative correlation was observed between Co–Pb pair. The strongest positive correlation was found in Pb–Cr pair, a situation quite similar to one encountered in plant and soil samples, evidencing their common origin in the three media. Ni–Cd pair in rice grains was significantly negatively correlated similar to soil. Cu–Ni and Co–Pb pairs were found to be significantly negatively correlated in plant and rice grain samples while they exhibited a significantly positive correlation in plant matrix, the reason may be traced in the phytoavailability of metals.

The correlation coefficient matrix for the metals in different media, that is, soil, plant, and grains is presented in Table 5. In case of soil versus plant metal correlation, the strongest positive correlation was observed between Cr contents in the two media, evidencing that the source of enhanced Cr levels in the plants originates from their enhanced levels in the soil. It was also supported by the high percentage of oxidizable fraction of Cr present in the soil. No such correlation was observed between Cr of soil and Cr of grains. It was indicative of the fact that although soil enhanced levels lead to absorption of Cr from soil, this excessive Cr was not translocated to the grains. It was also evidenced by a negative correlation between Cr(plants) and Cr(grains).

Pb of the soil was also significantly positively correlated with Pb of plants. Similarly Pb of soil was also significantly positively correlated with Pb contents of rice grains. As the grains constitute a direct edible part of plants, their accumulation of Pb is quite hazardous and may lead to various health hazards among the people consuming it. Similarly, Ni, Co, and Fe of soil were also found to be strongly positively associated with these metals in plant samples, but in case of rice grains only Ni was found to be significantly positively correlated. This matrix evidenced that enhanced levels of almost all the studied metals in the soil lead to an enhanced uptake by the arable parts of rice plants but these metals with the exception of Pb were not translocated to the grains, thus not posing any threat to human beings directly but indirectly they may constitute hazards because these arable parts may be used as food by the animals that constitute food for humans.

3.4. Source Apportionment Studies

3.4.1. Principle Component Analysis (PCA). The sources of various metals in soil, plants, and grain samples were determined in terms of varimax normalized factor loading (Table 6). Only two rotated factors were obtained for the total metal contents of various metals present in thirty-five soil samples collected from different rice fields with a cumulative eigenvalue of 88.53%. The first factor received major contribution from Co, Cd, Pb, and Cr, while the second factor being associated with an eigen value of 1.746 received major loadings from Fe and Ni. It is noteworthy that the metals arising from nitrate fertilizers, that is, Cd and Co, are grouped together in a single factor depicting their similar source.

The most significant sources of Fe in the soil are various fertilizers that are added to the soil to replenish various deficiency symptoms. It may also have geologic origins. It has been found that soils rich in Fe and Mn are also having enhanced As levels [38]. The sources of Pb in soil are traced in various fungicide and pesticide sprays that are used at various stages of crop production, containing Pb as an impurity [39]. It is known that phosphatic fertilizers are manufactured by using the phosphate ore, which is contaminated with different metals such as Pd, Cr, and Fe. These metal contaminants
Table 6: Varimax normalized factor loadings for metals in soil, plant, and grain samples.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Soil 1</th>
<th>Soil 2</th>
<th>Plant 1</th>
<th>Plant 2</th>
<th>Grain 1</th>
<th>Grain 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.069</td>
<td>0.834</td>
<td>0.413</td>
<td>0.808</td>
<td>−0.7</td>
<td>−0.070</td>
</tr>
<tr>
<td>Co</td>
<td>0.912</td>
<td>0.18</td>
<td>−0.555</td>
<td>0.322</td>
<td>−0.086</td>
<td>−0.809</td>
</tr>
<tr>
<td>Ni</td>
<td>−0.136</td>
<td>0.912</td>
<td>0.813</td>
<td>−0.042</td>
<td>0.266</td>
<td>0.809</td>
</tr>
<tr>
<td>Cd</td>
<td>0.787</td>
<td>−0.587</td>
<td>0.256</td>
<td>−0.86</td>
<td>0.628</td>
<td>−0.657</td>
</tr>
<tr>
<td>Pb</td>
<td>0.949</td>
<td>−0.275</td>
<td>0.895</td>
<td>0.131</td>
<td>0.701</td>
<td>0.528</td>
</tr>
<tr>
<td>Cr</td>
<td>0.977</td>
<td>0.016</td>
<td>0.927</td>
<td>0.099</td>
<td>0.807</td>
<td>0.110</td>
</tr>
<tr>
<td>Eigenvalue</td>
<td>3.566</td>
<td>1.746</td>
<td>2.875</td>
<td>1.516</td>
<td>2.453</td>
<td>1.689</td>
</tr>
<tr>
<td>% Total variance</td>
<td>59.43</td>
<td>29.11</td>
<td>47.92</td>
<td>25.27</td>
<td>40.89</td>
<td>28.15</td>
</tr>
<tr>
<td>Cumulative eigenvalue</td>
<td>3.566</td>
<td>5.312</td>
<td>2.875</td>
<td>4.391</td>
<td>2.453</td>
<td>4.142</td>
</tr>
<tr>
<td>Cumulative %</td>
<td>59.43</td>
<td>88.53</td>
<td>73.19</td>
<td>40.89</td>
<td>69.04</td>
<td>88.53</td>
</tr>
</tbody>
</table>

Also become a part of fertilizer and on application to soil lead to hazardous effects [40]. This Pb contamination of paddy soils may change the soil microorganisms and soil enzymatic activities and deteriorate the soil fertility, which may directly affect the rice physiological indices and results in rice yield decline and quality deterioration. Ultimately, Pb accumulates in human body through food chain and thus endangers human health [34].

These fertilizers contain not only higher amounts of Fe, Co, and Pb but also traces of Cd and Ni as impurities that constitute the sources of their enhanced levels in the soil. The levels of heavy metals determined by several authors in phosphate fertilizers were 0.1–170 mg kg$^{-1}$ Cd, 1–12 mg kg$^{-1}$ Co, 7–38 mg kg$^{-1}$ Ni, 7–225 mg kg$^{-1}$ Pb while in the nitrate fertilizers they were 0.05–8.5 mg kg$^{-1}$ Cd and 5.4–12 mg kg$^{-1}$ Co. Moreover, the heavy metals also form a part of the active compounds of pesticides. Thus repeated and excessive fertilizer and pesticide applications may lead to much enhanced concentrations of heavy metals in the soil [22].

Sewage sludge is commonly used in agriculture as soil conditioner/fertilizer due to easy availability and low costs [41]. But it may also contain substantial amounts of toxic metals such as Zn, Cu, Cr, Ni, Cd, and Pb [42–44], which are quite mobile due to the presence of organic matter in sewage sludge [45]. In addition to direct application, municipal sewage sludge disposed of through land filling is also a potential source of spreading toxic metals to nearby lands [46]. Thus, sewage sludge is also a major contributor of metals in agricultural lands and poses serious threats to human health and environment [47, 48].

The varimax normalized factor loadings were also recorded for the metal data of rice plant samples to trace the sources of various metals. Similar to the soil samples again, two rotated factors were obtained. The first factor being associated with a cumulative variance of 47.92% received major contribution from Ni, Pb, and Cr, thereby depicting similar origin of these metals in the rice plants from agrochemicals that are used simultaneously and contain these metals. The second factor received major contribution from two metals only, that is, Fe and Cd.

The rice grains are the edible part of the plant used throughout the world, so it is quite imperative to evaluate their quality in terms of total metal content. Thus varimax normalized rotation of metal data of rice grains yielded two rotated factors with cumulative variance of 69.04%. First factor received major loading for Pb and Cr similar to plant samples. Fe was another major contributor of this factor. Factor 2 was mainly associated with Co and Ni with an eigenvalue of 1.698.

The food chain (soil-plant-human) pathway is recognized as one of the major pathways for human exposure to soil contamination. However, the ingested dose of heavy metals is not equal to the absorbed pollutant dose in reality, as a fraction of the ingested heavy metals may be excreted, with the remainder accumulated in body tissues where they affect human health [19]. Similarly, only limited quantities of metals are absorbed into the upper parts of the plants, probably because the roots act as a barrier to the translocation of metals within the plant [49]. The phenomenon is thus responsible for different metal levels in different parts of plants.

3.4.2. Cluster Analysis. The clustering behavior of the selected metals in soil, plant, and grain samples was studied by cluster analysis and is depicted in Figure 2. In case of soil samples, the selected metals formed two primary clusters within linkage distance of 0.5. One of the primary clusters comprised of Fe and Ni depicting their similar origin. The second cluster comprised of Cr, Pb, Cd, and Co, all linked within linkage distance of 0.2, evidencing their close association.

In case of plant samples, Fe stood alone depicting its different source. Similar to plant samples Pb, Cr, and Ni were found to be associated closely within linkage distance of 0.5, depicting their common origin in plants and grains. On overall basis, the cluster analysis confirmed the findings of the principle component analysis.

4. Conclusion

The present study evidenced enhanced levels of all the studied metals in the paddy soil samples due to abundant and unmanaged use of agrochemicals. The sequential extraction procedure revealed that the oxidizable and reducible phases
of metals like Fe and Ni were predominant and they exhibited reduced mobility index values in the soil samples. Pb and Cd possessed high mobility due to their very high extractability in acid soluble fraction. The correlation coefficient matrix evidenced that enhanced metal levels in soil may lead to their accumulation in aerial parts of plants but not in edible parts of plants, that is, grains. A quite hazardous situation was observed where the rice grains in addition to aerial parts of plants also accumulated Pb, which may lead to various health hazards. Despite these hazards, rice plants may act a hyper-accumulators of Cr, Ni, Co, and Fe by accumulating these metals in their aerial parts but not in edible parts. The study also evidenced that there is a dire need to address the problem of agricultural soil pollution and to educate the farmers about the optimum and wise use of agrochemicals.

References


Submit your manuscripts at http://www.hindawi.com