# Assessment of co-contamination in soil samples from agricultural areas in and around Lucknow city, Uttar Pradesh, India

**Arpna Ratnakar and Shikha***

Department of Environmental Science, Babasaheb Bhimrao Ambedkar University, Vidya-Vihar, Raebareli Road, Lucknow 226 025, India

**An environmental evaluation of agricultural lands situated close to industrial areas in and around Lucknow city was carried out to determine the effect of co-contamination in the study area. Analysis of soil samples revealed the presence of mercury and cadmium at higher levels than their normal distribution in soil. Apart from heavy metals, the herbicide Butachlor was also detected in most of the soil samples studied. Co-contaminated soils pose a major threat to agricultural ecosystems since the presence of different concentrations of heavy metals may inhibit biodegradation of organic pollutants, which further affects metal bioavailabilty and phytoremediation.**

**Keywords:** Agricultural lands, co-contamination, heavy metals, industrial area, soil samples.

THE agricultural lands close to urban areas are subjected to various processes like traffic emissions, energy and fuel production, power transmission, mining, metal refining, intensive agriculture and dumping of sludge that contribute to contamination of soil[1]. Wastewater irrigation practices lead to the accumulation of heavy metals like nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), iron (Fe) and lead (Pb) in the soil and chronic exposure to heavy metals can lead to their accumulation in plant parts affecting plant growth[2], ground cover apart from having a negative impact on soil micro flora. Pesticides and agrochemicals are important inputs for improved yield and better quality crop production. However, an unplanned, erroneous and indiscriminate use of these organic compounds leads to the destruction of bio-control agents, pesticide residues in agro-ecosystems and environmental pollution, besides accumulating in the food chain[3].

Agricultural lands may be co-contaminated with both organic and inorganic substances, but limited work has been carried out for clean-up and monitoring of such co-contaminated lands. While studying such sites, it becomes important to consider the interactions of both organic and inorganic substances with respect to soil physico-chemical and biological properties that may affect both the form as well as availability of pollutants. Different metal concentrations have been shown to inhibit the microbial biodegradation of organics[4] and their further interaction with organic pollutants affects metal bioavailability[5].

In the present study, 15 representative agricultural soil samples from areas in and around Lucknow city, Uttar Pradesh (UP), India, were collected to assess the co-contamination of heavy metals and herbicides. Overall, the aim of the study was to assess the physico-chemical and microbial properties of soils which are co-contaminated with inorganic (heavy metals) and organic compounds (herbicides), and analysis of correlation matrix.

## Materials and methods

### *Study area*

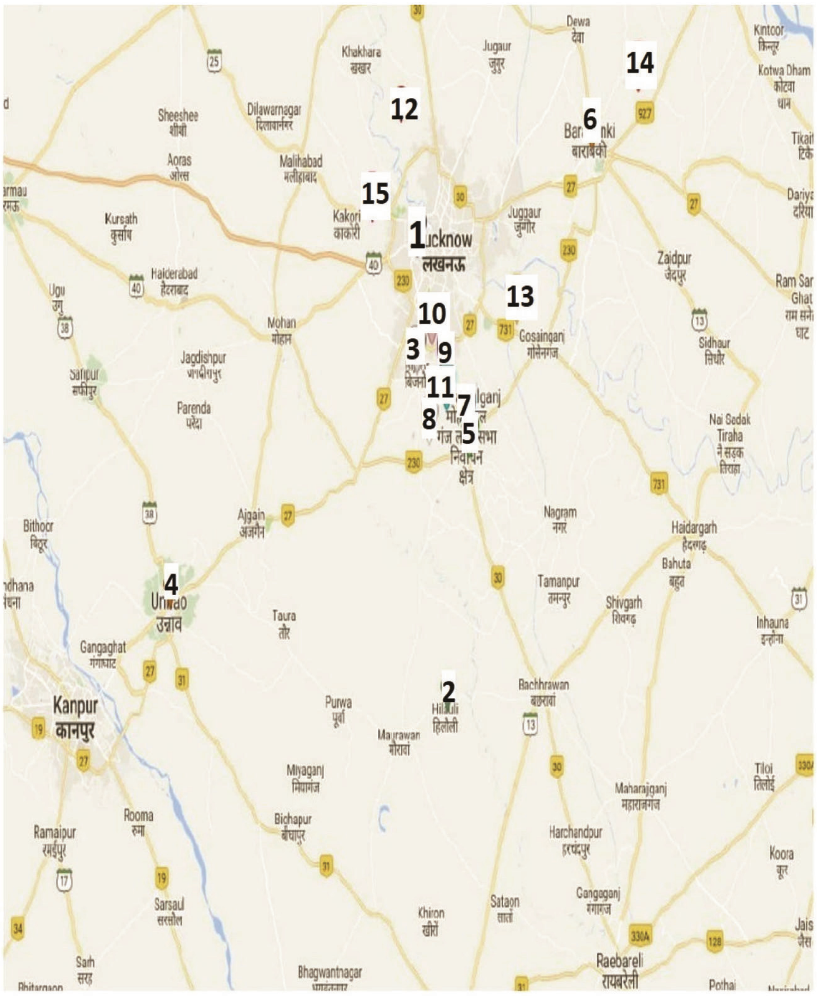
Lucknow, a large city in northern India, is the capital of UP. It is situated between 23°52′–31°28′N and 77°3′–84°39′E (ref. 6). The study area includes agricultural lands in and around Lucknow city (Figure 1). Industries such as brick kiln, leather tanning and electroplating are situated close to the study area.

### *Sampling and analysis*

For the present study, a total of 45 topsoil (0–15 cm) samples were collected from 15 different agricultural lands through Z-pattern of sampling. Next, 300 g of each soil sample was taken in a 50 m diameter area and a composite sample was formed. The samples were collected in polyethylene bags, properly labelled and stored in the laboratory at 4°C prior to analysis[7]. To obtain reference data, soil samples were collected from remotely situated agricultural lands, where no herbicides were used previously (control soil). These soil samples were processed similar to test samples from the fields.

The soil samples were air-dried, pulverized and sieved (2 mm sieve) prior to analysis. Analytical-grade reagents were used throughout the study.

*For correspondence. (e-mail: envscibbau@ymail.com)




| | |
|---|---|
| 1 | Aishbagh |
| 2 | Mohani |
| 3 | Bijnor |
| 4 | Unnao |
| 5 | Mohanlalganj |
| 6 | Barabanki |
| 7 | Mau |
| 8 | Diwanganj |
| 9 | Kalli West |
| 10 | Control |
| 12 | Kamlapur |
| 13 | Semarou |
| 11 | Kalli East |
| 14 | Suklai |
| 15 | Bhawaniganj |

*Map drawn with the help of Multiplottr (https://multiplottr.com/)

**Figure 1.** Study sites in and around Lucknow (UP).

### *Determination of physico-chemical parameters*

The physico-chemical parameters such as pH, electrical conductivity (EC), organic carbon (OC), organic matter (OM), moisture content (MC), texture, available nitrogen (N), phosphorus (P) and potassium (K) were determined following standard methodology[8–15]. For heavy metals (Pb, Hg, Cu, Cr, Ni, As, Cd, Mn, Fe) 1 g of each of the sieved soil samples was digested following the nitric/perchloric acid digestion procedure using Varian Spectra AA-250 plus Atomic Absorption spectrophotometer (AAS)[16].

### *Soil bacteria*

A spread-plate technique was used to estimate the soil bacterial population[17]. Colony-forming units per gram of soil (cfu/g) was calculated using the equation of Johnson and Case[18].

### *Pesticide estimation in soil using HPLC*

All the soil samples were air-dried at room temperature, pulverized and passed through 100 μm sieves and HPLC of soil samples was done using standard protocol given by Tekel and Stefan[19].

## Results and discussion

### *Physico-chemical properties of soil*

Tables 1 and 2 show average values of physical and chemical properties of soil samples respectively. The studied soil samples were found to vary between sandy loam and loam, which was in agreement to the texture observed in the studied area by Upadhyay and Sharma[20]. The pH of the soil samples ranged from 6.76 to 9.03, more towards neutral to alkaline in nature. Soil EC, an indicator of its salinity[21], was found to vary from 60 to

**Table 1.** Physical characteristics of soil samples (mean ± SD)

| Soil sampling site | Sand (%) | Silt (%) | Clay (%) | pH | EC (μS/cm) | MC (%) |
|---|---|---|---|---|---|---|
| Control | 35.2 ± 1.31 | 21.3 ± 1.41 | 43.5 ± 2.01 | 7.56 ± 0.36 | 80.21 ± 3.11 | 20.32 ± 0.17 |
| Barabanki | 41.9 ± 2.14 | 22.8 ± 1.42 | 35.3 ± 2.15 | 8.7 ± 0.163 | 119.63 ± 2.73 | 22.46 ± 0.58 |
| Suklai | 38.7 ± 1.3 | 23.2 ± 2.15 | 38.1 ± 2.03 | 8.466 ± 0.047 | 167.93 ± 3.41 | 32.23 ± 2.45 |
| Mohanlalganj | 35.5 ± 1.61 | 22.4 ± 0.71 | 42.1 ± 1.52 | 8.4 ± 0.00 | 202.33 ± 0.47 | 24.32 ± 0.55 |
| Bijnor | 42.3 ± 2.31 | 23.1 ± 1.34 | 34.6 ± 0.51 | 8.066 ± 0.047 | 123.23 ± 5.06 | 17.56 ± 0.37 |
| Mohani | 41.4 ± 0.29 | 22.8 ± 1.05 | 35.8 ± 0.07 | 8.366 ± 0.047 | 118.86 ± 4.81 | 14.08 ± 0.15 |
| Kamlapur | 39.8 ± 2.17 | 23.4 ± 0.045 | 36.8 ± 1.04 | 7.86 ± 0.047 | 109.86 ± 2.14 | 9.16 ± 0.12 |
| Unnao | 42.4 ± 0.46 | 23.1 ± 0.071 | 34.5 ± 1.71 | 8.73 ± 0.094 | 132.06 ± 2.62 | 19.20 ± 0.68 |
| Kalli East | 36.4 ± 1.63 | 24.9 ± 2.14 | 38.7 ± 3.16 | 6.76 ± 0.047 | 119.39 ± 0.40 | 22.34 ± 0.04 |
| Kalli West | 39.7 ± 0.78 | 21.78 ± 0.06 | 38.52 ± 2.14 | 7.26 ± 0.094 | 60.00 ± 1.29 | 17.75 ± 0.02 |
| Semarou | 43.1 ± 1.23 | 22.8 ± 2.52 | 34.1 ± 1.17 | 7.83 ± 0.047 | 163.94 ± 1.85 | 22.04 ± 0.04 |
| Mau | 36.5 ± 1.04 | 24.2 ± 0.061 | 39.3 ± 0.62 | 8.26 ± 0.047 | 139.32 ± 1.74 | 18.92 ± 0.54 |
| Diwanganj | 37.3 ± 0.05 | 23.2 ± 1.26 | 39.5 ± 0.39 | 9.03 ± 0.047 | 129.48 ± 1.69 | 33.52 ± 0.61 |
| Bhawaniganj | 38.6 ± 0.48 | 21.2 ± 2.11 | 40.2 ± 1.28 | 8.76 ± 0.047 | 271.18 ± 2.73 | 25.03 ± 0.23 |
| Aishbagh | 35.3 ± 0.73 | 22.7 ± 0.042 | 42 ± 2.10 | 7.33 ± 0.124 | 285.2 ± 0.73 | 31.24 ± 0.11 |
| Soil range | 35.2–43.1 | 21.2–24.9 | 34.1–43.5 | 6.76–9.03 | 60–285.2 | 9.16–33.52 |
| Soil average | 38.94 | 22.85 | 38.20 | 8.09 | 142.84 | 17.41 |

**Table 2.** Chemical characteristics of soil samples (mean ± SD)

| Soil sampling site | OC % | OM (%) | N (kg/ha) | P (kg/ha) | K (kg/ha) |
|---|---|---|---|---|---|
| Control | 2.12 ± 0.41 | 3.65 ± 0.13 | 58.23 ± 4.41 | 6.53 ± 0.72 | 96.41 ± 0.18 |
| Barabanki | 6.52 ± 0.81 | 11.25 ± 0.26 | 71.39 ± 3.38 | 10.86 ± 0.15 | 89.6 ± 0 |
| Suklai | 5.95 ± 1.32 | 10.25 ± 0.05 | 81.53 ± 5.43 | 16.06 ± 0.22 | 306.13 ± 0.57 |
| Mohanlalganj | 6.62 ± 0.65 | 11.41 ± 0.05 | 187.11 ± 4.79 | 15.97 ± 0.33 | 597.33 ± 1.15 |
| Bijnor | 6.75 ± 0.05 | 11.63 ± 0.50 | 317.78 ± 4.79 | 33.34 ± 0.47 | 769.06 ± 1.52 |
| Mohani | 6.73 ± 0.89 | 11.61 ± 0.59 | 127.53 ± 3.62 | 11 ± 0.08 | 365.86 ± 0.577 |
| Kamlapur | 7.19 ± 0.43 | 12.39 ± 0.26 | 251.92 ± 1.81 | 10.84 ± 0.07 | 548.8 ± 1.0 |
| Unnao | 6.07 ± 0.05 | 10.47 ± 0.19 | 291.64 ± 5.43 | 16.38 ± 0.07 | 291.2 ± 1.0 |
| Kalli East | 4.22 ± 0.05 | 7.28 ± 0.06 | 128.57 ± 3.13 | 31.31 ± 0.21 | 282.98 ± 2.51 |
| Kalli West | 3.21 ± 0.11 | 5.53 ± 0.16 | 97.21 ± 5.43 | 29.05 ± 0.039 | 477.86 ± 0.57 |
| Semarou | 3.64 ± 0.11 | 6.28 ± 0.23 | 163.07 ± 6.27 | 11.25 ± 0.15 | 160.90 ± 0.57 |
| Mau | 3.40 ± 0.05 | 5.87 ± 0.16 | 102.44 ± 1.81 | 22.23 ± 0.11 | 481.6 ± 2 |
| Diwanganj | 3.22 ± 0.1 | 5.56 ± 0.19 | 91.98 ± 1.81 | 18.95 ± 0.10 | 162.0 ± 2.3 |
| Bhawaniganj | 3.64 ± 0.11 | 6.27 ± 0.08 | 154.70 ± 3.62 | 10.7 ± 0.15 | 117.973 ± 2.08 |
| Aishbagh | 4.25 ± 0.20 | 7.33 ± 0.17 | 486.08 ± 3.13 | 37.3 ± 0.35 | 272.906 ± 2.51 |
| Soil range | 2.12–7.19 | 3.65–12.39 | 58.23–486.08 | 6.53–37.3 | 89.6–769.06 |
| Soil average | 4.90 | 8.45 | 174.07 | 18.78 | 431.90 |

285.2 μS/cm. The average MC of soil samples ranged from 9.16% to 33.52%.

OC content of the soils varied from 2.12% to 7.19% (Table 2). Soil OM was found to vary from 3.65% to 12.39% which was directly related to the content of OC in soil samples studied. The high OC content results in plants taking up nutrients more easily, and this leads to change in pH which improves soil condition for crop growth[22].

N, P and K are micronutrients essential for plant growth. The available N content varied from 58.23 kg/ha in control soil to the highest value in Aishbagh soil, i.e. (486.08 kg/ha; Table 2). The available N content of most of the soil samples was high. The average amount of P in soil ranged from 6.53 to 37.3 kg/ha in different agricultural sites. On the basis of the limits suggested by Muhr *et al.*[23], most of the soil samples (94%) were low (< 20 $P_2O_5$ kg/ha) in available P status and the rest were in medium range (20–50 $P_2O_5$ kg/ha).

Potassium is another important nutrient for crops. The available K content in soil samples varied from 89.6 kg/ha in Barabanki soil to 769 kg/ha in Bijnor soil (Table 2), which was highest among all the sites. Most of the soil samples (96%) were in medium range for K, i.e. 125–300 kg/ha (ref. 23).

## *Correlation matrix among different physico-chemical properties*

The relationships between different physico-chemical parameters were analysed by Pearson's correlation coefficient (Table 3). A high correlation coefficient (near +1 or –1) indicates good relationship between two variables;

**Table 3.** Correlation matrix among physico-chemical properties of soil

| | pH | EC (µS) | MC (%) | OC (%) | OM (%) | N (Kg/ha) | P (kg/ha) | K (kg/ha) | Sand (%) | Silt (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| EC (µS) | NS | 1 | | | | | | | | |
| MC (%) | 0.21 | 0.53* | 1 | | | | | | | |
| OC (%) | 0.29 | NS | –0.33 | 1** | | | | | | |
| OM (%) | 0.29 | NS | –0.33 | 0.99** | 1 | | | | | |
| N (kg/ha) | NS | 0.51 | 0.00 | 0.29 | 0.29 | 1 | | | | |
| P (kg/ha) | –0.50 | 0.13 | 0.20 | NS | NS | 0.52* | 1 | | | |
| K (kg/ha) | 0.31 | –0.16 | 0.23 | NS | NS | NS | NS | 1 | | |
| Sand (%) | 0.29 | –0.27 | –0.41 | 0.45 | 0.45 | NS | NS | NS | 1 | |
| Silt (%) | NS | NS | NS | 0.25 | 0.25 | NS | 0.37 | NS | NS | 1 |
| Clay (%) | NS | 0.316 | 0.40 | –0.51 | –0.51 | NS | NS | NS | –0.94** | –0.32 |

*Correlation is significant at 0.05 level. **Correlation is significant at 0.01 level.

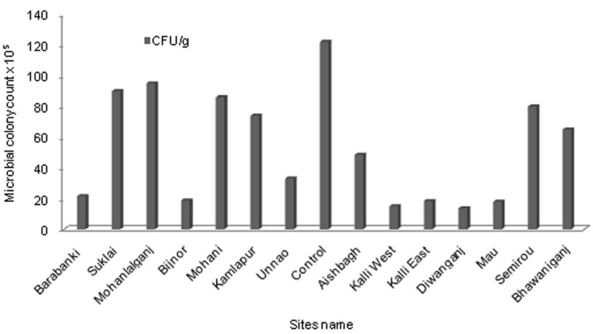



**Figure 2.** Soil bacteria count (CFU/g).

its concentration around 0 indicates no relationship between them at a significant level (0.05%). It can be strongly correlated, if $r > 0.7$, while if $r$ values lies between 0.5 and 0.7, it shows moderate correlation.

In Table 3, various notable significant correlations among different physico-chemical parameters have been summarized. pH established non-significant correlation with all parameters while showing negative correlation with $P$ ($r = –0.5$). EC showed positive relationship with MC ($r = 0.53$. $P > 0.05$) and the rest of the parameters did not reveal any significant relationship. MC had no significant relationship with any physico-chemical parameters studied.

Results revealed that OC showed positive correlation with organic matter ($r = 0.99$, $P > 0.01$) and negative correlation with clay particles ($r = –0.51$), while with the rest of the parameters no significant correlation was observed (Table 3).

Nitrogen showed positive correlation with phosphorus ($r = 0.52$, $P > 0.05$). Similar results have been reported by Ray and Mukhopadhyay[24]. Nitrogen established non-significant correlation with the rest of the parameters. With regard to phosphorus, relationships with all physico-chemical properties were statistically not significant. Phosphorus showed moderate relationship with nitrogen. Sand showed negative correlation with clay ($r = –0.94$, $P < 0.01$). Similar results for sand were observed by Kumar *et al.*[25] and no significant relationship was observed with the rest of the parameters.

## *Soil bacteria count*

The quantification of the number of soil bacteria is an indication of soil health, e.g. if there are $10^6$–$10^8$ culturable bacteria present per gram of soil, it would be considered a healthy soil. Results (Figure 2) revealed the highest bacterial population in control soil (122 CFU/g × $10^5$) and the lowest population was recorded in Diwanganj soil (13.7 CFU/g × $10^5$). A number less than $10^6$ per gram indicates poor soil health, which may be due to lack of nutrients as found in low OM soils, abiotic stress imposed by extreme soil pH values (<5 or >8), or toxicity imposed by organic/inorganic anthropogenic contaminants.

## *Distribution of heavy metals*

Soils have the natural ability to hold onto metals. Acidification in the soil causes some metals to bind less tightly with soil particles, except Hg. Metals freed in this way become available to plants to which they may or may not be toxic. Table 4 shows the concentration of heavy metals in the soil at different sampling sites.

Pb levels in the collected soil samples were in the range 1.25–59 mg/kg, which falls within the permissible limits set by the World Health Organization (WHO)[26].

Cr levels in the study sites ranged from 1.4–213.42 mg/kg with an average of 59 mg/kg. Concentration of Cr in some agricultural sites (Barabanki, Kamlapur, Unnao) exceeded the permissible level (50 mg/kg) for soils as given by Ministry of Agriculture, Fisheries and Food (MAFF)[27] and Council of the European Communities (EC)[28].

Hg concentration in the studied soil samples was between 0 and 24 mg/kg (Kalliwest). Its concentration in all the soil samples, except control soil, Mohani and Unnao was above the permissible limit (0.3–5 mg/kg; Table 5).

Fe had the highest mean concentration among all metals studied and its level ranged from 1500 to 6450 mg/kg with mean being 3157.36 mg/kg, while the concentration of Cu (0.57–5.00 mg/kg; Table 5) was found within the range given by WHO[29].

**Table 4.** Distribution of heavy metal and metal content at different sites

| | Heavy metal concentration (mg/kg) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sites | Pb | Cr | Hg | Fe | Cu | Ni | Cd | As | Mn |
| Control | 6.28 | 5.17 | 0.02 | 1500 | 0.57 | 0.01 | 5.51 | 0.00 | 101.31 |
| Barabanki | 59 | 194.05 | 8.3 | 4600 | 0.58 | 0.86 | 45.92 | 1.6 | 307.82 |
| Suklai | 36.75 | 78.22 | 7.1 | 5745 | 1.39 | 1.51 | 38.1 | 2.45 | 405.35 |
| Mohanlalganj | 46.5 | 47.5 | 7.5 | 4345 | 2.17 | 1.42 | 61.76 | 2.6 | 343.82 |
| Bijnor | 49 | 50.5 | 20 | 5355 | 1.58 | 1.38 | 20.98 | 1.69 | 325.35 |
| Mohani | 28.5 | 72.7 | ND | 6450 | 0.59 | 0.61 | 55.73 | 2.79 | 213.22 |
| Kamlapur | 1.25 | 213.42 | 10 | 2050 | 1.46 | 2.20 | 39.09 | 3.61 | 348.9 |
| Unnao | 24 | 188.67 | ND | 3762.5 | 0.75 | 0.87 | 40.85 | 3.75 | 307.82 |
| Kalli East | 48 | 8.24 | 14.4 | 2359.5 | 1.63 | 26.34 | 22.85 | ND | 458.4 |
| Kalli West | 20 | 1.4 | 24 | 1643.46 | 0.78 | 25.15 | 58.15 | ND | 243.36 |
| Semarou | 28.4 | 3.72 | 6.8 | 1881.75 | 0.93 | 21.57 | 61.95 | ND | 403.6 |
| Mau | 21.2 | 2.48 | 12.0 | 2042.4 | 1.09 | 12.82 | 52.18 | ND | 289.6 |
| Diwanganj | 19.2 | 5.24 | 5.2 | 1519.05 | 0.90 | 17.05 | 10.18 | ND | 332 |
| Bhawaniganj | 18.8 | ND | 19.2 | 2129.4 | 0.84 | 15.67 | 37.28 | ND | 289.2 |
| Aishbagh | 57.2 | 13.72 | 10.0 | 1977.36 | 5.00 | 19.32 | 17.39 | ND | 413.2 |
| Soil range | 1.25–59 | 0.0–213.42 | 0.0–24 | 1500–6450.0 | 0.57–5.00 | 0.01–26.34 | 5.51–61.76 | 0.0–3.75 | 101.31–458.4 |
| Soil average | 30.93 | 59.0 | 9.63 | 3157.36 | 1.35 | 9.78 | 37.86 | 1.23 | 318.86 |

**Table 5.** Mean values of heavy metals for paddy soils, worldwide normal surface soils, critical concentrations for contaminated soils, Indian standards, European Union standards, MEF compared with values of the present study

| Elements | Mean values For paddy soils [a] (mg/kg) | Mean values for worldwide normal surface soil [b] (mg/kg) | Critical soil concentration[c] (mg/kg) | Indian standard[d] (mg/kg) | European Union standard[e] (EU 2002; mg/kg) | Present study (mg/kg) |
|---|---|---|---|---|---|---|
| Pb | 23.3 | 22–44 | 100–400 | 250–500 | 300 | 32.95 |
| Cd | 0.34 | 0.37–0.78 | 3–8 | 3–6 | 3 | 38.89 |
| Cu | 20.7 | 13–24 | 60–125 | 135–270 | 140 | 1.37 |
| Cr | 64 | 12–83 | 75–100 | – | 150 | 72.06 |
| Mn | – | <1800 | 1500–3000 | – | – | 327.44 |
| Ni | – | 100* | 150* | 75–150 | 75 | 9.84 |
| As | – | 50* | 100 | – | 20 | 2.68 |
| Hg | – | 0.005–0.5* | 0.3–5* | – | – | 9.63 |
| Fe | – | – | – | 75–150 | – | 3276.02 |

[a–c]Data from refs 40–43. [d]Indian standards for agricultural soils[44]. [e]European standards for agricultural soils[45].

Concentration of Ni, As and Mn in the soil samples was within permissible limits (Table 5).

Cd level in all the soil samples was found between 5.51 and to 61.76 mg/kg, which was greater than the permissible limits (0.01–3.0 mg/kg) as observed by MAFF[27] and EC[28]. High Cd level in soil might be due to application of high doses of phosphate fertilizers and metal-based pesticides in agricultural crops[30].

## *Relationship among different heavy metals*

Pb showed positive correlation with Mn ($r = 0.51$, $P > 0.05$) and non-significant relationship with all heavy metals. Ni showed negative correlation with Cr ($r = –0.62$, $P < 0.05$) and strong negative correlation with As ($r = –0.75$, $P < 0.01$) and Fe ($r = –0.64$, $P < 0.01$). Fe showed significant correlation with Hg ($r = 0.50$), while with the rest of the heavy metals there was non-significant relationship. Similar result was also obtained for Ni by Tripathi and Mishra[31]. Hg showed negative correlation with As ($r = –0.38$) and non-significant relationship with the rest of the heavy metals (Table 6).

Cr showed strong positive correlation with As ($r = 0.82$, $P > 0.01$) and negative correlation with Ni ($r = –0.6$, $P > 0.05$). Cd and Cu displayed non-significant relationship with the rest of the metals. As showed strong positive relationship with Cr ($r = 0.82$, $P > 0.01$) and positive relationship with Fe ($r = 0.64$, $P > 0.05$) while the rest of the parameters showed no relationship with As.

## *Relationship among different physico-chemical parameters and heavy metals*

Pb showed significant relationship with EC ($r = 0.42$) and silt ($r = 0.26$). Similar results were observed by Aysen[32]. Hg showed positive correlation with phosphorus ($r = 0.55$,

**Table 6.** Correlation among heavy metals

| | Pb | Hg | Cd | Cu | Ni | As | Cr | Fe |
|---|---|---|---|---|---|---|---|---|
| Hg | 0.149296 | 1 | | | | | | |
| Cd | 0.023014 | 0.087683 | 1 | | | | | |
| Cu | 0.504283 | 0.126405 | –0.24 | 1 | | | | |
| Ni | 0.04694 | 0.508918 | –0.00917 | 0.225302 | 1 | | | |
| As | –0.02702 | –0.38481 | 0.292171 | –0.11392 | –0.75** | 1 | | |
| Cr | –0.00045 | –0.31468 | 0.169693 | –0.1655 | –0.62* | 0.82** | 1 | |
| Fe | 0.452597 | –0.21506 | 0.269598 | –0.10535 | –0.64** | 0.64** | 0.387993 | 1 |
| Mn | 0.51* | 0.218865 | 0.055346 | 0.506862 | 0.39265 | 0.023127 | 0.044867 | 0.023281 |

*Correlation is significant at 0.05 level. **Correlation is significant at 0.01 level.

**Table 7.** Correlation among heavy metals and different physic-chemical parameters of soil

| | pH | EC | MC | OC | OM | N | P | K | Sand | Silt | Clay |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Pb | –0.09 | 0.42 | –0.01 | 0.33 | 0.34 | 0.32 | 0.50 | –0.13 | 0.02 | 0.26 | –0.10 |
| Hg | –0.32 | 0.17 | –0.29 | –0.13 | –0.13 | 0.09 | 0.55* | 0.04 | 0.00 | –0.03 | 0.00 |
| Cd | 0.14 | 0.11 | –0.19 | 0.30 | 0.30 | –0.19 | –0.24 | –0.27 | 0.40 | –0.01 | –0.37 |
| Cu | –0.37 | 0.61* | –0.20 | 0.06 | 0.06 | 0.77** | 0.62* | –0.00 | –0.45 | 0.12 | 0.38 |
| Ni | –0.49 | 0.21 | –0.52* | –0.63* | –0.63* | 0.01 | 0.49 | 0.08 | –0.21 | 0.15 | 0.15 |
| As | 0.37 | –0.05 | 0.24 | 0.87** | 0.87** | 0.19 | –0.30 | –0.01 | 0.41 | 0.13 | –0.43 |
| Cr | 0.32 | –0.13 | 0.11 | 0.74** | 0.75** | 0.14 | –0.34 | –0.13 | 0.49 | 0.16 | –0.51* |
| Fe | 0.36 | 0.05 | 0.39 | 0.77** | 0.77** | 0.00 | –0.09 | –0.09 | 0.41 | 0.11 | –0.42 |
| Mn | –0.15 | 0.56* | –0.08 | 0.24 | 0.24 | 0.37 | 0.44 | 0.09 | 0.02 | 0.61* | –0.22 |

**Correlation is significant at 0.01 level. *Correlation is significant at 0.05 level.

$P > 0.05$), negative correlation with pH ($r = –0.32$) and non-significant relationship with the rest of the parameters.

Cd was found to show non-significant statistical relationship with the soil parameters studied. Cu showed positive correlation with EC ($r = 0.61$, $P > 0.05$) and N ($r = 0.77$, $P > 0.01$). Similar results were observed by Nauman and Khalid[33]. Cu also showed positive correlation with P ($r = 0.62$, $P > 0.05$) and negative correlation with sand ($r = –0.45$). Ni showed strong negative correlation with MC ($r = –0.52$, $P < 0.05$), OC and OM ($r = –0.63$, $P < 0.05$).

As showed strong positive correlation with OC and OM ($r = 0.87$, $P > 0.01$). Cr showed strong positive correlation with OC ($r = 0.74$, $P > 0.01$) and OM ($r = 0.75$, $P > 0.01$) and negative correlation with clay ($r = –0.51$, $P < 0.05$). Similar results were observed by Nauman and Khalid[39]. Fe showed positive correlation with OC and OM ($r = 0.77$, $P > 0.01$) and non-significant relationship with the rest of the physico-chemical parameters. This indicates that soils with high organic carbon content are rich in Fe. Mali *et al.*[34] reported similar correlation between OC and Fe content. Mn showed positive correlation with EC ($r = 0.56$, $P > 0.05$) and silt ($r = 0.61$, $P > 0.05$), and non-significant parameters relationship with the rest of the parameters (Table 7).

## *Cluster analysis of different heavy metals*

Figure 3 shows scatter analysis of different metals. Hg showed strong negative relation with Cr, while Cd showed positive correlation with Cr. Hg showed positive correlation with Pb and Cd. The results revealed that any soil having high concentration of Cr might have low amounts of Hg.

## *Pesticides*

In India approximately several thousand tonnes of herbicides are used for weed control, mainly in irrigated crops and plantations[35]. Chemical, biological and physical forces play an important role on the status of pesticides in soil. Pesticides remain or persist in the soil from days to years depending upon their type, OM, pH, soil moisture and temperature[36].

While collecting soil samples a survey was carried out to identify the pesticides used by farmers in agricultural lands in the selected sites. The survey revealed that majority of farmers used the herbicide Butachlor (*N*-butoxymethyl-2-chloro-2,6-diethylacetanilide) belonging to the acetanilide class. It is used as a selective pre-emergent herbicide[37]. Integration of inorganic (metals and heavy metals) and organic source of nutrients for crop production is the significant factor influencing herbicide behaviour in soils[38]. Butachlor has also been found at significant levels in agricultural areas around Delhi[25].

In the light of the aforementioned context, HPLC chromatogram of standard Butachlor was compared with that of extracts of untreated soil samples from different agricultural sites. Out of the 15 soil samples studied, only 8 soil revealed Butachlor residues. In the HPLC

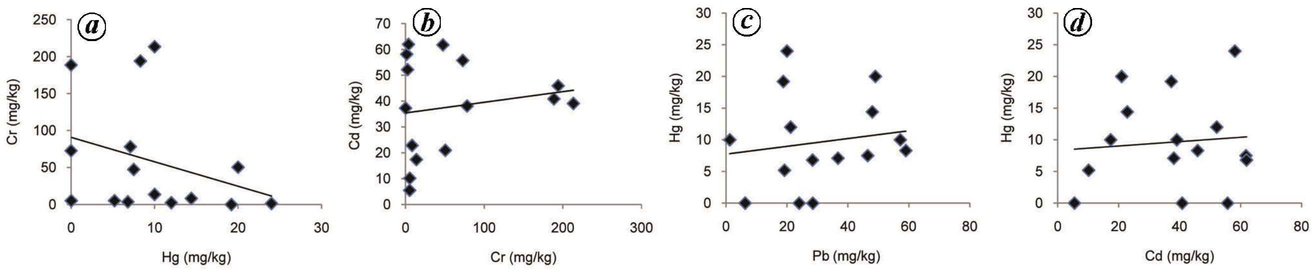



**Figure 3.** ***a***, Correlation between Hg and Cr; ***b***, Correlation between Cr and Cd; ***c***, Correlation between Hg and Pb; ***d***, Correlation between Hg and Cd.

**Table 8.** Pesticide concentration in soil samples from different sites

| Sampling site | Concentration (μg/kg) |
|---|---|
| Control | 1.21 (0.4) |
| Suklai | 4.78 (0.6) |
| Bijnor | 4.91 (0.8) |
| Kalli East | 46.56 (2.1) |
| Kamlapur | 43.93 (1.0) |
| Kalli West | 18.97 (0.9) |
| Mau | 111.88 (2.7) |
| Mohanlalganj | 5.60 (0.6) |
| Unnao | 12.06 (0.7) |

Each datum is the mean of triplicate analyses ($n = 3$).

chromatogram, several small peaks were present apart from the standard peak corresponding to Butachlor that revealed the presence of other pestide, herbicide or insectide residues corresponding to Atrazine (pesticide), Benomyl (pesticide), Cypermethrin (pesticide), Endosulfan (insecticide), Methyl Parathion (insecticide), Isoproturon (herbicide), Chloropyriphos (insecticide) and Dichlorvos (insecticide).

However, maximum residues of Butachlor in soil samples were preliminary compared with the corresponding residue limits used in other countries, considering the shortage of local standard for identifying soil pollution of the herbicides.

Table 8 summarizes the results on Butachlor residues determined in soil samples. The concentration of Butachlor in the soil samples ranged from 4.78 μg/kg to 111.8 μg/kg; the measured concentration at Kalli East (46.56), Kamlapur (43.93) and Mau (111.88) soils was above the maximum allowable concentration. The national regulations relevant for pesticide residues in agricultural soils define the maximum residue level for Butachlor as 40 μg/kg (ref. 39).

## Conclusion

The heavy metal concentration of soils in different land uses practicing extensive agricultural activities was analysed to assess soil quality in terms of its physicochemical properties. The data gave an insight into the level of co-contamination of agricultural areas with pesticide residues and heavy metals. Among the heavy metals tested, content of Hg and Cd was higher than the maximum permissible limits. Residues of several pesticides, herbicides and insecticides were detected in some of the soil samples. However, the presence of Butachlor exceeding the relevant minimum residual limit, indicated potential risk to the crop ecosystem apart from having a negative impact on human health. The observed heavy metals and pesticides in agricultural soils studied may be a matter of concern for future food chain accumulation and human health. Thus regular studies on herbicides and heavy metals are required to maintain soil health and contamination levels. Through regular assessment of heavy metals and herbicides in the soil possible sources of contamination as well as risks could be minimized, and mitigatory measures could be adopted thereof for bringing a large number of brown field sites into productive use.

1. Nouri, J., Khorasani, N., Lorestani, B., Karami, M., Hassani, A. H. and Yousefi, N., Accumulation of heavy metals in soil and uptake by plant species with phytoremediation potential. *Environ. Earth Sci.*, 2009, **59**(2), 315–323.
2. Sharma, R. K., Agrawal, M. and Marshall, F., Heavy metal contamination in vegetables grown in wastewater irrigated areas of Varanasi, India. *Bull. Environ. Contam. Toxicol.*, 2006, **77**(2), 312–318.
3. Khan, M. J., Zia, M. S. and Qasim, M., Use of pesticides and their role in environmental pollution. *World Acad. Sci. Eng. Technol.*, 2010, **72**,122–128.
4. Sandarin, T. and Maier, R., Impacts of metals on the biodegradation of organic pollutants. *Environ. Health Perspect.*, 2003, **111**, 1093–1101.
5. Gao, Y., Xiong, W., Ling, W. and Xu, J., Sorption of phenanthrene by soils contaminated with heavy metals. *J. Chemosphere*, 2006, **65**(8), 1355–1361.
6. www.nidm.gov.in/pdf/dp/Uttar.pdf (accessed on 20 April 2017).
7. Sun, S. H., Cai, H. Y., Chang, S. X. and Bhatti, J. S., Sample storage-induced changes in the quantity and quality of soil labile organic carbon. *Sci. Rep.*, 2015, **5**, 17496.
8. Brady, N. C., *The Nature and Properties of Soils*, McMillan, New York, 1996, 11th edn, p. 621.
9. Chopra, S. L. and Kanwar, J. S., *Analytical Agricultural Chemistry*, Kalyani Publishers, New Delhi, 2005.
10. American Society for Testing and Materials D 2216-98, Standard test method for laboratory determination of water (moisture) content of soil and rock by mass. Reprinted from the *Annual Book of ASTM Standards*, 1999.
11. Shirazi, M. A. and Boersma, L., A unifying quantitative analysis of soil texture. *Soil Sci. Am. J.*, 1984, **48**(1), 142–147.

12. Walkey, A. and Black., I. A., An examination of the Degtajareff method for soil organic matter determination and a proposed modification of the chromic acid titration. *Soil Sci*., 1934, **37**(1), 29–38.
13. Subbiah, B. V. and Asija, G. L., A rapid procedure for the determination of available nitrogen in soil. *Curr. Sci.*, 1956, **25**, 259–260.
14. Black, C. A., *Methods of Soil Analysis*, Academic Press, New York, USA, 1965, p. 367.
15. Olsen, S. R., Cole, C. V., Watanabe, F. S. and Dean, L. A., Estimation of available phosphorus in soils by extraction with sodium bicarbonate. Circular, US Department of Agriculture, Washington, DC, 1954, p. 19.
16. Odu, C. T. I., Babalola, O., Udo, E. J., Ogunkunle, A. O., Bakare, T. A. and Adeoye, G. O., Laboratory Manual for Agronomic Studies in Soils, Plants and Microbiology, Department of Agronomy, University of Ibadan, Nigeria, 1986, p. 83.
17. Martin, J. P., Use of acid rose Bengal and streptomycin in plate method for estimating soil fungi. *Soil Sci*., 1950, **69**, 215–232.
18. Johnson, T. R. and Case, C. L., *Laboratory Experiments in Microbiology*, Pearson Education, San Francisco: USA, 8th edn, 2007.
19. Tekel, J. and Stefan, H., Pesticide residue analyses in plant material by chromatographic methods: clean-up procedures and selective detectors. *J. Chromatogr. A*, 1996, **754**, 397–410.
20. Upadhyay, R. and Sharma, Y. K., Soil characteristics and their nutritional status in Lucknow District. *J. Biol. Chem. Res*., 2016, **33**(1), 578–585.
21. Solanki, H. A. and Chavda, N. H., Physico-chemical analysis with reference to seasonal changes in soils of Victoria Park Reserve Forest, Bhavnagar (Gujarat). *Life Sci. Leafl*., 2012, **8**, 62–68.
22. Aydinalp, C. and Marinova, S., Distribution and forms of heavy metals in some agricultural soils. *Pol. J. Environ. Stud*., 2003, **12**(5), 629–630.
23. Muhr, G. R., Datta, N. P., Sankarasubramoney, H., Dever, F., Laley, V. K. and Donahue, R. L., Critical test values for available N, P and K in different soils. In *Soil Testing in India*, US Agency for International Development, New Delhi. 1965, 2nd edn, pp. 120.
24. Ray, S. K. and Mukhopadhyay, D., A study on physicochemical properties of soils under different tea growing regions of West Bengal (India). *Int. J. Agric. Sci*., 2012, **4**(8), 325–329.
25. Kumar, B. *et al.*, Distribution of pesticides in sediments from Municipal Drains in Delhi, India. *Asi. J. Sci. Res*., 2011, **4**(3), 271–280.
26. WHO, Evaluation of certain food additives and contaminants (Forty-first report of the Joint FAO/WHO Expert Committee on Food Additives), WHO Technical Report Series, No. 837, World Health Organization, Geneva, 1993.
27. Ministry of Agriculture, Fisheries and Food and Welch Office Agriculture Department code of good agriculture practice for the protection of soil, Draft Consultation Document, MAFF, London, 1992; http://www.scirp.org (accessed on 20 November 2018).
28. Council of the European Communities, Directive 86278 EEC on the protection of the environment and in particular of the soil when sewage sludge is used, Brussels, OJL 181, 4.7, 1986, pp. 6–12.
29. WHO/FAO, Joint FAO/WHO Food standards program Codex Alimentation Commission, 13th session, Report of the Thirty Eighth session of the codex committee on food hygiene. ALINORM, Houston, USA, 2007.
30. Singh, S. and Kumar, M., Heavy metal load of soil, water and vegetables in peri-urban Delhi. *Environ. Monit. Assess.*, 2006, **120**(1–3), pp. 79–91.
31. Wong, S. C., Li, X. D., Zhang, G., Qi, S. H. and Min, Y. S., Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environ. Pollut.* 2002, **119**(1), 33–44.
32. Chandrajith, R., Dissanayake, C. B. and Tobschall, H. J., The abundances of rarer trace elements in paddy (rice) soils of Sri Lanka. *Chemosphere*, 2005, **58**(10), 1415–1420.
33. Kabata-Pendias, A., Agricultural problems related to excessive trace metal contents in soils. In *Heavy Metals: Problems and Solution* (eds Salomons, W., Forstner, U. and Mader, P.), Springer-Verlag, Berlin, Germany, 1995, p. 3–18.
34. Alloway, J. B., The origins of heavy metals in soils. In *Heavy Metals in Soils* (ed. Alloway, B. J.), Chapman & Hall. London, UK, 1995, pp. 29–39.
35. Awashthi, S. K., *Prevention of Food Adulteration Act No. 37 of 1954 Central and State Rules as Amended for 1999*, Ashoka Law House, New Delhi, 2000, 3rd edn, pp. 1–71.
36. European Union, Heavy metals in wastes. European Commission on Environment, EU, Brussles, Belgium, 2002.
37. Tripathi, A. and Misra, D. R., A study of physico-chemical properties and heavy metals in contaminated soils of municipal waste dumpsites at Allahabad, India. *Int. J. Environ. Sci*., 2002. **2**(4), 2024–2033.
38. Aysen, A., *International Conference on Agriculture and Biotechnology*, IACSIT Press, Singapore, 2013, vol. 60; http://doi:10.7763/IPCBEE.
39. Nauman, M. and Khalid, S. K., Heavy metals contamination of soils in response to wastewater irrigation in Rawalpindi region. *Pak. J. Agric. Sci*., 2010, **47**(3), 215–224.
40. Mali, V. S., Zende, N. A. and Verma, U. K., Correlation between soil physico-chemical properties and available micronutrients in salt affected soils. In Poster presentation, 17th WCSS, 14–21, Thailand, 2002, Symposium No. 33, p. 2220.
41. Kumar, B. *et al.*, Distribution of pesticides, herbicides, synthetic pyrethroids and polychlorinated biphenyls in sediments from drains of Delhi, India. *Organohalo. Comp*., 2008, **70**, 1120–1123.
42. Spark, K. M. and Swift, .R. S., Effect of soil composition and dissolved organic matter on pesticide sorption. *Sci. Total. Environ*., 2002, **298**, 147–161.
43. Chinnusamy, C., Janaki, P., Muthukrishnan, P. and Jeyaraman, S., Long term herbicidal weed management integrated with nitrogen nutrient in transplanted rice–rice cropping system of Tamil Nadu, India. *Pak. J. Weed Sci. Res*., 2012, **18**, 95–103.
44. Janaki, P., Meena, S. and Chinnusamy, C., Persistence and degradationof herbicides in rice, maize and soybean grown vertisols of Tamil Nadu, Southern India. In Proceedings of the 2nd International Conference on Novel and Sustainable Weed Management in Arid and Semi-Arid agro Ecosystem, Santorini, Athens, Greece, 7–10 September 2009.
45. The Official Gazette of the Republic of Serbia, Guideline on permitted concentrations of dangerous and harmful substances in soil and irrigation water and methods for their investigation, 1994, vol. 23, pp. 553–554.

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