Heavy metals abundance and distribution in soil, groundwater and vegetables in parts of Aligarh, Uttar Pradesh, India: implication for human health risk assessment

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Anthropogenic activities impact the natural environment, leading to the deterioration of its suitability for living organisms and human health. The present study investigated the concentration and distribution of potentially harmful elements Fe, Cr, Cu, Mn, Ni, Pb and Cd in the soil, groundwater and vegetables, and the consequent human health risk effects. Results revealed high content of Cu (mean = 331 mg kg\(^{-1}\)) and Zn (mean = 348.4 mg kg\(^{-1}\)) in the soils and exceeded permissible limits. Geo-accumulation Index (I\(_{geo}\)) values were high in respect of Cu (I\(_{geo}\) = 3.86, 3.16), and Zn (I\(_{geo}\) = 2.4, 1.6), indicating pollution in the industrial training institute (ITI) and Gular areas in Aligarh respectively. Groundwater from ITI and Gular recorded maximum content of Cr, Cu, Ni, Mn, Zn, Pb and Cd. Ni and Pb contents exceeded the highest permissible limits. Heavy metal pollution index (HPI) with mean HPI = 806.08 indicated serious groundwater contamination in the ITI and Gular areas. Content of heavy metals in vegetables appeared to be under permissible limit with some exception for Ni and Zn. Finally, the assessment of hazard index (HI) indicated that there was no potential risk to human health upon consumption of vegetables, whereas water ingestion posed serious human health hazard (HI = 2.62) in parts of Aligarh.

**Keywords:** Groundwater, hazard index, heavy metals, human health risk, soil, vegetables

HEAVY metal contamination is a matter of serious concern in different countries of the world\(^1\). The environmental deterioration due to heavy metal contamination, has intensified with the rapid increase of the global population and growth of industrial, agricultural and domestic activities\(^2\). Diversity and enhancement of heavy metal contamination is concomitant with the industrial revolution, massive urbanization and economic globalization, leading to food security and human health issues\(^3\).

Some heavy metals such as Fe, Cu and Zn are essential for living organisms; but excessive content of these metals may be detrimental to living organisms including the human beings\(^4,5\). Heavy metals may get enriched due to natural processes such as chemical weathering of minerals or volcanic activity and reach bioavailable levels\(^6\). However, the most concerning origin of heavy metal pollution is attributed to anthropogenic activities and high levels of contamination that are mainly reported from industrial areas\(^6,7\).

Non-enforcement of strict regulations and/or high cost of treatment processes have prompted most factories, particularly in the densely populated countries not to treat their waste before discharging it into an open land or water bodies. Furthermore, agriculture-related activities such as irrigation from wastewater, addition of sewage sludge (biosolids) and manures to agriculture fields, enhance the bioavailability of heavy metals from the soils and get ultimately transferred to vegetables and/or through groundwater, thus entering the human body via food chain and causing harm to human health\(^8\).

Aligarh has a population of around 1,211,000 (ref. 9). Due to its location in the Indo-Gangetic basin, the primary activity of the population in Aligarh is agriculture, and the total harvested area is around 565,553 ha. However, in recent decades urbanization and industrial activities have rapidly increased. By the end of 2018, large factories and small scale industries numbering 5506 have led to an increase in the built-up area by 6.85% within a span of 15 years\(^9\). Impact of this increase in industries and urbanization has not been examined in terms of heavy metal contamination and its potential risk to human health. This study assesses the heavy metal pollution in soil, water and plants in Aligarh region and the hazard that may arise from human exposure to heavy metals.

**Materials and methods**

**Study area**

Aligarh city lies in the western part of Uttar Pradesh, India (27°35’N and 77°29’E and 78°36’E). The geographical area is ~3650 sq. km. The study area is an alluvial plain comprising clay, silt, sand and gravels of...
Quaternary age. Climate is humid, subtropical (typical of North Central India), with monsoon season between June and September. Temperature varies widely from 41°C in June (summer) to 7.6°C in January (winter). The area receives an annual average precipitation of around 750 mm and most of the rainfall (~89%) occurs between July and August during south-west monsoon season.

Sample collection

The field work and sample collection were carried out in February 2018. Soil samples were collected from five locations: Industrial Training Institute (ITI) (S1 and S2), Gular (S3, S4 and S5), Mathura Road (S6), Upperkot (S7) and Talaspur (S8) (Figure 1). These places have different densities of industries with ITI being the densest to Talaspur area being sparse. Soil samples were collected from a depth of about 20–25 cm, each weighing 500 g and stored in clean plastic bags. While collecting the samples, care was taken to remove plant roots and pebbles.

Groundwater samples were collected from dug wells located in the immediate vicinity of the factories. All samples were collected and stored in clean polyethylene bottles of 1 litre capacity and 2–3 drops of HNO₃ were added to the water samples to acidify them (pH <2) to prevent precipitation and adsorption on the bottle walls.

The vegetable samples were collected using stainless steel trowel and knife, from the fields. They were also sampled from nearby markets. Approximately 500 g of each vegetable of seven species, namely Spinacia oleracea (spinach), Pisum sativum (peas), Solanum tuberosum (potato), Brassica oleracea var. capitata (cabbage), Brassica oleracea var. botrytis (cauliflower), Chenopodium album (Bathua) and Coriandrum sativum (coriander) were collected. All samples were stored in sealed plastic bags and taken to laboratory for further analysis.

Sample analysis

Soil samples were kept in plastic trays in dust-free place for 2–3 days to dry at room temperature. Dried soil samples were sieved to <2 mm grain size and powdered using agate mortar for further analysis. Each soil sample (0.5 g) was digested in 10 ml HF, 5 ml HNO₃ and 1 ml HClO₄ acid mixture in covered crucibles for 4 h at 90°C on a hot plate. After drying, 5 ml HNO₃ was added to the...
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residue and allowed to dry at the same temperature. After that, 20 ml 1 N HCl was added and heated at 90°C for 30 min. Finally, sample solution was filtered and diluted to 100 ml with double-distilled water.

Vegetables were cleaned using running tap water to remove dust and extraneous particles and chopped into small pieces after removing the non-edible parts. After that, they were dried in an oven at 90°C until a constant weight was achieved\(^\text{12}\). Then, the sample was powdered, homogenized and later ashed in a muffle furnace at 350–400°C. Later, 1 g of sample was mixed with 10 ml HNO\(_3\), 3 ml HClO\(_4\) and 2 ml HCl and heated on hot plate (at 60°C) for 30–45 min. Later, 10 ml of 1 N HCl was added to sample, and reheated until the mixture became transparent and was semi-dried. After cooling, the sample was filtered and diluted to 50 ml with double-distilled water.

Content of heavy metals (Fe, Cu, Zn, Pb, Ni, Mn and Cd) in the soil, groundwater and vegetables was determined by atomic absorption spectrometry (Thermo Scientific, M series) at the School of Environmental Sciences, Jawaharlal Nehru University (JNU), New Delhi. For the equipment calibration, certified single element standard solutions (Merck) were used. Additionally, reagent blanks were also used to measure the accuracy and precision of the analysis.

Data analysis

**Geo-accumulation index (I\(_\text{geo}\))**

The geo-accumulation index (I\(_\text{geo}\)), proposed by Muller\(^{13}\), is widely applied for assessing and quantifying heavy metal concentration in the sediments\(^6\). The I\(_\text{geo}\) is calculated using the equation

\[
I_{geo} = \log_2(C_d/1.5 \times B_0),
\]

where \(C_d\) is the concentration of metal in the soil sample, \(B_0\) geochemical background value of metal \(n\), after Turkish and Wedepohl\(^{14}\), and 1.5 was used as a correction factor for possible lithological variations. According to Muller\(^{13}\), there are seven classes of contamination based on I\(_\text{geo}\) values, viz. class 0 (I\(_\text{geo} \leq 0\)) indicating unpolluted, class 1 (0 < I\(_\text{geo} > 1\)) unpolluted to moderately polluted, class 2 (1 < I\(_\text{geo} > 2\)) moderately polluted, class 3 (2 < I\(_\text{geo} > 3\)) moderately to strongly polluted, class 4 (3 < I\(_\text{geo} > 4\)) strongly polluted, class 5 (4 < I\(_\text{geo} > 5\)) strongly polluted to extremely polluted, and class 6 (I\(_\text{geo} \geq 5\)) extremely polluted.

**Heavy metal pollution index**

This index is normally utilized for evaluating and assessing the overall impact of heavy metals on water quality. Heavy metal pollution index (HPI) is computed using eq. 3 (ref. 15)

\[
HPI = \frac{\sum_{i=1}^{n} (W_i Q_i)}{\sum_{i=1}^{n} W_i},
\]

where \(W_i\) is the unit weight of heavy metal, \(n\) the number of heavy metals considered, and \(Q_i\) is the sub-index of the \(i\)th heavy metal and is computed as

\[
Q_i = \sum_{i=1}^{n} \left( \frac{M_i}{S_i} \right) \times 100,
\]

where \(M_i\) is the examined value of the heavy metal, \(S_i\) is the recommended standard value for drinking water according to WHO guidelines\(^{16}\). The threshold value of HPI is 100, hence HPI value less than 100 can be considered low pollution of heavy metal, whereas HPI value greater than 100 may be considered as polluted water and harmful for human health.

**Transfer factor**

Transfer factor (TF) is used to evaluate the heavy metal transfer from soil to plants. Other terms, such as bioconcentration factor and the plant uptake factor, are used in quantifying heavy metal uptake by edible parts of the plants\(^3,11,12\). The heavy metal transfer from soil to plant can be quantified using eq. (4)

\[
TF = \frac{C_p}{C_s},
\]

where \(C_p\) is concentration of heavy metal in the plant, \(C_s\) is the concentration of heavy metal in the soil. TF > 1 indicates high metal accumulation in plant, TF ≈ 1 indicates non-influential metal uptake and TF < 1 indicates metal is excluded from plant uptake\(^{11}\).

**Health risk assessment**

The US environmental protection agency (USEPA) has evaluated the human health risk caused by the daily consumption of contaminated water and vegetables\(^{17}\). The exposure of human body to heavy metal occurs via different routes such as via ingestion, inhalation and dermal absorption\(^{12,15}\). In this study we only assessed the human health risk due to exposure to heavy metal by direct ingestion of water and vegetables. The exposure assessment is quantified as

\[
ADI_w = \frac{[C \times F \times IR \times E_I \times E_d]}{[BW \times AT]},
\]

\[
ADI_v = \frac{[C \times IR \times E_I \times E_d]}{[BW \times AT]},
\]

where ADI\(_w\) (mg/kg/day) and ADI\(_v\) (mg/kg/day) reflect average daily intake of metal via ingestion of vegetables.
and water respectively, C is the heavy metal concentration in vegetable (mg kg\(^{-1}\)), \(F\), conversion factor (0.085) used to convert vegetable from fresh weight to dry weight, IR represents ingestion rate for adults (0.240 kg day\(^{-1}\) and 2.51 day\(^{-1}\) for vegetable and water respectively), \(E_D\) represents the exposure frequency (365 days years\(^{-1}\)), \(E_{ch}\) the exposure duration (70 years), BW, the body weight, and AT represents the average exposure time for noncarcinogens.

Hazard quotient (HQ) is applied to determine the non-carcinogenic risk of heavy metals on human health\(^{17}\). The HQ can be quantified as the ratio between estimated dose and reference oral dose of the metal (\(R/D\)). The overall non-carcinogenic risk caused by more than one heavy metal can be assessed by Hazard index (HI), which is the summation of non-carcinogenic effects of heavy metals\(^{18}\).

\[
HQ_t = \frac{ADI_t}{R/D_t},
\]

\[
HQ_w = \frac{ADI_w}{R/D_w},
\]

\[
HI = \sum HQ_i.
\]

where \(R/D_t\) and \(R/D_w\) represent ingestion reference of vegetable and water respectively, \(HQ_t\) and \(HQ_w\) are the hazard quotients through ingestion of vegetable and water respectively, HI is hazard index and categorized into two levels – HI < 1 represents safe or low impact of heavy metals on human health, whereas HI ≥ 1 indicates greater detrimental risk on human health\(^{12,15}\).

**Results and discussion**

**Concentration of heavy metals in soil**

Soil samples were analysed to determine the concentration of Fe, Cr, Cu, Mn, Ni, Zn, Pb and Cd. The results are shown in Table 1 and Figure 2a. The Cu, Zn and Pb, along with Fe showed maximum concentration at the ITI site. The high abundance of these metals may be linked with the waste (solid and/or liquid) produced by lock

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**Table 1.** Heavy metal concentration in soil, groundwater and vegetables in Aligarh city

<table>
<thead>
<tr>
<th>Site no.</th>
<th>Fe</th>
<th>Cr</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Zn</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil (mg kg(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>24549</td>
<td>8.34</td>
<td>980.4</td>
<td>563.8</td>
<td>79.2</td>
<td>751.2</td>
<td>125.4</td>
<td>0.11</td>
</tr>
<tr>
<td>S2</td>
<td>34137.6</td>
<td>16.5</td>
<td>435.6</td>
<td>535</td>
<td>75.4</td>
<td>621.4</td>
<td>102.4</td>
<td>0.32</td>
</tr>
<tr>
<td>S3</td>
<td>25851</td>
<td>22.6</td>
<td>209.2</td>
<td>438.6</td>
<td>70.2</td>
<td>255</td>
<td>38.6</td>
<td>0.314</td>
</tr>
<tr>
<td>S4</td>
<td>26976.6</td>
<td>12.73</td>
<td>125.6</td>
<td>563</td>
<td>27.6</td>
<td>157.6</td>
<td>18.4</td>
<td>0.16</td>
</tr>
<tr>
<td>S5</td>
<td>23163</td>
<td>23.89</td>
<td>581.4</td>
<td>599.2</td>
<td>34.6</td>
<td>435</td>
<td>36.6</td>
<td>0.41</td>
</tr>
<tr>
<td>S6</td>
<td>33810</td>
<td>37.9</td>
<td>96.8</td>
<td>550.4</td>
<td>46.2</td>
<td>192.8</td>
<td>42.2</td>
<td>0.461</td>
</tr>
<tr>
<td>S7</td>
<td>30332.4</td>
<td>21.4</td>
<td>27.6</td>
<td>588.4</td>
<td>140.4</td>
<td>242.6</td>
<td>27.6</td>
<td>0.36</td>
</tr>
<tr>
<td>S8</td>
<td>25195.8</td>
<td>26.2</td>
<td>191.4</td>
<td>561.2</td>
<td>33.4</td>
<td>131.8</td>
<td>63.2</td>
<td>0.332</td>
</tr>
<tr>
<td>Mean ±</td>
<td>28001.9</td>
<td>20.32 ± 331 ±</td>
<td>549.95 ± 63.38 ±</td>
<td>348.43 ± 56.8 ±</td>
<td>0.29 ±</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SD</td>
<td>4237.6</td>
<td>9.88</td>
<td>320</td>
<td>49.3</td>
<td>37.18</td>
<td>230.44</td>
<td>38</td>
<td>0.14</td>
</tr>
<tr>
<td>EU(^{a})</td>
<td>–</td>
<td>140</td>
<td>150</td>
<td>–</td>
<td>75</td>
<td>300</td>
<td>300</td>
<td>3</td>
</tr>
<tr>
<td>ISP(^{b})</td>
<td>–</td>
<td>135–270</td>
<td>–</td>
<td>75–150</td>
<td>300–600</td>
<td>250–300</td>
<td>3–6</td>
<td></td>
</tr>
<tr>
<td>Groundwater (mg l(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>–</td>
<td>0.077</td>
<td>0.481</td>
<td>0.015</td>
<td>0.087</td>
<td>2.121</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>S2</td>
<td>–</td>
<td>0.069</td>
<td>0.435</td>
<td>0.015</td>
<td>0.074</td>
<td>2.00</td>
<td>0.03</td>
<td>0.015</td>
</tr>
<tr>
<td>S3</td>
<td>–</td>
<td>0.054</td>
<td>0.41</td>
<td>0.003</td>
<td>0.065</td>
<td>0.198</td>
<td>0.09</td>
<td>0.00</td>
</tr>
<tr>
<td>S4</td>
<td>–</td>
<td>0.049</td>
<td>0.31</td>
<td>0.003</td>
<td>0.073</td>
<td>0.178</td>
<td>0.08</td>
<td>0.00</td>
</tr>
<tr>
<td>S5</td>
<td>–</td>
<td>0.067</td>
<td>0.27</td>
<td>0.386</td>
<td>0.072</td>
<td>0.423</td>
<td>0.12</td>
<td>0.02</td>
</tr>
<tr>
<td>S6</td>
<td>–</td>
<td>0.062</td>
<td>0.21</td>
<td>bdl</td>
<td>0.051</td>
<td>0.37</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>S7</td>
<td>–</td>
<td>0.073</td>
<td>0.25</td>
<td>0.349</td>
<td>0.057</td>
<td>0.756</td>
<td>0.1</td>
<td>0.00</td>
</tr>
<tr>
<td>S8</td>
<td>–</td>
<td>0.068</td>
<td>0.36</td>
<td>0.002</td>
<td>0.066</td>
<td>0.138</td>
<td>0.034</td>
<td>0.00</td>
</tr>
<tr>
<td>Mean ±</td>
<td>–</td>
<td>0.6 ± 0.34 ± 0.11 ±</td>
<td>0.07 ± 0.77 ±</td>
<td>0.06 ± 0.01 ±</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SD</td>
<td>0.04</td>
<td>0.01</td>
<td>0.10</td>
<td>0.18</td>
<td>0.01</td>
<td>0.82</td>
<td>0.04</td>
<td>0.003</td>
</tr>
<tr>
<td>WHO(^{c})</td>
<td>0.1</td>
<td>0.5</td>
<td>1.5</td>
<td>1</td>
<td>0.07</td>
<td>5</td>
<td>0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>USEPA(^{d})</td>
<td>3</td>
<td>0.1</td>
<td>1.3</td>
<td>0.05</td>
<td>0.1</td>
<td>5</td>
<td>–</td>
<td>0.005</td>
</tr>
<tr>
<td>ISP(^{e})</td>
<td>0.3</td>
<td>–</td>
<td>0.05</td>
<td>0.1</td>
<td>–</td>
<td>5</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>Vegetables (mg kg(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peas</td>
<td>127.9</td>
<td>bdl</td>
<td>11.1</td>
<td>21.8</td>
<td>2.05</td>
<td>52</td>
<td>1.4</td>
<td>bdl</td>
</tr>
<tr>
<td>Potato</td>
<td>82.2</td>
<td>bdl</td>
<td>2.6</td>
<td>11.1</td>
<td>bdl</td>
<td>12.5</td>
<td>0.2</td>
<td>0.05</td>
</tr>
<tr>
<td>Cabbage</td>
<td>33.4</td>
<td>0.57</td>
<td>2.45</td>
<td>30.35</td>
<td>0.91</td>
<td>23.25</td>
<td>2.1</td>
<td>0.33</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>103.75</td>
<td>0.88</td>
<td>9.15</td>
<td>38.45</td>
<td>48.95</td>
<td>88.05</td>
<td>0.78</td>
<td>0.126</td>
</tr>
<tr>
<td>Batna</td>
<td>168.0</td>
<td>bdl</td>
<td>9.6</td>
<td>78.3</td>
<td>bdl</td>
<td>40.25</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>Spinach</td>
<td>205.45</td>
<td>0.66</td>
<td>7.4</td>
<td>69.4</td>
<td>1.37</td>
<td>35.05</td>
<td>1.9</td>
<td>0.205</td>
</tr>
<tr>
<td>Coriander</td>
<td>135.35</td>
<td>3.3</td>
<td>4.8</td>
<td>30</td>
<td>9.21</td>
<td>18.5</td>
<td>3.89</td>
<td>bdl</td>
</tr>
<tr>
<td>Mean ±</td>
<td>122.29 ± 0.70 ± 6.73 ±</td>
<td>39.91 ± 13.32 ±</td>
<td>38.51 ± 1.24 ±</td>
<td>0.22 ±</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SD</td>
<td>56.36</td>
<td>0.15</td>
<td>3.48</td>
<td>24.81</td>
<td>23.75</td>
<td>25.69</td>
<td>0.85</td>
<td>0.10</td>
</tr>
<tr>
<td>FAO/WHO(^{f})</td>
<td>450</td>
<td>–</td>
<td>40</td>
<td>–</td>
<td>–</td>
<td>60</td>
<td>0.5</td>
<td>2.0</td>
</tr>
<tr>
<td>ISP(^{g})</td>
<td>–</td>
<td>20</td>
<td>30</td>
<td>–</td>
<td>1.5</td>
<td>50</td>
<td>2.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

bdl, Below detection limit, \(\text{EU}^{a}\), \(\text{ISP}^{b}\), \(\text{WHO}^{c}\), \(\text{USEPA}^{d}\), \(\text{ISF}^{e}\) and \(\text{FAO/WHO}^{f}\) are the permissible limit values set by these organizations.

\(HI = \sum HQ_i\).
manufacturing industries in the area. Other metals, viz. Mn, Ni, Cr and Cd recorded their maximum concentrations in other sites (Gular, Talaspur and Mathura Road). However, when compared to the guidelines from standard agencies such as EU\textsuperscript{19} and Indian standard (IS)\textsuperscript{20}, the heavy metal contents in these areas were found to be within standard limits except for Cu and Zn. The Cu concentration exceeded by 62.5\%, the standard prescribed by EU and by 37.5\% by the IS. The enrichment of Cu in ITI was approximately 5 times the standard limit and two times in Gular. Zn exceeded the standard limit by two times in ITI.

Soil pollution assessment

The $I_{\text{geo}}$ is applied for quantifying the intensity of anthropogenic activity contaminating the surface and subsurface soil\textsuperscript{6-11}. The result of $I_{\text{geo}}$ calculations is given in Supplementary Table 1 and presented in Figure 3.\textsuperscript{a} The calculations revealed that the soil depicted uncontaminated to moderately contaminated status for Cd (0.03) in Mathura Road (S6); Pb content of 0.49 was obtained in Mathura Road (S6), and 0.36 and 0.28 in Gular area (S3 and S5 respectively). The Pb content was classified as moderately polluted in the ITI (S2: 1.07) and Talaspur (S8: 1.7). The highest $I_{\text{geo}}$ value of Pb observed was 2.06 (class 3; moderately to heavily polluted) which was recorded in S1 of ITI area. The Zn concentration had maximum $I_{\text{geo}}$ values in ITI area, i.e. moderately to heavily contaminated soil. Zn recorded low grade pollution in Gular area (S5), and uncontaminated to moderately contaminated in rest of the sites. However, Talaspur sample (S8) did not show any contamination of Zn. The Ni content in Upperkot area corresponded to uncontaminated to moderately contaminated values. Cu was the most contaminant metal in the soils of the study area. Its $I_{\text{geo}}$ values ranged from uncontaminated in Upperkot soil (S7) to heavily contaminated soil with $I_{\text{geo}} = 3.8$ and 3.1 in the ITI and Gular areas respectively. In Talaspur and Mathura Road, the soil was moderately polluted to unpolluted with reference to Cu.

The quality of soil indicated serious level of contamination, particularly in case of Cu, Zn and Pb, and to a lesser extent of Cd. This can be directly linked with the industrial activities in the area. Cu and Zn are the primary raw materials used for brass used for lock manufacturing; hence they are the main contaminants in the soils of Aligarh. Paint industry along with deposition from air contributes to the contamination of Pb. Mathura refinery is the major contributor of Pb contaminant via air in the study area.

Concentration of heavy metals in groundwater

Water contaminated by heavy metals could adversely affect human health either by direct ingestion of contaminated water or via the food chain. The results of heavy metal analysis of groundwater are shown in Table 1 and Figure 2.\textsuperscript{b} The maximum content of Cd, Cu, Cr, Ni and Zn was found in the samples from ITI area, and maximum...
Table 2. HPI resulting from various heavy metals in groundwater

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Mean (Mi) (mg l\textsuperscript{–1})</th>
<th>Highest permitted value (Si)</th>
<th>Unit weight (W\textsubscript{i} = K/Si)</th>
<th>Sub-index Q\textsubscript{i}</th>
<th>W\textsubscript{i} × Q\textsubscript{i}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.067</td>
<td>0.1</td>
<td>0.026</td>
<td>58.57</td>
<td>1.54</td>
</tr>
<tr>
<td>Cu</td>
<td>0.330</td>
<td>2</td>
<td>0.001</td>
<td>14.73</td>
<td>0.019</td>
</tr>
<tr>
<td>Mn</td>
<td>0.151</td>
<td>1</td>
<td>0.003</td>
<td>5.66</td>
<td>0.015</td>
</tr>
<tr>
<td>Ni</td>
<td>0.066</td>
<td>0.07</td>
<td>0.038</td>
<td>92.66</td>
<td>3.49</td>
</tr>
<tr>
<td>Zn</td>
<td>0.668</td>
<td>5</td>
<td>0.001</td>
<td>116.61</td>
<td>0.061</td>
</tr>
<tr>
<td>Pb</td>
<td>0.064</td>
<td>0.05</td>
<td>0.053</td>
<td>135</td>
<td>7.12</td>
</tr>
<tr>
<td>Cd</td>
<td>0.01</td>
<td>0.003</td>
<td>0.879</td>
<td>1305</td>
<td>1146.79</td>
</tr>
</tbody>
</table>

∑W\textsubscript{i} = 1.0, ∑W\textsubscript{i} × Q\textsubscript{i} = 806.08, ∑HPI = 806.08.

Figure 3. (a) Geo-accumulation index (I\textsubscript{geo}) and (b) transfer factor of heavy metals from soil to vegetables.

The concentration of Mn was found in water from Gular area. With exceptions for Ni and Pb, the mean value of the other metals were all under permissible limits given by WHO\textsuperscript{16}, USEPA\textsuperscript{21} and the Indian Standard Institution (ISI)\textsuperscript{22}. The Ni content recorded in the ITI area was 17% above the highest permissible limit, and Pb content recorded in the Gular area was 28% above the highest permissible limit.

**Water pollution assessment**

HPI is an effective tool for assessing water quality in any area\textsuperscript{15}. The anthropogenic source of contamination is the discharge of industrial and domestic wastewater into rivers or open areas, which could reach the groundwater aquifer via direct percolation or influent process. The HPI value in the study area was 806.08 (Table 2), which exceeded the threshold value of 100 (ref. 11). Accordingly, the HPI calculations indicated critical contamination of groundwater by metals. Consequently, based on the guidelines given by USEPA\textsuperscript{21}, the water was considered unsuitable for potable use.

**Concentration of heavy metals in vegetables**

The vegetable samples were analysed to determine the toxicity transferred to the plants from soil, and the results are shown in Table 1 and represented in Figure 2c. The mean metal content values, except for Ni, in different vegetables were under the permissible limits recommended by FAO/WHO\textsuperscript{23} and IS\textsuperscript{20}. Ni showed concentration above the permissible limit set by IS. This excessive content of Ni was detected in cauliflower, coriander and peas (48.95 mg kg\textsuperscript{–1}, 9.21 mg kg\textsuperscript{–1} and 2.05 mg kg\textsuperscript{–1} respectively). Zn content in cauliflower, compared to FAO/WHO guideline values\textsuperscript{23}, was found to be above the permissible limit by 46%, and in peas by 4% based on IS guidelines\textsuperscript{20}. The maximum content of Pb was detected in coriander and was the only value that exceeded the admissible limit by 55%. Maximum concentration of Cd was found in cabbage in which it exceeded the FAO/WHO\textsuperscript{23} guidelines by 65%.

**Pollution assessment in vegetables**

In order to assess contamination in plants, TF was applied to determine the enrichment of heavy metal from soils to plants (Supplementary Table 2). Cd had the highest TF value among the heavy metals and its maximum content was found in cabbage (1.07), followed by spinach and cauliflower (0.66 and 0.40 respectively). Cauliflower also showed high TF ratio of Ni (0.77). However, the calculated TF ratios for different plants investigated in this study indicated low uptake of heavy metals by plants from soils\textsuperscript{24}. 
**Human health risk assessment**

Human health risk due to exposure to heavy metals was evaluated in the present study following the guidelines of USEPA\(^1\), and the results are presented in Table 3. In this study, it was considered that the human health risk was caused by direct ingestion of water and vegetables. Accordingly, the results showed that HQ due to vegetable consumption was less than 1, and the maximum value obtained was for Ni (0.83, with ingestion via cauliflower). The results also indicated non-significant detrimental impact on human health through vegetable consumption, as HI for most metals was less than 1 (HI < 1), except for cauliflower whose concentration accounted for human health risk HI = 1.7. Similar results regarding food contamination (HI > 1) were reported from other cities in India and Pakistan due to anthropogenic intervention\(^25,26\).

On the contrary, the assessment of water pollution revealed high risk via water ingestion. Despite HQ values of almost all heavy metals being less than unity (HQ < 1), Cd had recorded HQ values greater than unity in the ITI and Gular areas (2.4 and 1.3 respectively). Further, the HI values calculated from the metal abundances in groundwater were higher than 1 in all the locations (average HI = 2.6) indicating risk to human health. Groundwater in the study area was unsuitable for drinking and domestic use. Groundwater in ITI and Gular areas in particular recorded the highest HI values (4.5 and 4.02 respectively). This might be due to the density of industries in these two locations in comparison to other areas\(^7\).

**Conclusion**

Investigation of heavy metals in soil, groundwater and vegetables of Aligarh area leads to the conclusion that soil contains the highest proportion of heavy metals followed by plant and groundwater (Supplementary Figure 1). Amongst the five locations from where samples were collected, the soil samples from ITI and Gular recorded higher levels of Cu and Zn contamination. The soil contamination assessed by \(I_{geo}\) index confirmed high contamination level in the ITI and Gular areas indicating that contamination might be arising from lock manufacturing industries. Groundwater from ITI area recorded maximum content of Cd, Cu, Cr, Ni and Zn, whereas the maximum content of Mn and Pb was detected in groundwater from Gular area. Among these metals, only Ni and Pb contents exceeded the highest permissible limits set by WHO, USEPA and ISI. Nonetheless, HPI calculations revealed critical contamination of groundwater and unsuitability for domestic use. In the case of vegetables, all heavy metals except for Ni and Zn, were within permissible limits. Ni and Zn exceeded IS and FAO/WHO standard values in cauliflower, coriander and peas. However, TF ratios for different plants investigated in this study indicated low uptake of heavy metals by the plants from the soils. Thus, human health risk assessment from the data leads to the conclusion that HI less than 1 in case of vegetables indicates abundance of heavy metal in the vegetables of the study area, and has non-significant detrimental impact on human health except from cauliflower. On the contrary, the assessment of water pollution revealed high risk on human health via water ingestion. HI values for water samples were higher than 1 in all the locations (average HI = 2.6) indicating that well water in the study was unsuitable for domestic use.

**Declaration of interests.** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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17. USEPA, Regional Screening Level (RSL) Summary Table, Wash-ington DC, USA, 2013.


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