Heavy metals in soil, finger millet and weeds due to nutrient management practices under a 43-year-old long term fertilizer experiment

Metais pesados no solo, no milheto e nas ervas daninhas devido às práticas de gerenciamento de nutrientes em um experimento de fertilização de longo prazo de 43 anos

Metales pesados en el suelo, el mijo y las malas hierbas debido a las prácticas de gestión de nutrientes en un experimento de fertilización a largo plazo de 43 años de duración

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ABSTRACT
Chemical fertilizers contain traces of heavy metals and long-term use of fertilizers in agriculture could lead to the accumulation of heavy metals in the soil. Specific amounts of fertilizers and manure have been consistently applied for the past 43 years. Soil and plant samples were collected and quantified for heavy metals. The results revealed that the application of FYM and inorganic fertilizers led to a higher concentration of heavy metals in surface soil and decreased with soil depth. The application of 100% RDF resulted in higher concentrations of metals in samples of finger millet and all the heavy metals were below toxic limits. The PLI of heavy metals was found to have a value <10, indicating that soils are less polluted. Cd and Pb had BCF values of <1 for grain and straw, which indicates a lower concentration of metals in soil than those taken up by plants, while >1 for As and Cr indicates a higher uptake in grain and straw than in soil.

Keywords: fertilizers, finger millet, heavy metal, treatments, uptake, weeds.

RESUMO
Os fertilizantes químicos contêm traços de metais pesados e o uso prolongado de fertilizantes na agricultura pode levar ao acúmulo de metais pesados no solo. Quantidades específicas de fertilizantes e esterco foram aplicadas de forma consistente nos últimos 43 anos. Amostras de solo e plantas foram coletadas e quantificadas para metais pesados. Os resultados revelaram que a aplicação de FYM e fertilizantes inorgânicos levou a uma maior concentração de metais pesados na superfície do solo e diminuiu com a profundidade do solo. A aplicação de 100% de RDF resultou em concentrações mais altas de metais em amostras de milho e todos os metais pesados estavam abaixo dos limites tóxicos. O PLI dos metais pesados apresentou um valor <10, indicando que os solos estão menos poluídos. O Cd e o Pb apresentaram valores de BCF <1 para grãos e palha, o que indica uma concentração mais baixa de metais no solo do que aqueles absorvidos pelas plantas, enquanto que >1 para As e Cr indica uma absorção maior nos grãos e na palha do que no solo.

Palavras-chave: fertilizantes, painço, metais pesados, tratamentos, absorção, ervas daninhas.
RESUMEN
Los fertilizantes químicos contienen trazas de metales pesados y su uso prolongado en la agricultura podría provocar la acumulación de metales pesados en el suelo. Durante los últimos 43 años se han aplicado sistemáticamente cantidades específicas de fertilizantes y estiércol. Se recogieron muestras de suelo y plantas y se cuantificaron en busca de metales pesados. Los resultados revelaron que la aplicación de FYM y fertilizantes inorgánicos provocó una mayor concentración de metales pesados en el suelo superficial y disminuyó con la profundidad del suelo. La aplicación de 100% RDF dio lugar a mayores concentraciones de metales en muestras de mijo y todos los metales pesados estaban por debajo de los límites tóxicos. El PLI de los metales pesados resultó tener un valor <10, lo que indica que los suelos están menos contaminados. El Cd y el Pb presentaron valores de FBC <1 para el grano y la paja, lo que indica una menor concentración de metales en el suelo que los absorbidos por las plantas, mientras que >1 para el As y el Cr indica una mayor absorción en el grano y la paja que en el suelo.

Palabras clave: fertilizantes, mijo, metales pesados, tratamientos, absorción, malas hierbas.

1 INTRODUCTION

The world is becoming more dependent on agriculture than it has ever been because of population increase and growing food demand. Global agriculture and food security face enormous challenges. In most emerging countries, population expansion and growing prosperity have led to previously unheard-of levels of demand for food and other agricultural items. The Food and Agriculture Organization (FAO) forecasts that to fulfil the world's food demand in 2050, the world's annual output of crops and animals will need to grow by 60% from 2006 [1].

Soil is the most important natural resource, and its quality is determined by management decisions made about the majority of factors that impact agricultural sustainability and production. The physical, chemical, and biological characteristics of soil have been adversely altered by pollution, both organic and inorganic, worldwide, resulting in a significant decline in soil quality. The green revolution boosted fertilizer usage, which enhanced food grain yield in India; nevertheless, prolonged use of NPK fertilizers would also increase the concentration of heavy metals in agricultural soil.

Heavy metals exhibit metallic properties such as malleability, cation stability, ductility, conductivity, and ligand selectivity. While some are required in trace amounts by both plants and animals, their quantity in soil is rather low, and they become hazardous when consumed in significant amounts. Important heavy metals include Cu, Zn, Mn, Co,
Fe, and so forth; nevertheless, metals such as Cd, Ni, Pb, Cr, and Hg are not essential for plants or animals [2]. Based on their relative amounts, all of the micronutrient cations iron, manganese, copper, zinc, and nickel are classified as heavy metals and show toxicity as well as deficiency in plants. Arsenic, lead, cadmium, chromium, mercury, selenium, and other heavy metals and metalloids are hazardous to animals, including humans and plants. These days, the environment is full of dangerous metals that are very damaging and dangerous to all living creatures. It becomes poisonous when a certain concentration of heavy metals is attained. The build-up of heavy metals in the soil also results in increased erosion and infertility. It also inhibits microbial enzyme activity and reduces the variety of flora and fauna populations. These metals are taken by the roots of grazing plants and animals and enter the food chain because they cannot biodegrade. Humans may be exposed to metals via their diet, drink, air, ground (by dust inhalation and consumption), or skin (due to dermal absorption of contaminants from soil and water). While certain metals, like aluminum, may be removed by natural mechanisms, other metals build up in the body and food chain and cause long-term problems [3] [4].

Long-term fertilizer experiments (LTFE) are crucial for comprehending the complex relationships between plant, soil, and climate management techniques as well as their long-term effects on soil productivity [5]. Extensive manure and fertilizer studies provide valuable information regarding the impact of regular application of fertilizers with varying proportions of organic and inorganic materials on the physical and chemical properties of soil. They also provide a good basis for monitoring changes in these properties. Together with the primary components needed for plant nutrition and development, these manures and fertilizers also include trace metals as contaminants. These metals may accumulate in the soil, be taken up by plants, and then go up the food chain to affect animals and humans, claim [6]. Thus, an effort was made to estimate the level of heavy metal contamination in finger millet grains and soil. The objectives of the current studies were to: a) estimate the amounts of farmyard manure and continuous fertilizer applications that contribute to soil profiles containing cadmium, lead, arsenic, and chromium; and b) investigate the impact of continuous fertilization under long-term fertilizer experiments on heavy metal contamination of crops.
2 MATERIALS AND METHODS

2.1 CHARACTERISTICS OF SITE

The location of the experimental site is 12°58’ N latitude and 77°35’ E longitude. It began with the finger millet crop in 1978 at the research farm of the Gandhi Krishi Vignana Kendra, University of Agricultural Sciences, Bangalore, as part of the All India Co-ordinated Research Project for Dryland Agriculture (AICRPDA). Agro-ecological sub-region (AESR) AESR 8.1 and agro-ecological region (AER) AER 8 include the experimental site. The zone receives 920.4 mm of rain a year on 56 rainy days, with a range of 528 to 1374 mm. The months of May (101 mm) and August (130 mm) until September (197 mm) saw the highest amounts of precipitation in the area. The Alfisols that make up the soil experiment site are classified as fine, kaolinitic, isohyperthermic, Typic Kandiustalf, and Vijayapura series. These lateritic, yellowish-red soils are produced from granite and gneiss in a subtropical, semi-arid environment. The experimental site's soil had a sandy clay loam texture, a pH of 5.0 that was slightly acidic, electrical conductivity of 0.20 dS m⁻¹, low levels of organic carbon (0.40%), and low levels of nitrogen, phosphorus, and potassium that were readily accessible (200, 8, and 132.8 kg ha⁻¹, respectively).

2.2 EXPERIMENTAL DESIGN AND TREATMENT DETAILS

The experiment was laid out in a randomized complete block design, consisting of eight treatments with three replications. The different treatment combinations were a) absolute control, b) 100% NPK, c) FYM, d) FYM + 100% NPK, e) FYM + 50% NPK, f) MR, MR+100% NPK, and g) MR+50% NPK. The recommended dose of N:P:K for finger millet is 50:50:25 respectively and farmyard manure (FYM) and maize residue (MR) were applied (FYM) 10 and 5 mg ha⁻¹ respectively. The experimental field was ploughed twice with a bullock-drawn cultivator, to protect the movement of soil from one plot to another and laid into 13 m X 3.3 m plots. Finger millet GPU-28 medium duration variety (110-115 days to maturity) having resistance to blast with yield potential of 3500-4000 kg ha⁻¹. Farmyard manure and maize residue were sourced from the Zonal Agricultural Research Station of the University of Agricultural Sciences, Bangalore, on average FYM had As, Cr, Cd, and Pb were 2.71, 0.24, 0.73, and 2.68 respectively whereas maize residue
had As, Cr, Cd, Pb were 2.71, 0.24, 0.73 and 2.68 respectively on a dry weight basis. The chemical fertilizers for the study were urea, single super phosphate, and muriate of potash. The P and K were applied as basal at the time of sowing, N was applied in two equal splits, half dose at the time of sowing and the remaining dose was top dressed at 30 days after sowing. FYM and MR were applied uniformly in respective plots on a dry weight basis and spread manually three weeks before sowing. No irrigation was given throughout the crop duration.

2.3 CROP MANAGEMENT

The chemical fertilizers were broadcasted into the plots as per the treatments and mixed thoroughly with soil before sowing. Finger millet variety GPU-28 was sown with the onset of monsoon i.e., on 26th July 2021. Gap filling was done two weeks after sowing to ensure optimum plant population. Weeds were controlled manually after 20 days after sowing. Finger millet was harvested at maturity on 14th November 2021. At maturity, the ear heads of finger millet were harvested first and the remaining biomass was harvested manually using a sickle just above the ground (about 5 cm). The ear heads and biomass were sun-dried for 2-3 days on the threshing floor and later threshed manually. Grain and straw yields were recorded separately adjusting the seed moisture content to 14%.

2.4 DATA COLLECTION

At maturity, finger millet plants from border rows were discarded to avoid the border effect and ear heads in each plot were harvested manually, sundried, and threshed manually and grain yield was adjusted to 14% moisture. The remaining stover was harvested plot-wise recorded and expressed in kg ha⁻¹. The total organic carbon content in FYM and maize residue was determined by the wet oxidation method [7]. The heavy metal content in grain and straw was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Ametek-Spectogenesis, Germany). The uptake by grain and stover was derived by multiplying respective nutrient content with their yields.
2.5 SOIL SAMPLING AND ANALYSIS

Soil samples were collected treatment-wise from three different depths viz., 0-15, 15-30 and 30-60 cm. These soil samples were analysed for soil pH and electrical conductivity [8], soil organic carbon was analysed using Walkley and Black’s rapid titration method [9] and heavy metals viz., arsenic, cadmium, chromium and lead by DTPA extraction method [10].

2.6 SOIL POLLUTION INDEX

The data obtained by analyzing heavy metal content in soil was put forth further to assess the degree of soil contamination by soil pollution index (SPI) and pollution load index (PLI). The SPI is the ratio of the heavy metal concentration in the study area to the geometric mean of the background concentration [11].

\[
\text{Soil Pollution Index} = \frac{C_i}{S_i} \times 100 \quad (1)
\]

Where, \(C_i\) is the measured concentration of the examined metals in the soils and \(S_i\) is the geochemical background concentration of the metals.

The pollution load index (PLI) is the mean value for all SPI values of all the considered metals.

\[
\text{PLI} = \sqrt[n]{C_1 \times C_2 \times C_3 \times C_4 \ldots C_n} \quad (2)
\]

Where \(C_1, C_2, C_3\ldots\) are soil pollution index of particular heavy metal. It is classified as either low (PLI≤10), moderate (10<PLI≤20), high (20<PLI≤50), or extremely high contamination (PLI>50).

2.7 BIOCONCENTRATION FACTOR

It represents the ratio of metal concentration in the plants to the metal concentration in the soil. BCF is classified as low translocation (BCF<1) and high translocation (BCF≥1) [12].
\[
BCF = \frac{\text{Heavy metal content in plant (mg kg}^{-1}\text{)}}{\text{Heavy metal content in soil (mg kg}^{-1}\text{)}}
\] (3)

2.8 DATA ANALYSIS

The generated data were subjected to statistical tests by using a Randomized Complete Block Design (RCBD) and an analysis of variance (ANOVA) was performed following standard procedures for randomized block design [13]. The F-test was used to test significant differences between treatment means. The significant differences between treatments were compared with the critical difference (C.D.) at a 5% level of probability.

3. RESULTS AND DISCUSSION

3.1 HEAVY METAL CONTENT IN FERTILIZERS AND MANURES

The chemical fertilizers used in this experiment from the inception are urea, single super phosphate and muriate of potash to supply nitrogen, phosphorus and potassium respectively. Farmyard manure and maize residues were used as sources of organic matter. Fertilizer samples were collected to analyse the As, Cd, Cr and Pb. Higher As (11.62 mg kg\(^{-1}\)), and Pb (7.11 mg kg\(^{-1}\)) were recorded in muriate of potash whereas cadmium (4.37 mg kg\(^{-1}\)) and Cr (22.32 mg kg\(^{-1}\)) were found in single super phosphate. Farmyard manure contains higher As (2.73 mg kg\(^{-1}\)), Cd (0.78 mg kg\(^{-1}\)), Cr (24.27 mg kg\(^{-1}\)) and Pb (9.63 mg kg\(^{-1}\)) compared to maize residues (Table 1). Heavy metal content in chemical fertilizers, is mainly due to the heavy metal content in the raw materials, used in the manufacture of fertilizers [14]. Similarly, the heavy metal content in the farmyard manure is due to the heavy metal content in the feed and maize residue is due to heavy metals in the soil [15] [16].

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Fertilizer/M</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Urea</td>
<td>4.21±0.25</td>
<td>0.33±0.026</td>
<td>3.49±0.18</td>
<td>0.78±0.02</td>
</tr>
<tr>
<td>2</td>
<td>SSP</td>
<td>7.37±0.78</td>
<td>4.37±0.025</td>
<td>22.32±1.53</td>
<td>2.81±0.27</td>
</tr>
<tr>
<td>3</td>
<td>MOP</td>
<td>11.62±0.38</td>
<td>0.09±0.19</td>
<td>5.31±0.18</td>
<td>7.11±0.32</td>
</tr>
<tr>
<td>4</td>
<td>FYM</td>
<td>2.73±0.13</td>
<td>0.78±0.21</td>
<td>24.27±1.69</td>
<td>9.63±1.75</td>
</tr>
<tr>
<td>5</td>
<td>MR</td>
<td>0.15±0.01</td>
<td>0.046±0.03</td>
<td>11.53±0.05</td>
<td>0.326±0.03</td>
</tr>
</tbody>
</table>

Values indicate mean± standard deviation (n=3), MR: Maize Residue

Source: The Authors

Table 1. Heavy metal content (mg kg\(^{-1}\)) in fertilizer and manure used in the experimental soil
3.2 SOIL PROPERTIES

The data about soil quality parameters like Ph, EC and organic carbon was detailed and discussed in Table 2.

Generally, soil pH is sensitive to management practices like fertilizer and manure application. The initial values of soil physicochemical properties under present investigation were pH 5.0, EC 0.20 dS m\(^{-1}\), soil organic carbon 0.40%, available N 200 kg ha\(^{-1}\), P\(_2\)O\(_5\) 8.70 kg ha\(^{-1}\) and K\(_2\)O 132.80 kg ha\(^{-1}\). Results depicted that continuous application of only inorganic fertilizers decreased the soil pH at 3.56 (T\(_2\)) in comparison to control pH 4.63. Application of FYM and FYM + NPK treatments enhanced the soil pH up to 5.91 in comparison to other treatments. Soil pH recorded an increasing trend with increasing depth irrespective of the treatment. The physical and chemical characteristics of the soil varied significantly between the treatments in the current study. The pH of the soil, in particular, varied both within and across treatments throughout time. When it came to soil qualities, pH was the main factor influencing the bioavailability of heavy metals in the soil solution [17].

<table>
<thead>
<tr>
<th>Treatment</th>
<th>pH</th>
<th>EC (dS m(^{-1}))</th>
<th>Organic carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-15</td>
<td>15-30</td>
<td>30-60</td>
</tr>
<tr>
<td>T(_1): Control</td>
<td>4.63</td>
<td>4.72</td>
<td>4.83</td>
</tr>
<tr>
<td>T(_2): 100% NPK</td>
<td>3.56</td>
<td>3.67</td>
<td>3.72</td>
</tr>
<tr>
<td>T(_3): FYM</td>
<td>5.91</td>
<td>6.14</td>
<td>6.17</td>
</tr>
<tr>
<td>T(_4): FYM+ 100% NPK</td>
<td>5.73</td>
<td>5.88</td>
<td>5.91</td>
</tr>
<tr>
<td>T(_5): FYM+50% NPK</td>
<td>5.72</td>
<td>5.98</td>
<td>5.97</td>
</tr>
<tr>
<td>T(_6): MR</td>
<td>4.92</td>
<td>5.13</td>
<td>5.36</td>
</tr>
<tr>
<td>T(_7): MR + 100% NPK</td>
<td>4.31</td>
<td>4.47</td>
<td>4.56</td>
</tr>
<tr>
<td>T(_8): MR + 50% NPK</td>
<td>4.52</td>
<td>4.68</td>
<td>4.82</td>
</tr>
</tbody>
</table>

S.E.m ±: 0.169 ± 0.174 ± 0.179 ± 0.005 ± 0.005 ± 0.006 ± 0.048 ± 0.051 ± 0.047
CD@5%: 0.509 ± 0.520 ± 0.539 ± 0.015 ± 0.017 ± 0.019 ± 0.146 ± 0.158 ± 0.143

MR: Maize Residue
Source: The Authors

The electrical conductivity (EC) of soil indicated the soluble salts of the soil. The EC value for most of the soils irrespective of treatments was below 0.081 (T\(_3\)) dS m\(^{-1}\) throughout the soil depths viz., 0-15, 15-30 and 30-60 cm. The findings of the present study showed that adding manure and fertilizer changed the soil EC in a significant way. This could be explained by changes in EC in soil solution brought on by the ionization of salts in the soil and water as well as the release of ionic species during the reduction
process. High levels of electrical conductivity in soil solutions indicated that there were hazardous ions of heavy metals present in the soil environment.

After pH, the most important soil parameter is organic carbon which governs the bioavailability of heavy metals and subsequent uptake by plants. Application of FYM along with NPK increased the soil organic carbon content of the soil to 0.64% in comparison to the control (0.22%) in 0-15 cm soil depth and the same trend was also observed with 15-30 and 30-60 cm. An essential component, organic carbon can form an insoluble or soluble compound with heavy metals based on its molecular weight. The complex structure will determine whether heavy metals migrate or stay in the soil. In our investigation, we found that the soil treated with FYM + 100% NPK had an almost three times higher organic carbon percentage than the control and there was a marginally significant increase in organic carbon percentage across all treatments.
Table 3. Effect of long-term application of nutrient management practices on heavy metal (mg kg$^{-1}$) content in soil

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Arsenic</th>
<th>Cadmium</th>
<th>Chromium</th>
<th>Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-15</td>
<td>15-30</td>
<td>30-60</td>
<td>0-15</td>
</tr>
<tr>
<td>T1: Control</td>
<td>0.051</td>
<td>0.050</td>
<td>0.049</td>
<td>0.086</td>
</tr>
<tr>
<td>T2: 100% NPK</td>
<td>0.063</td>
<td>0.061</td>
<td>0.062</td>
<td>0.107</td>
</tr>
<tr>
<td>T3: FYM</td>
<td>0.057</td>
<td>0.057</td>
<td>0.054</td>
<td>0.097</td>
</tr>
<tr>
<td>T4: FYM+ 100% NPK</td>
<td>0.072</td>
<td>0.071</td>
<td>0.069</td>
<td>0.107</td>
</tr>
<tr>
<td>T5: FYM+50% NPK</td>
<td>0.068</td>
<td>0.068</td>
<td>0.064</td>
<td>0.103</td>
</tr>
<tr>
<td>T6: MR</td>
<td>0.055</td>
<td>0.056</td>
<td>0.051</td>
<td>0.098</td>
</tr>
<tr>
<td>T7: MR + 100% NPK</td>
<td>0.068</td>
<td>0.066</td>
<td>0.065</td>
<td>0.099</td>
</tr>
<tr>
<td>T8: MR + 50% NPK</td>
<td>0.065</td>
<td>0.063</td>
<td>0.062</td>
<td>0.098</td>
</tr>
<tr>
<td>S.Em</td>
<td>0.002</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>CD @ 5%</td>
<td>0.006</td>
<td>0.003</td>
<td>0.003</td>
<td>0.005</td>
</tr>
</tbody>
</table>

MR: Maize Residue
Source: The Authors
3.3 DISTRIBUTION OF HEAVY METALS IN SOIL PROFILE

In the present investigation, the annual fertilizer consumption rate was 50, 50 and 25 kg ha\(^{-1}\) for nitrogen, phosphorus and potassium respectively in the experimental soil. Results revealed that the DTPA extractable heavy metals like As, Cd, Cr and Pb were present in soil solution in a very minute quantity (Table 3). Although in the present long-term fertilizer experiment, heavy metals in the soil increased after fertilization this can be observed in the heavy metal concentration in the soil without fertilizer application (control). Amongst the treatments, the maximum build-up of DTPA extractable As, Cd, Cr and Pb in the surface layer was recorded at 0.072, 0.107, 0.093 and 1.171 mg kg\(^{-1}\) respectively in the case of 100% NPK+FYM treated plot. Results also depicted that the accumulation of different heavy metals in the experimental site recorded a declining trend with increasing depth of the soil. The overall results showed that the build-up of heavy metals in the soils under long-term fertilizer experiments is not alarming after 43 years of cultivation. The application of both organic and inorganic fertilizers to agricultural soil was the cause of the increased metal build-up [18].

Samples of surface soil from each treatment plot in the current investigation showed significantly higher concentrations of hazardous metals than soil at lower depths. The NPK + FYM treatment often had the highest concentration among the treatments, whereas the control plots showed the lowest and researchers found that contamination in cultivated fields was caused by fertilizer additions such as single super phosphate-containing heavy metals [19]. The main sources of heavy metals are phosphatic fertilizers, such as superphosphate, which is made from phosphatic rocks [20] [21]. The plant mostly takes up heavy metals from the top 0–15 cm layer of the soil. Heavy metals and other contaminants have been mostly influencing the top 15 cm of soil due to human activity in recent years [22]. The distributions of heavy metals were similarly well controlled by soil texture. In general, the distribution of hazardous metals in soils and sediments was determined by soil texture [23]. Clayey soils chelated large amounts of harmful metals because they included more moisture and organic matter [24]. The concentration of metals in agricultural soils was increased by the use of fungicides, pesticides, organic manures, and commercial fertilizers [25] [26].

The main factors for lead build-up in agricultural soils are the application of sludge and manure as well as air deposition [27]. According to several studies, the main causes of heavy metal pollution in soils are irrigation water, animal dung, and fertilizer
application [28]. However, the findings of our experiments showed that the majority of the heavy metals, such as As, Cd, Cr and Pb were present in the fertilizers, farmyard manure and maize residue used in the current study.

Table 4: Effect of long-term application of organic and inorganic sources of nutrients on Cr, Ni, Cd and Pb content (mg kg$^{-1}$) in grain and straw of finger millet

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Arsenic Grain</th>
<th>Arsenic Straw</th>
<th>Cadmium Grain</th>
<th>Cadmium Straw</th>
<th>Chromium Grain</th>
<th>Chromium Straw</th>
<th>Lead Grain</th>
<th>Lead Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$_1$: Control</td>
<td>0.052</td>
<td>0.107</td>
<td>0.006</td>
<td>0.014</td>
<td>0.045</td>
<td>0.189</td>
<td>0.040</td>
<td>0.080</td>
</tr>
<tr>
<td>T$_2$: 100% NPK</td>
<td>0.102</td>
<td>0.198</td>
<td>0.015</td>
<td>0.040</td>
<td>0.096</td>
<td>0.536</td>
<td>0.074</td>
<td>0.353</td>
</tr>
<tr>
<td>T$_3$: FYM</td>
<td>0.089</td>
<td>0.186</td>
<td>0.011</td>
<td>0.021</td>
<td>0.077</td>
<td>0.320</td>
<td>0.058</td>
<td>0.125</td>
</tr>
<tr>
<td>T$_4$: FYM + 100% NPK</td>
<td>0.097</td>
<td>0.208</td>
<td>0.012</td>
<td>0.033</td>
<td>0.085</td>
<td>0.419</td>
<td>0.069</td>
<td>0.233</td>
</tr>
<tr>
<td>T$_5$: MR</td>
<td>0.092</td>
<td>0.193</td>
<td>0.009</td>
<td>0.028</td>
<td>0.085</td>
<td>0.249</td>
<td>0.051</td>
<td>0.091</td>
</tr>
<tr>
<td>T$_6$: MR + 100% NPK</td>
<td>0.085</td>
<td>0.175</td>
<td>0.009</td>
<td>0.019</td>
<td>0.071</td>
<td>0.205</td>
<td>0.048</td>
<td>0.145</td>
</tr>
<tr>
<td>T$_7$: MR + 50% NPK</td>
<td>0.094</td>
<td>0.199</td>
<td>0.012</td>
<td>0.026</td>
<td>0.089</td>
<td>0.431</td>
<td>0.061</td>
<td>0.256</td>
</tr>
<tr>
<td>T$_8$: MR + 50% NPK</td>
<td>0.090</td>
<td>0.185</td>
<td>0.012</td>
<td>0.022</td>
<td>0.088</td>
<td>0.331</td>
<td>0.056</td>
<td>0.234</td>
</tr>
<tr>
<td>S.Em$^+$</td>
<td>0.002</td>
<td>0.006</td>
<td>0.004</td>
<td>0.006</td>
<td>0.039</td>
<td>0.031</td>
<td>0.009</td>
<td>0.038</td>
</tr>
</tbody>
</table>

MR: Maize Residue
Source: The Authors

3.4 HEAVY METALS CONTENT IN FINGER MILLET GRAIN AND STRAW

The presence of trace elements in fertilizers implied that their long-term application had the potential to induce soil contamination. The heavy metals e.g. As, Cd, Cr and Pb were recorded in straw and grain of finger millet. In finger millet straw, the concentration of heavy metals like As, Cd, Cr and Pb showed an increasing tendency due to the application of different fertilizers and organic manures compared to control (Table 4). Heavy metal content in finger millet straw recorded some remarkable significance under different treatments. The maximum Cr concentration in millet straw was recorded as 0.536 mg kg$^{-1}$ under the treatment received 100% NPK and a minimum concentration of 0.189 mg kg$^{-1}$ was obtained in control, where no fertilizer and FYM was applied. The concentration of Cd in millet straw was ranging from 0.014 mg kg$^{-1}$ to 0.033 mg kg$^{-1}$. Similarly, the content As and Pb in straw 0.208 and 0.233 mg kg$^{-1}$ respectively were enhanced with the application of FYM with 100% NPK. However, the application of FYM aggravated the content of heavy metals in straw along with fertilizers. It was due to the higher content of heavy metals in FYM itself. Experimental results revealed that the concentration of different toxic heavy metals like As, Cd, Cr and Pb were evenly distributed at low concentrations in grain and straw at various treatments. The results depicted that finger millet grain contained heavy metals, namely As (0.097 mg kg$^{-1}$), Cd
(0.012 mg kg\(^{-1}\)), Cr (0.085 mg kg\(^{-1}\)) and Pb (0.069 mg kg\(^{-1}\)), whereas in finger millet straw relatively higher concentrations of different heavy metals like As (0.208 mg kg\(^{-1}\)), Cd (0.033 mg kg\(^{-1}\)), Cr (0.419 mg kg\(^{-1}\)) and Pb (0.233 mg kg\(^{-1}\)).

3.5 SOIL POLLUTION INDEX AND POLLUTION LOAD INDEX

The data obtained by analysing heavy metal content in soil was put forth further to obtain the soil pollution index and pollution load index (Table 5). Long-term application of farmyard manure and maize residue with different dosages of the recommended fertilizer builds up heavy metal concentrations in the soil. The soil sample results recorded a higher soil pollution index for As, Cd, Cr and Pb in treatment T\(_4\) that received FYM 10 t ha\(^{-1}\) + 100% RDF under finger millet monocropping i.e., 0.35, 3.57, 0.12 and 1.38 respectively. A lower soil pollution index of 0.25, 2.87, 0.06 and 0.67 was recorded for As, Cd, Cr and Pb respectively in the control treatment (T\(_1\)) where fertilizer and organic residues were not applied.

Table 5: Soil pollution index and pollution load index for heavy metals in soil

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Soil pollution index</th>
<th>PLI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
<td>Cd</td>
</tr>
<tr>
<td>T(_1): Control</td>
<td>0.25</td>
<td>2.87</td>
</tr>
<tr>
<td>T(_2): 100% NPK</td>
<td>0.31</td>
<td>3.57</td>
</tr>
<tr>
<td>T(_3): FYM</td>
<td>0.28</td>
<td>3.23</td>
</tr>
<tr>
<td>T(_4): FYM+ 100% NPK</td>
<td>0.35</td>
<td>3.57</td>
</tr>
<tr>
<td>T(_5): FYM+50% NPK</td>
<td>0.33</td>
<td>3.43</td>
</tr>
<tr>
<td>T(_6): MR</td>
<td>0.27</td>
<td>3.27</td>
</tr>
<tr>
<td>T(_7): MR + 100% NPK</td>
<td>0.33</td>
<td>3.30</td>
</tr>
<tr>
<td>T(_8): MR + 50% NPK</td>
<td>0.32</td>
<td>3.27</td>
</tr>
</tbody>
</table>

MR: Maize Residues
Source: The Authors

The plots treated with both FYM and fertilizer showed higher PLI values compared to other treatments; this is due to the addition of heavy metals by fertilizer and FYM. The PLI of the different treated plots imply the total degree of pollution. In our study, the PLI value was <10 which means soils were low polluted with heavy metals. The pollution index (PI) values of all seven heavy metals (As, Cd, Cr, Cu, Ni, Pb, and Zn) studied in agricultural soil adjacent to the industrial region of Korea ranged from 0.1 to 0.4 for top and subsoils indicating that these soils are not polluted [29]. The pollution load index (PLI) values using seven heavy metals ranged from 0.10 to 0.24 for the top and subsoils and the number was categorized into Group 2, which is unpolluted.
3.6 BIOCONCENTRATION FACTOR

Heavy metals like arsenic and chromium show >1 BCF value in both grain and straw except T₄, which indicates that finger millet crop has a high affinity towards these heavy metals and their value is higher in plants than in soil (Table 6). Among different heavy metals, As had the highest BCF for grain and straw (1.62 and 3.26 in T₂ and T₃ respectively) followed by chromium (1.16 and 6.09 in T₈ and T₂ respectively).

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Grain</th>
<th>Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
<td>Cd</td>
</tr>
<tr>
<td>T₁: Control</td>
<td>1.02</td>
<td>0.07</td>
</tr>
<tr>
<td>T₂: 100% NPK</td>
<td>1.62</td>
<td>0.14</td>
</tr>
<tr>
<td>T₃: FYM</td>
<td>1.56</td>
<td>0.11</td>
</tr>
<tr>
<td>T₄: FYM+100% NPK</td>
<td>1.35</td>
<td>0.11</td>
</tr>
<tr>
<td>T₅: FYM+50% NPK</td>
<td>1.35</td>
<td>0.09</td>
</tr>
<tr>
<td>T₆: MR</td>
<td>1.55</td>
<td>0.09</td>
</tr>
<tr>
<td>T₇: MR+100% NPK</td>
<td>1.38</td>
<td>0.12</td>
</tr>
<tr>
<td>T₈: MR+50% NPK</td>
<td>1.38</td>
<td>0.12</td>
</tr>
</tbody>
</table>

MR: Maize Residue
Source: The Authors

The bioconcentration factor of heavy metals is essential to investigate the human health risk index and it explains the transfer and bioavailability of heavy metals from soil to plants. Both grain and straw had BCF values of <1 for Cd and Pb which indicates a lower concentration of these heavy metals in soil than those taken up by plants, while >1 for As and Cr indicates a higher uptake of arsenic and chromium in grain and straw than in soil. The accumulation of heavy metals in agricultural soils increases heavy metal uptake by plants.

4 CONCLUSION

After 43 years of agriculture, it was determined overall that the amounts of heavy metals in the soils under long-term experimentation are not concerning. The DTPA-extractable heavy metal levels among the treatments increased with the addition of fertilizer and farmyard manure but they remained below allowable limits. Urea, SSP, MOP, FYM, and maize residues contain varied amounts of arsenic, cadmium, chromium, and lead. This could lead to an increase in the building of metal in the soil. When the heavy metal content of the grain was calculated to evaluate its quality, it was discovered
As, Cd, Cr, and Pb, were present. The results showed that the current study had BCF values less than unity (<1) for Cd and Pb indicating low translocation of metals while more than unity (>1) for As and Cr indicates high metal uptake by plants from soil. Heavy metals evaluated for PLI are classified as low indicating soils were less polluted with heavy metals. To create a database of heavy metal contamination in soil and plants across the nation's many agroclimatic zones, more research is needed.

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