**Evaluation of Levels of Cadmium, Chromium and Lead in Bio Fertilizer from Various Feed Stocks and in Inorganic Fertilizers Used in Kenya**

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**Authors’ contributions**

This work was carried out in collaboration among all authors. Author JGK designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors CGN and PN managed the analyses of the study. Author EGG managed the literature searches. All authors read and approved the final manuscript.

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**ABSTRACT**

This study was conducted to compare the levels of selected heavy metals (Pb, Cr and Cd) in inorganic fertilizers and bio slurry from different feed stocks. Bio slurry samples from chicken droppings, cow dung and pig wastes were analyzed for levels of selected heavy metals. Inorganic fertilizers for analysis DAP, CAN, Urea and NPK were procured from local market in Juja town next to Jomo Kenyatta University of Agriculture and Technology (JKUAT). Bio slurry samples were collected from Githunguri Sub County in Kiambu County and from mini digesters set up at JKUAT. Concentrations of Cd, Cr, and Pb were determined by Flame Atomic Absorption Spectrophotometer (Shimadzu 6200). Inorganic fertilizers were found to contain detectable amounts of lead metal. DAP had the highest amount of Pb at 0.03 mg/l followed by CAN (0.02 mg/l) Urea and NPK had 0.01 mg/l.
1. INTRODUCTION

World over there is a steady increase in demand for food supply. To meet this demand application of fertilizer is indispensable in modern agriculture [1]. Phosphorous is critical macronutrient necessary for plant growth. Phosphorus is mostly obtained from mined rock phosphate and is often combined in mineral fertilizers with sulphuric acid, nitrogen, and potassium [2]. It is estimated that rock phosphate reserves could be exhausted in the next 50–100 years. Phosphate rock (PR) is the major source for the production of most of the world’s phosphate fertilizers. The source of the phosphate is an important issue as different heavy metals may be introduced into the agricultural land along with the fertilizer [3]. Repeated application over extended periods of time and an increase in application frequency favor metal accumulation and bio transfer. Depending on soil composition and the presence of metals in the reused waste, specific chemical and physical associations can cause the accumulation of these pollutants in soil [4]. Several heavy metals such as iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), cobalt (Co), or molybdenum (Mo) are essential for the growth of organisms. Others have a single function and only in some organisms such as vanadium (V) in some peroxidases and in V-nitrogenases or nickel (Ni) in hydrogenases. Other heavy metals are always toxic to organisms: cadmium (Cd), lead (Pb), uranium (U), thallium (Tl), chromium (Cr), silver (Ag), and mercury (Hg) [5]. Concentration of above 0.1% of all heavy metals except iron in the soil become toxic to plants and therefore change the community structure of plants in a polluted habitat [5].

Analysis of phosphate fertilizer before its application to the soil for plant growth should be carried out to determine the concentration of heavy metals [6]. Phosphate rock (PR) contains various metals as minor constituents in the ores. Varying amounts of these elements are transferred to P fertilizers in production processes, and later are applied to soils with these fertilizers. Some other heavy metals of possible significance are: arsenic (As), chromium (Cr), lead (Pb), mercury (Hg), nickel (Ni), and vanadium (V). However, these metals are of less concern than Cd, either because they are not as readily absorbed by plants from P-fertilized soils or their apparent relative effects on human health are less than that of Cd. Cadmium (Cd) is the heavy metal of great interest because potentially it may be harmful to human health. Animal manures may contain Cd and other heavy metals, but at lower concentrations. Therefore, no buildup of heavy metals would be expected from moderate manure application rates on agricultural lands.

Extensive use of inorganic fertilizers leads to serious environmental concerns such as increased greenhouse gas emission during production of the fertilizers as well as heavy metal uptake and accumulation by food crops. In addition, chemical fertilizer could eliminate the beneficial microbial as well as insect community of soil [1]. Nitrate leaching and surface/ground water pollution due to increased use of fertilizer is directly related to human health problems. Similarly, freshwater contamination by chemical fertilizer/fertilizer residue is one of the major causes of eutrophication. Nitrogen and phosphorus contained in wastewaters are the primary causes of environmental eutrophication in surface waters [7]. Human food chain toxicity is influenced by application of inorganic and organic fertilizer, since they contain not only major elements necessary for plant nutrient growth but also variable qualities of heavy metals [8]. Many of these problems can be solved by utilization of bio slurry fertilizer.

Application of organic amendments such as compost and digestate to agricultural land has a number of beneficial effects. The first one is the supply of plant nutrients [9]. Recycling of organic wastes within agriculture can reduce the need for mineral fertilizer and restore organic carbon deficiency in the soil [10]. Use of organic waste in agriculture would be more sustainable than using inorganic commercial fertilizers. Many of the

Keywords: Fertilizer; bio-slurry; heavy metal; bioaccumulation; toxin; agriculture; food safety.
problems arising from the use inorganic fertilizers can be surmounted by utilization of bio-fertilizers. It may not be practical to completely replace the inorganic fertilizers by bio-fertilizer; however, bio-fertilizers have the potential to supplement the synthetic fertilizers and to significantly reduce its use [11].

2. MATERIALS AND METHODS

2.1 Sample Collection and Pre-treatment

The study was conducted between January 2018 and December 2018 a period of one year. Samples for this study were collected from Githunguri sub-county, Kiambu County in Kenya. The site was chosen due to intensity of biogas technology adoption by dairy farmers in the sub county. Miniature biogas digesters were set up at Jomo Kenyatta University of Agriculture and Technology and the digesters were fed with cow dung, chicken litter and swine waste and allowed to undergo anaerobic digestion. Bio slurry samples were collected from the digesters and stored in clean, sealable and airtight bags. Inorganic fertilizers; DAP CAN, Urea and NPK, were procured from local market in Juja town. The slurry was sieved and the liquid content analyzed for the dissolved nutrients. Physical parameters of the samples (pH, EC and TDS) were determined onsite. The undigested manure samples were allowed to dry in the air at 35°C and relative humidity of 30– 60 percent for 24 hours and ground using a mortar and pestle to increase the surface area.

The following codes were used for the selected samples:

GR- raw cow dung from Githunguri (Slurry before feeding digester)
GD- digested cow dung slurry from Githunguri
CD – cow dung slurry sample Jkuat mini digester
CH- Chicken litter slurry Jkuat mini digester
PG – Pig waste slurry Jkuat mini digester
UREA, NPK, CAN and DAP – inorganic fertilizers

2.2 Determination of Heavy Metals in selected Inorganic Fertilizers and in Bio Slurry

Levels of heavy metals (Pb, Cd, and Cr) in prepared samples of bio-slurry and inorganic fertilizers were determined. Standard solutions (1000 mg/L) of Pb(NO₃)₂, Cd(NO₃)₂, and Cr(NO₃)₂ were purchased from Sigma-Aldrich®. Calibration standards for each metal were prepared by serial dilution of procured stock solutions. 1 g each of selected inorganic fertilizers and bio slurry samples were digested with concentrated HNO₃ at 80°C. Fertilizer samples were digested in a beaker with concentrated HNO₃ according to the procedure of the Association of Official Analytical Chemists. The beakers were swirled gently until white fumes indicated full digestion. The digested samples were cooled to ambient temperature, filtered and adjusted to 50 ml with distilled water prior to analysis. The bio-fertilizer samples were swirled with concentrated HNO₃ at 80°C until the solution turn white. Finally, the digest was filtered through Whatman No. 42 and diluted to 50 ml with distilled water prior to analysis. Concentrations of Cd, Cr, and Pb were determined by Flame Atomic Absorption Spectrophotometer (Shimadzu 6200).

3. RESULTS AND DISCUSSION

Results of the study are presented in Table 1 and Fig. 1.

Using 3 standard deviation of the reagent blank the detection limits for the respective metals were determined to be Cd 0.0081 mg/l, Cr 0.0070 mg/l, and Pb 0.0084 mg/l.

Chicken litter and pig waste slurries had lead metal levels below detection limit. Cow dung samples both raw and digested from Githunguri had low levels of Pb ranging from 0.01 to 0.02 mg/l, these results are similar to literature [2]. All the inorganic fertilizers had detectable amounts of lead metal. DAP had the highest amount of Pb at 0.03 mg/l followed by CAN (0.02 mg/l) Urea and NPK had 0.01 mg/l each.

Cow dung from the mini digesters and chicken litter had Cd level below detection limits. On the other hand, pig waste had small amounts of Cd at about 0.02 mg/l. Cow dung samples from Githunguri contained Cd (0.06 mg/l) which were relatively higher than in pig waste.

All the four inorganic fertilizers contained Cd with the highest levels being in the phosphorous containing fertilizers DAP (0.41 mg/l) and NPK (0.48 mg/l).

Cr was found to be present in all samples, the highest in bio slurry samples being 0.09 mg/l in
Table 1. Heavy metals (mg/l) in slurry filtrates and selected inorganic fertilizers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb</th>
<th>Cd</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDS1</td>
<td>bdl</td>
<td>bdl</td>
<td>0.04±0.01</td>
</tr>
<tr>
<td>CDS2</td>
<td>bdl</td>
<td>bdl</td>
<td>0.03±0.00</td>
</tr>
<tr>
<td>CDS3</td>
<td>bdl</td>
<td>bdl</td>
<td>0.02±0.00</td>
</tr>
<tr>
<td>PGS1</td>
<td>bdl</td>
<td>0.02±0.00</td>
<td>0.03±0.00</td>
</tr>
<tr>
<td>PGS2</td>
<td>bdl</td>
<td>0.01±0.00</td>
<td>0.03±0.00</td>
</tr>
<tr>
<td>PGS3</td>
<td>bdl</td>
<td>bdl</td>
<td>0.02±0.00</td>
</tr>
<tr>
<td>CHS1</td>
<td>bdl</td>
<td>0.01±0.00</td>
<td>0.06±0.01</td>
</tr>
<tr>
<td>CHS2</td>
<td>bdl</td>
<td>bdl</td>
<td>0.04±0.01</td>
</tr>
<tr>
<td>CHS3</td>
<td>bdl</td>
<td>bdl</td>
<td>0.05±0.02</td>
</tr>
<tr>
<td>DG1</td>
<td>bdl</td>
<td>0.01±0.00</td>
<td>0.04±0.01</td>
</tr>
<tr>
<td>GR1</td>
<td>0.02±0.00</td>
<td>0.01±0.00</td>
<td>0.04±0.01</td>
</tr>
<tr>
<td>DG2</td>
<td>bdl</td>
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</tr>
<tr>
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<td>0.05±0.00</td>
</tr>
<tr>
<td>DG3</td>
<td>0.01±0.00</td>
<td>0.06±0.00</td>
<td>0.06±0.00</td>
</tr>
<tr>
<td>GR3</td>
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<td>0.02±0.01</td>
<td>0.07±0.00</td>
</tr>
<tr>
<td>UREA</td>
<td>0.01±0.00</td>
<td>0.28±0.00</td>
<td>0.06±0.00</td>
</tr>
<tr>
<td>NPK</td>
<td>0.01±0.00</td>
<td>0.48±0.00</td>
<td>0.01±0.00</td>
</tr>
<tr>
<td>CAN</td>
<td>0.02±0.00</td>
<td>0.15±0.01</td>
<td>0.08±0.02</td>
</tr>
<tr>
<td>DAP</td>
<td>0.03±0.00</td>
<td>0.41±0.01</td>
<td>0.03±0.01</td>
</tr>
</tbody>
</table>

± Standard deviation of 3 replications  bdl - below detection limit

Fig. 1. Heavy metal levels in filtrate slurry and selected inorganic fertilizers

Cow dung collected from Githunguri. CAN had the highest level of Cr (0.08 mg/l) among the inorganic fertilizers.

All the commercial fertilizers had substantial amounts of heavy metals. NPK had the highest amount of cadmium followed by DAP, Urea and CAN. Fertilizers with high Phosphorous content contain higher amounts of heavy metals since their origin are phosphate rocks which are mined in areas with heavy metal deposits. It is evident from figure 1 that most of the study bio slurry had on average low levels of the selected heavy metals than commercial inorganic fertilizers. Consequently, from the results bio slurry appears to be a better choice of fertilizers with respect to heavy metal pollution and the resulting bio accumulation that may be attributed to the metals.

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inputs to agricultural soils should be a strategic aim of soil protection policies [12].

4. CONCLUSION

The outcome of this study indicate that bio-slurry can be better alternative fertilizers with lower levels of heavy metals when compared to some inorganic fertilizers. We conclude that bio-slurry are a safer fertilizer with respect to heavy metals pollution and their subsequent bio-accumulation.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES


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