Evaluation of commonly used fertilizers, fish and poultry feeds as potential sources of heavy metals contamination in food

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Abstract: An experiment was conducted at the Department of Agricultural Chemistry, BAU to assess the heavy metal status in different feed and fertilizer samples collected from Sadar and Trisal upazilas of Mymensingh district. The feed samples included poultry and fish feeds, whereas, fertilizer samples included DAP, TSP, MOP, gypsum and zinc sulphate (ZnSO₄). AAS analysis of Cd, Cr and Pb showed variable levels of contamination in the fertilizer and feed samples. In case of feed samples, Cd, and Pb contents in fish feed collected from Sadar upazila was 0.159 and 3.581 mg kg⁻¹, respectively and that of Trisal upazila was 0.441 and 153.824 mg kg⁻¹, respectively. The content of Cd was 0.008 mg kg⁻¹ in poultry feed but in fish feed it was 0.441 mg kg⁻¹. The Cr content in both poultry and fish feeds collected from Sadar and Trisal upazilas were below the detection level. In general, heavy metals contaminations were higher in different fish feed samples compared to that of poultry feed samples, especially in samples from Trisal upazila.The Cd contents in DAP, TSP, MOP, gypsum and ZnSO₄ collected from Sadar upazila were 1.560, 14.749, 0.137, 0.906 and 10.312 mg kg⁻¹, respectively, and that of Trisal upazila were 1.780, 15.662, 3.988, 1.180 and 3.165 mg kg⁻¹, respectively. The Cr contents in DAP, TSP, MOP, gypsum and ZnSO₄ collected from Sadar upazila were 60.392, 206.667, 15.882, 24.314 and 11.373 mg kg⁻¹, respectively. Whereas, mean Cr concentrations DAP, TSP, MOP and gypsum from Trisal upazila were 54.118, 168.431, 16.078 and 26.863 mgkg⁻¹, respectively. However, in ZnSO₄,Cr was below the detection limit. Again, Pb contents in DAP, TSP, MOP, Gypsum and ZnSO₄ collected from Sadar upazila were 12.633, 45.729, 33.586, 13.319 and 30.014 mg kg⁻¹, respectively, and that of Trisal upazila were 4.062, 46.919, 101.205, 21.681 and 6.676 mg kg⁻¹, respectively. In general, heavy metal contamination levels in different fertilizer samples collected from Mymensingh Sadar were higher compared to that of Trisal upazila. The results showed that despite the close proximity of the market locations, heavy metal contents may vary in fertilizer and feed samples indicating various supply chains of these essential inputs are in place and calls for greater degree of quality monitoring from the government point of view.

Keywords: heavy metal contamination; poultry and fish feeds; fertilizers; Bangladesh

1. Introduction
In most developing countries like Bangladesh, attempts to increase food production and consumption are undermined by rapid population growth, migration from rural to urban areas and widespread land degradation. Population pressure continues to place a severe burden on productive capacity in the most developing countries like ours. However, the increasing population of the country needs an urgent supply of food for balancing the growing population with an increased food production (Nabulo et al., 2012). Nowadays, our country faces acute population pressure. But adopting modern agricultural practices, our country ensures the food demand of growing population in spite of having shortage of land. Bangladesh has managed to triple its rice production since its independence. Adoption of modern technologies accompanied by increased food
production may facilitate metal contamination in our food chain. Heavy metal contamination may occur due to factors including irrigation with contaminated water, the addition of fertilizers which may be contaminated with trace and heavy metals and metal based pesticides, industrial emissions, transportation, post harvesting process, storage and/or sale (Ali et al., 2013). Such heavy metal contaminations of food have a long term effect on our heath as well as our next generation.

Again, heavy metals contaminate the food at various stages along the food production line. Due to depletion of soil nutrients, agricultural application of chemical fertilizers is increasing globally. As human population continues to increase, putting pressure on food production systems, mainly crop and livestock production, the increase in the demand for food also raises but soil fertility deteriorates with time. This has led to substantial increase in application of plant nutrients, including inorganic fertilizers in the last 50 years to increase food production in order to satisfy human population demand (Ashraf, 2006). More than 30 million metric tons of phosphate fertilizers are annually consumed worldwide to increase crop production and land reclamation (Khater, 2008). Studies have shown that heavy metals in fertilizers can accumulate in soil and become readily available to plants (Modaihsh et al., 2004). For some time, there has been serious concern about the simultaneous input of unwanted trace elements, present in the mineral fertilizers, like Cd and Cr. Therefore, long-term application of fertilizers can redistribute and elevate toxic heavy metals such as As, Cd and Pb in soil and consequently, contribute to increased bioaccumulation of the heavy metals in the food chain.

More than half of the people of Bangladesh are based on agricultural and livestock farming. The poultry and fish sector is an integral part of farming systems and have created both direct and indirect employment opportunity, improved food security and enhanced supply of quality protein to people’s meals and reducing poverty level in rural and urban areas of Bangladesh. About 44% of human daily intake of animal protein comes from livestock and poultry products (HIES, 2010). The demand for fish, meat and egg has been expanding dramatically with income growth, population growth, urbanization and dietary changes. Recognizing this fact, some immoral feed producer are now using industrial wastes and by-product, especially from tanneries and dying industries, poultry litter to obtain high profit from the poultry and fish feeds. Due to this contamination in feed and food sector, heavy metals enter into our food chain and finally heavy metals are ending up in the food on our plate. Recently, it has been noted that some of the commercial feed producers failed to meet up with standards for the requirement of fish and in many ways, the source of raw material for the production of the feeds tends to be contaminated with heavy metals (Indrajit et al., 2011). There is very little information on the status of heavy metals in fish and poultry feeds produced by different feed industries, especially, at the local levels. Moreover, mineral supplements are occasionally added to poultry and fish feeds so as to fulfill the requirement. Unfortunately, most of the time, studies conducted on poultry feeds in India, Bangladesh, Pakistan and various other places around the world, have shown the presence of high concentration of heavy metals like Cr, Cd, Pb, Hg, Ni, etc. purely due to anthropogenic reasons (Mahmood et al., 2004; Hossain et al., 2007; Imran et al., 2014).

The risk associated with the exposure to heavy metals present in foodstuffs represents a concern to human health (Wang and Du, 2013; IARC, 1990; Flora et al., 2012). Hence, in recent years the increasing demand of food safety has accelerated research initiatives regarding the risk associated with consumption of food contaminated by heavy metals (Mansour et al., 2009). So, it has become an urgent issue to analyze the heavy metals in primary produce and raw materials. In Bangladesh, there is very little reliable works have been conducted to analyze the potential health risks from heavy metal contaminated fertilizer and feeds. In this context, the present study aimed to to assess the extent of heavy metal (Cd, Cr and Pb) contamination levels in commonly used fertilizer and feeds in the two selected upazilas of Mymensingh a major producer of agricultural and fisheries products.

2. Materials and Methods
2.1. Selection of markets
Notun Bazar and Mesua Bazar from Mymensingh Sadar upazila; and Pouro Market and Dorirampur Bazar from Trisal upazila were selected for sample collection. These four markets are representative market place for the locations as well as commodities selected.

2.2. Collection of poultry, fish feed and fertilizer samples
For this study, fish and poultry feeds and different fertilizer samples were collected from Mymensingh Sadar and Trisal upazillas of Mymensingh district. Equal numbers of fertilizers samples (three for each sample) were collected equally from Mymensingh Sadar and Trisal upazilas. The collected fertilizer samples were TSP, DAP, MoP, gypsum and zinc sulphate.
Poultry feed samples were collected equally from Mymensingh Sadar and Trisal upazilas. Collected feed samples have the following companies—Quality Feeds Limited, Madina Poultry Feed, United Feeds Ltd. etc. There are many commercial feeds which are being used by the farmers of Mymensingh district for production of fishes. Fish feed samples were collected equally from Mymensingh Sadar and Trisal upazila. Collected feed samples have the following companies—Quality Feeds Ltd., C. P Bangladesh Company Ltd., Fresh Feed, Usha Feeds Limited., Provitia Feed Ltd. Etc. Most collected fish feeds were locally produced.

Poultry feed, fish feed and fertilizer samples were finally selected as study samples for the analysis. Six samples of each commodity of poultry feed, fish feed and fertilizer having at least 500g weight were collected from three different vendors in every selected market. Then the samples were kept into air tight zip lock bags. The bags were properly labeled with unique codes. All sampling were done during the month of November 2016 and February 2017.

2.3. Sample processing

After collection, the samples were air dried and kept in individual paper bag with proper labeling and oven dried (Model no: KD 400 NUVE, Turkey) at 60°C for 48 hours until a constant weight was obtained. The dried samples were finely ground by an electric grinder (Model no: IKA A11B). Then the ground samples were kept in polythene zipper bags labeled with specific code number until subsequent analysis.

2.4. Sample digestion

Exactly 1 g of each feed samples was taken into a conical flask. Then 10 ml of di-acid mixture (HNO₃:HClO₄ = 2:1) was added into the conical flask. The samples were digested at 150°C until the white fumes appear. About 2 mL of H₂O₂ was added and heated until the digest became colorless. Then the samples were cooled. After cooling, the samples were filtered through Whatman No. 42 filter paper.

In case of fertilizer samples, exactly 1g of sample was taken into a conical flask. Then 50 mL of 50% HCl (1:1 dilution) was added into the sand bath. The samples were digested at 180°C in hot plate until the samples reached to about 2 ml. Then the samples were cooled. After cooling the samples, the samples were filtered through Whatman No. 42 filter paper to remove unwanted suspended materials. After filtering both fertilizer and feed samples, the digests were made up to 50 mL volume by deionized water and kept in labeled air tight polyvinyl bottles. Then the samples were stored in the refrigerator until analysis.

2.5. Analysis of heavy metals

Determination of different elements (Cd, Cr and Pb) in fertilizer, poultry and fish feed samples was done by using a Flame AAS (Model no: SHIMADZU, AA-7000, Japan). Mono element hollow cathode lamp was employed for the determination of each metal of interest. At first, the AAS was calibrated following the manufacturer’s recommendation. The filtered samples were run directly for the determination of heavy metals in the samples. Then, the concentration of the metals in fertilizer, poultry and fish feed samples was recorded directly by AAS.

2.6. Data compilation and processing

All data were subjected to analysis of variance (ANOVA) using statistical software MiniTab version 17.0 (MiniTable State College, PA, USA).

3. Results and Discussion

3.1. Heavy metals in poultry feeds

Collected poultry feed samples were analyzed. They showed variable amount of Cd, Cr and Pb. The mean concentration and associated standard deviation of Cd, Cr and Pb in poultry feed samples are presented in Table 1.

The concentration of Pb in poultry feed ranged between 0-0.729 mg kg⁻¹ (Figure 1). Statistical analysis by MiniTAB 17 revealed that there was significant difference in Pb content in poultry feed collected from Mymensingh Sadar and Trisal. The mean Pb content in feed sample from Mymensingh Sadar was 0.073 mg kg⁻¹. However, Pb was not detected from the samples collected from Trisal (Table 1).

The concentration of Cd in poultry feed ranged between 0-0.023 mg kg⁻¹ (Figure 1). Statistical analysis by MiniTAB 17 revealed that there was significant difference in Cd content. The mean Pb content in feed sample from Trisal was 0.008 mg kg⁻¹. However, Cd was not detected from the samples which were collected from Mymensingh (Table 1). The feed samples collected from the certain locations have Cr concentration below detectable limit by AAS.
The results for Pb and Cd in obtained in this study were lower than 1.10-7.85 mg kg\(^{-1}\) and 23.2-32.6 mg kg\(^{-1}\) obtained by Okoye et al. (2011) and Mahesar (2010) in their analysis of poultry feeds, respectively. Bukar and Saeed (2014) also found Pb (ranged from 0.56±0.26 to 0.47±0.13 mg kg\(^{-1}\)) in poultry feed within the permissible limits while Cd levels (ranged from 2.26±0.67 to 1.20±0.51 mg kg\(^{-1}\)) in all samples exceeded the permissible limit by regulatory bodies. In the present study, however, Cd and Pb in all the poultry feed samples met the heavy metal standards set by EC (2003) (2 and 5 ppm for Cd and Pb, respectively) and NRC (2005) (30 and 10 ppm, respectively) contrasting the results of Jothi et al. (2016) who found higher levels of both Cr and Pb where Pb exceeded the standard set by EC.

3.2. Heavy metals in fish feed

Collected fish feed samples were analyzed. They showed variable amount of Cd, Cr and Pb. The mean concentration and associated standard deviation of Cd, Cr and Pb in fish feed samples are presented in Table 1. The concentration of Pb in fish feed ranged between 0-446.443 mg kg\(^{-1}\) (Figure 1). Statistical analysis by MiniTAB 17 revealed that there was significant difference in Pb content in fish feed collected from Mymensingh Sadar and Trisal. The mean Pb concentration in fish feed was determined in Mymensingh and Trisal were 3.581 and 153.824 mg kg\(^{-1}\), respectively (Table 1 and Figure 1).

The concentration of Cd in fish feed ranged between 0.0913-0.4566 mg kg\(^{-1}\) (Figure 1). Statistical analysis by MiniTAB 17 revealed that there was no significant difference in Cd content in fish feed collected from Mymensingh Sadar and Trisal. The mean Cd content in fish feed was determined in Mymensingh and Trisal were 0.1598 and 0.4414 mg kg\(^{-1}\), respectively (Table 1). The feed samples collected from the certain locations have Cr concentration below detectable limit by AAS.

Table 1. Cadmium, Cr and Pb contents in different feed samples collected from Sadar and Trisal upazilas of Mymensingh district.

<table>
<thead>
<tr>
<th>Items</th>
<th>Location</th>
<th>Pb (mg kg(^{-1})) Mean</th>
<th>SD</th>
<th>Cr (mg kg(^{-1})) Mean</th>
<th>SD</th>
<th>Cd (mg kg(^{-1})) Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish feed</td>
<td>Trisal</td>
<td>153.824</td>
<td>253.446</td>
<td>ND</td>
<td>-</td>
<td>0.441</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>Mymensingh</td>
<td>3.581</td>
<td>5.583</td>
<td>ND*</td>
<td>-</td>
<td>0.160</td>
<td>0.060</td>
</tr>
<tr>
<td>Poultry feed</td>
<td>Trisal</td>
<td>ND*</td>
<td>-</td>
<td>ND*</td>
<td>-</td>
<td>0.008</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>Mymensingh</td>
<td>0.248</td>
<td>0.417</td>
<td>ND*</td>
<td>-</td>
<td>ND*</td>
<td>-</td>
</tr>
</tbody>
</table>

*ND- Not detected

Reference standards
EC (2003) 5 ppm - 2 ppm
NRC (2005) 10 ppm - 30 ppm

Figure 1. Box plot showing the comparative Cd (a) and Pb (b) contents (mean and range) in fish and poultry feeds collected from Mymensingh Sadar and Trisal upazilas.

Here, the fish feed samples from Trisal upazila exceeded the permissible limit set by both EC and NRC. However, Cd levels of all samples were below the international standards. The values of Trisal samples were much higher than that reported by Kundu et al. (2017) (ranged from 7.671 to 12.232 mg kg\(^{-1}\)) who collected feed samples from Muktagachha Upazila of Mymensingh district. The Pb content of feed samples from...
Mymensingh Sadar showed more resemblance with the Kundu et al. (2017) result. They also reported higher levels of Cd in the feed samples (ranged from 8.082 to 9.771 mg kg$^{-1}$) unlike the present study.

### 3.3. Heavy metals in fertilizer

Analysis of heavy metals in five different fertilizers showed variable amount of Pb, Cr and Cd. The results are presented in Table 2.

The concentration of Pb, Cr and Cd in DAP fertilizer ranged between 2.16-17.16 mg kg$^{-1}$, 40.59-64.12 mg kg$^{-1}$ and 0-0.0913 mg kg$^{-1}$, respectively (Figure 2). Statistical analysis by MiniTab 17 revealed that except Pb, there was no significant differences in Cd and Cr contents in DAP collected from Mymensingh Sadar and Trisal. The mean Pb, Cr and Cd contents in DAP fertilizer from Mymensingh were 12.633, 60.392 and 1.560 mg kg$^{-1}$, respectively; while in Trisal these were 4.062, 54.118 and 1.781 mg kg$^{-1}$, respectively (Table 2).

The concentration of Pb, Cr and Cd in TSP fertilizer ranged between 40.73-50.73 mg kg$^{-1}$, 111.765-230 mg kg$^{-1}$ and 0.776-31.118 mg kg$^{-1}$, respectively (Figure 2). Statistical analysis by MiniTab 17 revealed that there was no significant differences in Pb, Cd and Cr contents in TSP collected from Mymensingh Sadar and Trisal. The mean Pb, Cr and Cd contents in TSP fertilizer from Mymensingh were 45.729, 206.667 and 14.749 mg kg$^{-1}$, respectively; while in Trisal these were 46.919, 168.431 and 15.662 mg kg$^{-1}$, respectively (Table 2).

### Table 2. Cadmium, Cr and Pb contents in different fertilizer samples collected from Sadar and Trisal upazilas of Mymensingh district.

<table>
<thead>
<tr>
<th>Items</th>
<th>Location</th>
<th>Pb</th>
<th>Cr</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean** SD</td>
<td>Mean SD</td>
<td>Mean SD</td>
<td>SD</td>
</tr>
<tr>
<td>Gypsum</td>
<td>Trisal</td>
<td>21.681a 9.101</td>
<td>26.863 1.891</td>
<td>1.180 0.765</td>
</tr>
<tr>
<td></td>
<td>Mymensingh</td>
<td>13.319b 4.185</td>
<td>24.314 6.123</td>
<td>0.906 0.197</td>
</tr>
<tr>
<td>MoP</td>
<td>Trisal</td>
<td>101.205a 70.059</td>
<td>16.078 0.340</td>
<td>3.988a 3.369</td>
</tr>
<tr>
<td></td>
<td>Mymensingh</td>
<td>33.586b 8.66</td>
<td>15.882 1.765</td>
<td>0.137b 0.165</td>
</tr>
<tr>
<td>TSP</td>
<td>Trisal</td>
<td>46.919 2.887</td>
<td>168.431 49.076</td>
<td>15.662 15.179</td>
</tr>
<tr>
<td></td>
<td>Mymensingh</td>
<td>45.729 5.000</td>
<td>206.667 28.225</td>
<td>14.749 1.839</td>
</tr>
<tr>
<td>ZnSO$_4$</td>
<td>Trisal</td>
<td>6.676b 11.551</td>
<td>ND</td>
<td>3.165b 0.414</td>
</tr>
<tr>
<td></td>
<td>Mymensingh</td>
<td>30.014a 13.906</td>
<td>11.373a 19.698</td>
<td>10.312a 7.509</td>
</tr>
<tr>
<td>DAP</td>
<td>Trisal</td>
<td>4.062b 1.798</td>
<td>54.118 12.155</td>
<td>1.781 1.561</td>
</tr>
<tr>
<td></td>
<td>Mymensingh</td>
<td>12.633a 3.934</td>
<td>60.392 5.951</td>
<td>1.560 0.058</td>
</tr>
</tbody>
</table>

*ND- Not detected
** Figures with different letters are significantly different at 5% level using the Tukey method.

The concentration of Pb, Cr and Cd in MoP fertilizer ranged between 22.87-157.87 mg kg$^{-1}$, 14.117-17.647 mg kg$^{-1}$ and 0-6.874 mg kg$^{-1}$, respectively (Figure 2). Statistical analysis by MiniTab 17 revealed that Pb and Cd contents were significantly different in MoP fertilizers collected from Mymensingh Sadar and Trisal. The mean Pb, Cr and Cd contents in MoP fertilizer from Mymensingh were 33.586, 15.882 and 0.137 mg kg$^{-1}$, respectively; while in Trisal these were 101.205, 16.078 and 3.988 mg kg$^{-1}$, respectively (Table 2).

The concentration of Pb, Cr and Cd in gypsum fertilizer ranged between 8.557-32.157 mg kg$^{-1}$, 19.412-31.176 mg kg$^{-1}$ and 0.639-2.055 mg kg$^{-1}$, respectively (Figure 2). Statistical analysis by MiniTab 17 revealed that except Pb, no significant differences was found for Cd and Cr contents in DAP collected from Mymensingh Sadar and Trisal. The mean Pb, Cr and Cd contents in DAP fertilizer from Mymensingh were 13.319, 24.314 and 0.906 mg kg$^{-1}$, respectively; while in Trisal these were 21.681, 26.863 and 1.180 mg kg$^{-1}$, respectively (Table 2).

The concentration of Pb, Cr and Cd in zinc sulphate fertilizer ranged between 0-40.779 mg kg$^{-1}$, 0-34.118 mg kg$^{-1}$ and 1.644-14.840 mg kg$^{-1}$, respectively (Figure 2). Statistical analysis by MiniTab 17 revealed that all three heavy metal contents were significantly different in zinc sulphate fertilizers collected from Mymensingh Sadar and Trisal. The mean Pb, Cr and Cd contents in MoP fertilizer from Mymensingh were 30.014, 11.373 and 10.312 mg kg$^{-1}$, respectively. In fertilizers collected from Trisal Cr was below the detection limit. However, Pb and Cd contents were 6.676 and 3.165 mg kg$^{-1}$, respectively (Table 2).

From the results, it was apparent that TSP had the highest contamination of all three metals analysed. The Pb and Cd contents in MoP, especially in samples from Trisal, were also high. Among the two sampled locations, except for Pb, little difference was observed considering Cd and Cr contents in most fertilizers analysed. However, heavy metal contents vary greatly in zinc sulphate collected from the two locations. Wang and Li
As presented by Benson et al. (2014), Atafar et al. (2010) and Sultana (2010), phosphate and micronutrient fertilizers, and liming materials contain elevated levels of arsenic, cadmium, and lead compared to other fertilizer types. The results for Pb contents observed in the present study were much higher than the reports presented by Benson et al. (2014), Atafar et al. (2010) and Sultana (2010) who studied heavy metal load in various NPK fertilizers. On the contrary, Cd levels in the present study were lower than the values found in same reports.

**Figure 2.** Box plot showing the comparative Pb, Cr and Cd contents (mean and range) in TSP, DAP, MOP (a-c); gypsum and zinc sulphate (d-f) fertilizers collected from Mymensingh Sadar and Trisal upazilas.

### 4. Conclusions
There have been heightened concerns about human health, the environment and the sustainability of farming practices arising from the use of commercial fertilizers as well as animal feeds that contain elevated amounts of toxic trace metals. In this context, the research was conducted to assess the heavy metal and trace element concentrations in some fertilizer and feed samples collected from two locations of Mymensingh District. High
variations in the concentration of heavy metals especially for Pd were found in all samples among the two locations due to the variation in point sources of collection and marketing. Again, no matter how close the sample locations, for some metal elements significant concentration differences were observed in the studied materials. However, the present study has given partial information about contamination status within the study sites but not enough data about the whole country. To understand about the overall contamination status throughout the country, more science based experiment with larger sample size covering all regions should be conducted.

Conflict of interest
None to declare.

References


