Chromium from tannery waste in poultry feed: A potential cradle to transport human food chain

Sobur Ahmed*, Fatema-Tuj-Zohra1, Md. Shiblee Hider Khan1 and Md. Abul Hashem2

Abstract: Raw skin trimmings (RST), wet blue shaving dusts (WSD), and low-chrome wet-blue scraps (LCWS) are protein-rich tannery wastes which are used as one of the main ingredients for manufacturing of poultry feeds. These feeds may contain toxic chromium, which accumulates in the poultry and cause chrome contamination in human food chain. It is a major concern for humans consuming these poultry as part of their regular diet. In this study, tannery wastes, 12 brands of poultry feeds, broiler chickens (Gallus gallus domesticus) nourished on chrome containing feed were collected for the investigation of total chromium present and circulated through the process of ingestion and digestion. The chromium content of RST and all poultry feed samples were found to be below 0.03 mg/kg, except the samples of WSD, LCWS, starter feed (FS10), and grower feed (FS11), which were 29854.4 ± 0.9, 14902.0 ± 1.01, 618.3 ± 0.9 and 3.02 ± 0.07 mg/kg, respectively. The chromium in protein concentrate made from WSD and LCWS were 21535.4 ± 1.01 and 13421.8 ± 0.04 mg/kg, respectively. Various body parts of chickens were found to be contained the element in the range of 0.42 to 0.84 mg/kg. Hence, there is a potential human health risk through consumption of contaminated poultry meat as it exceeded the daily adequate intakes (AIs) level.

ABOUT THE AUTHORS

Sobur Ahmed, Fatema-Tuj-Zohra, and Md. Shiblee Hider Khan belong to the same working group at the Institute of Leather Engineering and Technology, University of Dhaka, Dhaka 1209, Bangladesh. Their research interests are in the domain area of leather science with waste management and pollution control. Ahmed has published a book and 15 research papers in the national and international reputed journals. Fatema has published a book and 10 research papers in the national and international journals.

Md. Abul Hashem is an assistant professor in the Department of Leather Engineering at Khulna University of Engineering and Technology, Bangladesh with research interest in the leather engineering and waste management. He published 22 research articles in different national and international journals.

PUBLIC INTEREST STATEMENT

Bangladesh is a densely populated developing country where poultry is one of the main cheap sources of protein as human diet. A few farms reared poultry using feed made from tannery solid waste. About 80% protein-rich solid wastes generated from tannery during leather processing and 90% of these leather processed by chrome tanning method. Chromium was detected in the collected poultry feeds made from wet blue scraps and saving dusts. The chromium content was found to be accumulated in the body parts of chickens reared with the chrome-containing poultry feed. Trace amounts of chromium (III) is essential for certain metabolic functions in the human body. However, excessive heavy metals may cause serious adverse effects on human health. Chromium did not found in the poultry feed prepared from raw skin trimmings. Hence, the consumption of poultry meat reared by these feeds may not be exposed to health hazards.
1. Introduction

Metal pollutants are potentially toxic elements, which are potentially harmful for human health when transported via the food chain (Arain et al., 2009; Kabay et al., 2005). Many researchers have investigated the toxicological effects of chromium on the human health ingested through different food items (Bratakos, Lazos, & Bratakos, 2002; Cubadda, Giovannangeli, Iosi, Raggi, & Stacchini, 2003; Tinggi, Reilly, & Patterson, 1997; Uluozlu, Tuzen, & Soylak, 2009). It has been found that chromium (III) in trace amounts is essential for certain metabolic functions in the human body (Kalidhasan, Ganesh, Sricharan, & Rajesh, 2009). On the other hand, chromium (VI) can be toxic and carcinogenic (Matos, dos Reis, Costa, & Ferreira, 2009; Yalçin & Apak, 2004). About 90% tanning industries use basic chromium sulfate (BCS) during tanning, (Aravindhan, Madhan, Rao, Nair, & Ramasami, 2004); this chromium sulfate binds with the collagen protein to make stabilize it against degradation. On an average, only 60% of the entire chromium used is taken up by the pelt, while the remaining 40% chromium expelled through solid and liquid wastes, especially as spent chrome liquor (Fabiani, Ruscio, Spadoni, & Pizzichini, 1997).

Solid wastes generated in tannery industries mainly consist of skin trimmings, keratin wastes, fleshing wastes, chrome shaving wastes, and buffing wastes (Kanagaraj, Velappan, Babu, & Sadullah, 2006). Chrome shaving dusts, wet blue scraps, and buffing dusts contain huge amount of chromium. It is reported that chrome shaving dusts contain chromium in the range of 10.68 ± 1.98 mg/g (Swarnalatha, Srinivasulu, Srimurali, & Sekaran, 2008). Disposing of this high chromium content solid wastes as land fill or dumping these may cause leaching of chromium to groundwater and thus cause its entry into the human food chain. In Bangladesh, every year 5.9 × 10^4 tons of hides and skins (bovine, sheep, lamb, goat, and kid) are used are raw material for leather production (Food and Agriculture Organization of the United Nations [FAO], 2013), leading to huge amounts of solid wastes being generated by the tanneries. Injudicious disposal of solid wastes from the tanneries cause environmental pollution, which ultimately has detrimental effects on human health when exposed it through various agencies (Sundar, Raghavarao, Muralidharan, & Mandal, 2011). Due to the generation of solid, liquid, and gaseous pollutants, Department of Environment (DoE), Bangladesh has categorized tanneries as a ‘red’ category industry. Many research groups have already investigated different ways to manage the solid wastes originating from the tanneries (Cabeza et al., 1998; Ravindran & Sekaran, 2010; Shanmugam & Horan, 2009).

In Bangladesh, several large and many small mills are converting the solid wastes into protein concentrates without following any appropriate standard operating procedure. This protein concentrate is mixed with other ingredients to prepare poultry feeds. Each large mill produces 200–250 tons of protein concentrate per day (Hossain et al., 2007). Transfer of chromium into poultry may occur through these feeds, which then enters into the human food chain. It is very important to know the quantity of chromium present in the feed and the amount of chromium transmitted to the body parts of chicken which are consumed as human food.

In this study, an investigation was carried out to determine and quantify the chromium content in (1) solid wastes used in producing protein concentrate, (2) prepared poultry feed, and (3) different body parts of chicken which were reared by selected feed.
2. Materials and methods

2.1. Sampling
Raw skin trimmings, chrome shaving dusts, and wet blue scraps were collected from Hazaribagh tannery area, Dhaka in an uncontaminated polyethylene bags. Poultry feed samples for broiler chickens (Gallus gallus domesticus) were collected from a poultry farm of Dhaka city and marked as: (a) starter feed, (b) grower feed, and (c) finisher feed. Two chickens reared on the feeds containing chrome were collected from the same poultry farm. The legs of both the chickens were cleaned with deionized water and wiped with non-adhesive tissue paper. The chickens were weighed after proper drying and denoted as A (1.5 kg) and B (1.3 kg). The chickens were slaughtered with sharp stainless steel knife by slitting the throat.

2.2. Sample preparation
The slaughtered chickens were hung upside down for 30 min to allow all the blood to be drained. Then every part of the chickens, i.e. meat, liver, heart, gizzard, and bones were separated with stainless steel knife; each part was washed with deionized water and air-dried on Petri dishes. All glassware and stainless steel knife were sterilized at oven for 72 h at 125–130°C. Then, samples were cut into small pieces with stainless steel knife and each type was mixed homogenously. Clean and hygienic conditions were maintained at all times to prevent contamination.

2.3. Reagents
All stock solutions were prepared from analytical grade reagent. The chrome shaving dusts and wet blue scraps were digested with nitric acid (Merck, India), hydrochloric acid (Merck, India), and sulfuric acid (Merck, India). The feed samples were digested with nitric acid and perchloric acid (BDH, England). Freshly prepared double deionized water was used in all the experiments. Prepared samples were kept in acid-washed plastic polymer bottles.

2.3.1. Acid digestion
Different methods were used for preparation of different types of samples. All the samples were conditioned following standard IUC method before analysis.

2.3.2. Acid digestion of raw skin trimmings, shaving dusts, and wet blue scraps
For preparing the raw skin trimmings, shaving dusts, and wet blue scraps, about 50 mg of samples were poured into the digestion vessel and 3 mL of nitric acid (HNO₃) was added, in which 1 mL of hydrochloric acid (HCl) and 3 mL of sulfuric acid (H₂SO₄) was added. The mixture was gently swirled manually for 10 min before the vessel was stoppered. Then it was digested with microwave digester at 190°C and 35 bar pressure for 20 min. The obtained solution was cooled, filtered, and diluted to 25 mL (Huq & Didar-Ul-Alam, 2005).

2.3.3. Acid digestion of poultry feed
About 0.4 g of the feed sample was taken and 5 mL of nitric acid (HNO₃) was added to it. The mixture was left standing for 1 h. After 1 h, 3 mL of perchloric acid (HClO₄) was added to the sample and it was left standing for 30 min. After 30 min, the sample was digested at 200°C on a hot plate. The digested sample was diluted to 25 mL and filtered through Whatman 44 filter paper (Hossain, Barreto, & Silva, 1998).

2.3.4. Acid digestion of organ
The biological samples (body parts of chicken) were washed with distilled water and then air dried. They were conditioned for 72 h at 60°C to remove the moisture. The samples were then cut into small pieces and each type was mixed homogeneously. About 0.4 g of these samples was taken in a beaker and left for 1 h after 5 mL of nitric acid (HNO₃) being added to it. Then, 3 mL of perchloric acid (HClO₄) was added to it and left for 30 min. After 30 min the sample was digested at 200°C on a hot plate. The solution obtained was diluted to 25 mL and filtered with Whatman 44 filter paper (Hossain et al., 1998).
2.4. Determination of chromium

Acid digested aliquot was analyzed with the use of atomic absorption spectroscopy (SHIMADZU, AA-7000) in order to quantify the chromium content. Direct flame (air-acetylene) at the wavelength of 357.9 nm was employed at this stage of the procedure. The detection limit of the atomic absorption spectroscopy for chromium was 0.03 mg/kg. The machine was calibrated and ISO 17025 certified.

3. Results and discussion

3.1. Chromium content in tannery waste and protein concentrate

The chromium concentration in the tannery waste and protein concentrate is shown in Table 1. It is clear from the data that out of the three raw materials, two contained high amounts of chromium. The chromium content in the wet blue shaving dust (WSD) was 29,854.4 ± 0.9 mg/kg and in the low-chrome wet blue scraps (LCWS) was 14,902.0 ± 1.01 mg/kg. In the raw skin trimmings, chromium content was below 0.03 mg/kg.

The chromium content in the 12 different poultry feeds is shown in Table 2. Out of 12 poultry feeds tested, only 2 contained chromium. The chromium content in the samples FS10 (starter feed) and FS11 (finisher feed) were 618.3 ± 0.9 and 3.02 ± 0.07 mg/kg, respectively. The chromium content in the remaining 10 feed samples was less than 0.03 mg/kg.

3.2. Chromium content in the body parts of chicken

Standard poultry feeds in Bangladesh are made by adding various ingredients, e.g. maize, wheat, soya oil cake, barley, and ground rice with protein concentrate. It was observed that in the poultry farm used for sampling, three types of feed were used to rear the chickens. The transport mechanism of chromium from tannery waste to human food chain through poultry feed is shown in Figure 1.

| Table 1. Chromium content in tannery waste and protein concentrate |
|---------------------------------------------------------------|
| **Tannery waste** | **Cr (mg/kg)** | **Protein concentrate** | **Cr (mg/kg)** |
| Raw skin trimmings | <0.03 | Made from the RST | <0.03 |
| Wet blue shaving dust | 29,854.4 ± 0.9 | Made from the WSD | 21,535.4 ± 1.01 |
| Low-chrome wet-blue scraps | 14,902.0 ± 1.01 | Made from the LCWS | 13,421.8 ± 0.04 |

| Table 2. Chromium content in different poultry feed |
|---------------------------------------------------|
| **Sample ID** | **Sample type** | **Cr content (mg/kg)** |
| FS1 | Starter feed | <0.03 |
| FS2 | Grower feed | <0.03 |
| FS3 | Finisher feed | <0.03 |
| FS4 | Starter feed | <0.03 |
| FS5 | Grower feed | <0.03 |
| FS6 | Finisher feed | <0.03 |
| FS7 | Starter feed | <0.03 |
| FS8 | Grower feed | <0.03 |
| FS9 | Finisher feed | <0.03 |
| FS10 | Starter feed | 618.3 ± 0.9 |
| FS11 | Grower feed | 3.02 ± 0.07 |
| FS12 | Finisher feed | <0.03 |
Figure 2 shows chromium accumulation in the different body parts of the chicken sample A and sample B.

It is clear from Figure 2 that the chromium accumulated in the different body parts, i.e. meat, bone, heart, gizzard, and liver of the chickens reared with chrome-containing poultry feed samples FS10 and FS11. The chromium content in the heart and gizzard of chicken B (wt. 1.3 kg) was much lower than that of chicken A (wt. 1.5 kg), whereas it was higher in the bone of chicken B. The highest amount of chromium was found in the heart of chicken A, i.e. 0.84 mg/kg.

3.3. Adequate intakes of chromium

Table 3 shows the adequate intakes (AIs) of chromium required or acceptable for humans, from infant to above 50 years. It is evident that a minuscule amount of chromium is required for humans of all ages. In case of infants, per day requirement of chromium is 0.2 μg; whereas, for children (8 years), it is 75 times higher than that of infants. In addition, for the average male aged of 9–50,

| Age          | Infants and children (μg/day) | Male (μg/day) | Female (μg/day) | Pregnancy (μg/day) | Lactation (μg/day) |
|--------------|-------------------------------|---------------|-----------------|--------------------|--------------------|
| 0–6 months   | 0.2                           |               |                 |                    |                    |
| 7–12 months  | 5.5                           |               |                 |                    |                    |
| 1–3 years    | 11                            |               |                 |                    |                    |
| 4–8 years    | 15                            |               |                 |                    |                    |
| 9–13 years   | 25                            | 21            |                 |                    |                    |
| 14–18 years  | 35                            | 24            | 29              | 44                 |                    |
| 19–50 years  | 35                            | 25            | 30              | 45                 |                    |
| >50 years    | 30                            | 20            |                 |                    |                    |
this daily chromium intake requirement is higher than the requirement of the average female in the same age group. Moreover, during pregnancy, a female's requirement for adequate intake of chromium is higher than the normal daily requirement.

4. Conclusions
In this study, chromium was found in the starter and grower poultry feed, however, it was below the detection limit in the finisher feed. The toxic chromium was found to accumulate in the body parts of chickens reared by chrome-containing poultry feed. Transfer of excessive chromium in human food chain through chicken meat is harmful for human health, though a trace amount of chromium is required for humans of all ages. Protein concentrate made from raw trimmings were quite safe to be used in poultry feed preparation as they were found to be free of heavy metals like chromium. De-chroming of shaving dust and wet blue scraps are indispensable for safe production of protein concentrate and poultry feed. Cost-effective protein concentrate can be produced from de-chromed shaving dusts, wet blue scraps, and fresh raw skin trimmings, and in conjunction with vegetable protein, can be used in the preparation of safe and nutritious poultry feed.

Funding
The authors received no direct funding for this research.

Author details
Sobur Ahmed
E-mail: soburahmed@du.ac.bd
Fatema-Tuj-Zohra
E-mail: fatema.ilet@du.ac.bd
Md. Shiblee Hider Khan
E-mail: shibleehider@gmail.com
Md. Abul Hashem
E-mail: mahashem@moli.kuet.ac.bd
1 Institute of Leather Engineering and Technology, University of Dhaka, Dhaka 1209, Bangladesh.
2 Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna 9203, Bangladesh.

Citation information
Cite this article as: Chromium from tannery waste in poultry feed: A potential cradle to transport human food chain, Sobur Ahmed, Fatema-Tuj-Zohra, Md. Shiblee Hider Khan, & Md. Abul Hashem, Cogent Environmental Science (2017), 3: 1312767.

References
Arain, M. B., Kazi, T. G., Boig, J. A., Jamali, M. K., Afri, H. I., Shah, A. Q., Jalbani, N., & Sarfraz, R. A. (2009). Determination of arsenic levels in lake water, sediment, and foodstuff from selected area of Sindh, Pakistan: Estimation of daily dietary intake. Food and Chemical Toxicology, 47, 242–248.

Aravindhan, R., Madhan, B., Rao, J. R., Nair, B. U., & Ramasami, T. (2004). Biomagnification of chromium from tannery wastewater: An approach for chrome recovery and reuse. Environmental Science and Technology, 38, 300–306.

Bhattacharyya, M. S., Lazor, E. S., & Bhattacharya, S. M. (2002). Chromium content of selected Greek foods. The Science of the Total Environment, 290, 47–58.

Cabeza, L. F., Taylor, M. M., DiMaio, G. L., Brown, E. M., Marmer, W. N., Cerri, R., Cob, J. (1998). Processing of leather waste: Pilot scale studies on chrome shavings. Isolation of potentially valuable protein products and chromium. Waste Management, 18, 211–218.

Cubadda, F., Giovannangeli, S., Iosi, F., Ragi, A., & Stacchini, P. (2003). Chromium determination in foods by quadrupole inductively coupled plasma-mass spectrometry with ultrasonic nebulization. Food Chemistry, 81, 463–468.

Cubadda, F., Giovannangeli, S., Iosi, F., Ragi, A., & Stacchini, P. (2003). Chromium determination in foods by quadrupole inductively coupled plasma-mass spectrometry with ultrasonic nebulization. Food Chemistry, 81, 463–468.

Fabiani, C., Ruscio, F., Spadoni, M., & Pizzicini, M. (1997). Chromium (III) salts recovery process from tannery wastewaters. Desalination, 108, 183–191.

Food and Agriculture Organization of the United Nations (FAO). (2013). World statistical compendium for raw hides and skins, leather and leather footwear, 1993–2012.

Hossain, A. M. M. M., Monir, T., Rezwan-Ul-Haque, A. M., Kazi, M. A. I., Islam, M. S., & Elahi, S. F. (2007). Heavy metal concentration in tannery solid wastes used as poultry feed and the ecotoxicological consequences. Bangladesh Journal of Scientific and Industrial Research, 42, 397–416.

Hossain, S. M., Barreto, S. L., & Silva, C. G. (1998). Growth performance and carcass composition of broilers fed supplemental chromium from chromium yeast. Animal Feed Science and Technology, 71, 217–228.

Haque, M. M., & Didar-Ul-Alam, M. D. (Eds.). (2005). A handbook on analysis of soil, plant and water (pp. 246). Bangladesh: BACER-DU, University of Dhaka.

Kabany, N., Solak, Özge, Arda, M., Topal, Ümmühan, Yüksel, M., Troichczuk, A., & Streit, M. (2005). Packed column study of the sorption of hexavalent chromium by novel impregnated resins containing alioquix 336: Effect of chloride and sulfate ions. Reactive and Functional Polymers, 64, 75–82.

Kalihasan, S., Ganesh, M., Sricharan, S., & Rajesh, N. (2005). Extractive separation, determination of chromium in tannery effluents and electroplating waste water using tribenzylamine as the extractant. Journal of Hazardous Materials, 165, 886–892.

Kanagaraj, J., Velappan, K. C., Babu, N. K., & Sadullah, S. (2006). Solid wastes generation in the leather industry and its utilization for cleaner environment: A review. Journal of Scientific and Industrial Research, 65, 541–546.

Matos, G. D., dos Reis, E. B., Costa, A. C. S., & Ferreira, L. C. (2000). Speciation of chromium in river water samples contaminated with leather effluents by flame atomic absorption spectrometry after separation/preconcentration by cloud point extraction. Microchemical Journal, 92, 135–139.
Ravindran, B., & Sekaran, G. (2010). Bacterial composting of animal fleshing generated from tannery industries. Waste Management, 30, 2622–2630. http://dx.doi.org/10.1016/j.wasman.2010.07.013

Shanmugam, P., & Horan, N. J. (2009). Optimising the biogas production from leather fleshing waste by co-digestion with MSW. Resource Technology, 100, 4117–4120. http://dx.doi.org/10.1016/j.biortech.2009.03.052

Sundar, V. J., Raghavarao, J., Muralidharan, C., & Mandal, A. B. (2011). Recovery and utilization of chromium-tanned proteinous wastes of leather making: A review. Critical Reviews in Environmental Science and Technology, 41, 2048–2075. http://dx.doi.org/10.1080/10643389.2010.497434

Swarnalatha, S., Srinivasulu, T., Srimurali, M., & Sekaran, G. (2008). Safe disposal of toxic chrome buffing dust generated from leather industries. Journal of Hazardous Materials, 150, 290–299. http://dx.doi.org/10.1016/j.jhazmat.2007.04.100

Tinggi, U., Reilly, C., & Patterson, C. (1997). Determination of manganese and chromium in foods by atomic absorption spectrometry after wet digestion. Food Chemistry, 60, 123–128. http://dx.doi.org/10.1016/S0308-8146(96)00328-7

Uluozlu, O. D., Tuzen, M., & Soylak, M. (2009). Speciation and separation of Cr(VI) and Cr(III) using coprecipitation with Ni2+/2-Nitroso-1-naphthol-4-sulfonic acid and determination by FAAS in water and food samples. Food and Chemical Toxicology, 47, 2601–2605. http://dx.doi.org/10.1016/j.fct.2009.07.020

Yalçın, S., & Apak, R. (2004). Chromium (III, VI) speciation analysis with preconcentration on a maleic acid-functionalized XAD sorbent. Analytical Chimico Acta, 505, 25–35. http://dx.doi.org/10.1016/S0003-2670(03)00498-7