Heavy Metal Residue in Milk of *Holstein Friesian* Dairy Cows Supplemented by Urea Molasses Multi-Nutrient Block Containing Cement Substituted by Tapioca Meal

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Abstract. Urea Molasses Multi-Nutrient Block (UMMB) is a feed supplement for dairy cows, comprising fillers and adhesives. Cement is the most commonly used adhesive in UMMB; however, it consists of inorganic materials that may lead to the precipitation of heavy metals in dairy products, such as milk. In contrast, tapioca meal exhibits similar adhesive properties and is considered a viable substitute for cement in UMMB. This research aimed to evaluate the impact of substituting cement with tapioca meal as an adhesive in UMMB on heavy metal residues, specifically lead (Pb), cadmium (Cd), and mercury (Hg), in cow's milk. A total of 20 lactating *Holstein Friesian* dairy cows were organized into five dietary treatments according to a completely randomized design, with four cows serving as replicates for each treatment. The dietary treatments included UMMB with 100% cement adhesive (T0); a mixture of 75% cement and 25% tapioca meal (T1); 50% cement and 50% tapioca meal (T2); 25% cement and 75% tapioca meal (T3); and 100% tapioca meal (T4). The milk's Pb, Cd, and Hg concentrations were subsequently measured. Results indicated that the treatment had a significant effect ($P<0.05$) on Pb levels, while no significant effects ($P>0.05$) were observed for Cd and Hg. The concentrations of Pb and Cd in the milk across all treatments ranged from 0.009 to 0.01 ppm and 0.10 to 0.11 ppm, respectively. Notably, Hg residues were not detected in the milk samples. Consequently, it can be concluded that tapioca meal is an effective alternative to cement as an adhesive in UMMB. Furthermore,

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UMMB supplemented with tapioca meal is superior due to its organic composition.

1 Introduction

Milk production and its composition are influenced by various factors, particularly the nutrients cows consume. Nutrients are chemical substances in feedstuffs that can be mobilized and utilized for basal maintenance, production, and reproduction [1]. The urea molasses multi-nutrient block (UMMB) represents a cost-effective technology that enhances ruminant productivity and holds significant potential for improving livestock nutrition in Indonesia. In several countries, UMMB has been utilized as a feed supplement for beef cattle, dairy cows, and small ruminants. Utamy et al. [2] reported that UMMB feed supplements can boost postpartum Bali cattle's daily gain and overall performance. Typically, UMMB is produced from a combination of molasses, urea, and either cement or lime as an adhesive, along with bran and various protein-rich by-products, salt, and water, all mixed and processed into a solid, compact block [3]. Our previous study also examined the use of UMMB [2].

UMMB comprises fillers and adhesives, with cement being a commonly used adhesive material. However, cement dust contains heavy metals such as chromium, nickel, cobalt, lead, and mercury, which can be detrimental to the environment, particularly soil, and adversely affect vegetation, human health, animal health, and the ecosystem [4]. While small amounts of heavy metals are essential for maintaining good health, excessive exposure can lead to toxicity and serious health risks. Heavy metal toxicity may result in decreased energy levels and adversely affect the functioning of critical organs, including the brain, lungs, kidneys, liver, and blood composition. Prolonged exposure can lead to progressive physical, muscular, and neurological degenerative conditions that may resemble diseases such as multiple sclerosis, Parkinson's disease, Alzheimer's disease, and muscular dystrophy. In some cases, repeated long-term exposure to certain metals and their compounds has been linked to cancer risk [5].

Cement contains heavy metals that can be detrimental to human health; therefore, substituting cement with safer adhesive alternatives is essential. Tapioca meal presents a viable substitute for cement, as it exhibits similar adhesive properties [6]. This study aimed to investigate the impact of substituting cement with tapioca meal as an adhesive in Urea-Molasses Multi-Nutrient Blocks (UMMB) on the levels of heavy metal residues—specifically lead (Pb), cadmium (Cd) and mercury (Hg)—in cow's milk.

2 Materials and methods

2.1 Study Site and Materials

The study was located with precision in Lebang Village, situated in the Cendana Sub-district of Enrekang Regency, from January to February 2023. We thoroughly analyzed heavy metal residues in milk samples at the Chemical Feed Laboratory in the Faculty of Animal Science at Hasanuddin University, Makassar. The UMMB feed supplement is expertly formulated and includes rice bran, urea, coconut cake meal, essential minerals, tapioca meal, cement (serving as an adhesive), vitamins, and salt.

2.2 Research Implementation

All feed ingredients were measured according to the specified formulations and thoroughly mixed using a hand mixer. The mixtures were then formed into rounds and

pressed with suitable equipment. Additionally, the UMMB was placed in a dehydrator at 70°C for approximately 15 hours before being fed to lactating Holstein Friesian dairy cows. The study was conducted for 60 days with a 7-day feed adaptation period. Dairy cows were kept in group cages side by side, with the size of each cage being 5 m × 2 m. The process of providing forages was fed twice a day, at 08.00 AM and 04.00 PM. Tofu dregs were fed once at 07.00 PM. The rate of feed given was 3% (dry matter basis) of the dairy cow's body weight. The UMMB was placed on the side of the feed and fed as much as 500 g/head/day.

A total of 20 lactating Holstein Friesian cows were divided into 5 dietary groups in a completely randomized design. Each treatment had 4 cows as replicates. The dietary treatments consisting of UMMB are presented below:

T0 = UMMB with 100% of cement adhesive
T1 = UMMB with 75% of cement and 25% of tapioca meal T2 = UMMB with 50% of cement and 50% of tapioca meal T3 = UMMB with 25% of cement and 75% of tapioca meal T4 = UMMB with 100% of tapioca meal adhesive

2.3 Parameters Study

The parameters observed in this study included heavy metal residues in milk, specifically Pb, Hg, and Cd, which were analyzed using the atomic absorption spectrophotometry (AAS) method.

2.4 Data analysis

Data obtained in the present study were subjected to analysis of variance to determine the effect of diets containing different levels of cement on heavy metal residues in cow's milk, and the differences between the means were determined by the least significant difference at $p < 0.05$.

3 Results and discussion

The results of heavy metal residues in dairy cow milk are presented in Table 1.

Table 1. Heavy metal residues in Holstein Friesian dairy cow milk.

Parameters	Treatments (ppm)					Significance
	T0	T1	T2	T3	T4	
Pb	0,11±0,000[a]	0,11±0,000[a]	0,11±0,000[a]	0,105±0,004[b]	0,105±0,004[b]	P=0,014
Hg	x	x	x	x	x	ns
Cd	0,010±0,000	0,009±0,000	0,009±0,000	0,009±0,000	0,009±0,000	ns

Pb= Lead; Hg= Mercury, and Cd= Cadmium; x= not exist; ns= non-significant; [ab]Means with different superscripts in a row differ significantly ($p < 0.05$).

The provision of UMMB resulting from the substitution of cement with tapioca starch as an adhesive material had a significant effect ($P < 0.05$) on Pb levels in *Friesian Holstein* dairy milk but no significant effect ($P > 0.05$) on Hg and Cd levels. Pb levels in *Friesian Holstein* dairy milk decreased as cement substitution with tapioca starch decreased. So, it is suspected that the residual Pb metal found in milk is produced from the cement adhesive material used in the manufacture of UMMB in this study. The high level of Pb in all treatments is suspected that Pb is not only found in cement as an adhesive material but also possibly comes from Pb-contaminated feed crops. Grasslands close to the highway are very easily contaminated with

Pb. Pb is widely produced from motor vehicle fumes and corroded road dividers [7]. Dust from motor vehicles can accumulate on the surface of plant leaves or other parts of the plant [8]. Cement dust contains heavy metals such as chromium, nickel, cobalt, lead, and mercury, which harm biotic environments such as soil and impact vegetation, human health, animal health, and ecosystems [9].

The highest Pb levels in *Friesian Holstein* dairy milk were in the P0, P1, and P2 treatments at 0.11 ppm and the lowest were in the P3 and P4 treatments at 0.105 ppm. Pb levels in all treatments exceeded the maximum limit that is safe for consumption. The maximum limit of lead in milk is 0.02 ppm according to Codex Alimentarius, EU, and Iranian National Standards [10]. Consuming Pb-contaminated cow's milk is very harmful to the body. Pb can affect the neurological system and the most severe is encephalopathy, which is a response to very high doses of Pb that causes irritability, headaches, loss of focus, memory loss, mental dullness, and hallucinations [11].

No residual levels of mercury (Hg) were detected in *Friesian Holstein* dairy milk, as indicated in Table 2. The low Hg levels in UMMB are believed to prevent its absorption into the resulting milk products. Additionally, the absence of Hg residues in dairy products can be attributed to the intricacies of the cow's digestive system. The digestion process of UMMB does not lead to significant Hg levels reaching the milk synthesis process. The digestive system of dairy cows involves several stages, starting from the mouth, esophagus, rumen, reticulum, omasum, abomasum, small intestine, and large intestine [12]. Nutrient absorption occurs in the small intestine, where the absorbed nutrients are transported by the blood to various parts of the body. Milk fat, lactose, and protein are synthesized in the cell from precursors that are absorbed from the blood and released into the milk through apocrine, merocrine, or holocrine secretion. Milk's water, minerals, and vitamin components primarily enter the alveolus lumen through diffusion, although some may be bound to other compounds [13].

In this research, it was found that *Friesian Holstein* dairy milk meets the standard as it does not contain any Hg residues, which can cause serious neurological diseases. Heavy metals such as mercury can lead to decreased IQ, memory, autism, and abnormalities of the eyes and tongue. The contamination of heavy metals Pb and Cd usually originates from the environment, including water, grass, feed additives, drugs, and farm equipment. Cd contamination can occur through pastures, crops, contaminated soil, and feed containing chemical elements. It's important to note that heavy metals can be present in dairy products and by-products at varying levels due to factors such as raw milk contamination, processing methods, utensils, packaging materials, and water supply for feed crops.

Cd levels decreased with decreasing cement levels in the manufacture of UMMB. The highest Cd level in *Friesian Holstein* dairy milk is in the P0 treatment, which is 0.010 ppm, and the lowest is in the P1, P2, P3, and P4 treatments, which is 0.009 ppm, which is still within safe limits for consumption (<0.01 ppm) [15-16]. Consuming milk contaminated with Cd exceeds the standard that has been set can cause serious health problems. According to the World Health Organization (WHO), consuming Cd beyond the standard has a great potential to cause neurodegenerative disorders, ESRD, breast cancer, prostate cancer, bone demineralization, and diabetes [17].

The levels of cadmium (Cd) diminished as the cement content in the production of UMMB was decreased. The highest concentration of Cd detected in Friesian Holstein dairy milk occurred in the P0 treatment, with a measurement of 0.010 ppm, while the lowest concentrations were found in treatments P1, P2, P3, and P4, all at 0.009 ppm. These levels are still within the safe consumption threshold of less than 0.01 ppm. However, consumption of milk with Cd levels exceeding these limits can lead to serious health concerns. The World Health Organization (WHO) has indicated that high levels of Cd intake may be associated

with neurodegenerative disorders, end-stage renal disease (ESRD), breast cancer, prostate cancer, bone demineralization, and diabetes [17].

4 Conclusion

The concentrations of mercury (Hg) and cadmium (Cd) in milk did not show significant changes due to the different dietary treatments. However, the lead (Pb) concentration in milk was notably lower in the T3 and T4 treatments than in the T0, T1, and T2 treatments. This suggests tapioca meal can effectively replace cement as an adhesive in UMMB. Additionally, UMMB supplements containing tapioca meal are preferable due to their organic nature and ability to decrease lead levels in cow milk. Consuming milk with heavy metal levels exceeding the recommended limit is important to note that it can lead to serious health issues.

Data availability statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author contribution statement
Renny Fatmyah Utamy: Conceptualization, Methodology, Investigation, Validation, Writing- Original draft preparation. Rio Saputra: Data curation, Writing- Reviewing and Editing. Ambo Ako: Investigation, Writing- Reviewing and Editing. Hasbi Hasbi: Investigation, Writing- Reviewing and Editing. Muhammad Hatta: Investigation, Writing- Reviewing and Editing. Zyahrul Ramadan: Investigation, Writing- Reviewing and Editing. Rara Mufliha: Investigation, Writing- Reviewing and Editing. Tasya Tasya: Investigation, Writing- Reviewing and Editing. Andi Fitri Nurbina: Investigation, Writing- Reviewing and Editing. Andi Mutfaidah: Investigation, Writing- Reviewing and Editing. I Dewa Ayu Mahayani: Investigation, Writing- Reviewing and Editing. Utlul Ilma Navia: Investigation, Writing- Reviewing and Editing. Andi Arif Rahman: Investigation, Writing- Reviewing and Editing. Siti Annisa Sukri: Investigation, Writing- Reviewing and Editing. Mohammad Mijanur Rahman: Investigation, Writing- Reviewing and Editing.

References

1. A. Pramono, E. Handayanta, D. T. Widayati, P. P. Putro, and Kuston, "Dietary protected feed supplement to increase milk production and quality of dairy cows," *Sci. Eng.* **193**, 1–4 (2017).
2. R. F. Utamy, A. Ako, A. L. Toleng, and M. Yusuf, "Performance of an-estrus postpartum Bali cattle by additional feed of multiple nutrient molasses based on Indigofera," *Earth Environ. Sci.* **492**, 1–5 (2020).
3. Yanuartono, A. Nururrozi, S. Indarjulianto, H. Purnamaningsih, N. Haribowo, and A. D. Oktawan, "Effect supplementation of urea molasse multinutrient block (UMMB) on the weight gain average of Heifers Peranakan Ongole breed," *Life Sci.* **1**, 39–43 (2018).
4. V. O. E. Akpambang, G. C. Ebuzeme, and J. O. Akinola, "Heavy metal contamination of topsoil around a cement," *Environ. Pollutants and Bioavailability* **34**(1), 12–20 (2022).

5. M. Jaishankar, T. Tseten, N. Anbalagan, B. B. Mathew, and K. N. Beeregowda, "Toxicity, mechanism and health effects of some heavy metals," *Interdiscip. Toxicol.* **7**(2), 60–72 (2014).

6. I. J. Opara, C. D. Ossi, and C. O. Okoudu, "Formulation of cassava starch-based adhesive," *Int. J. Adv. Res.* **5**(7), 26–33 (2017).

7. K. Adachi, and Y. Tainosho, "Characterization of heavy metal particles embedded in tire dust," *Environ. International* **30**, 1009–1017 (2004).

8. T. Stafilov, and V. Jordanovska, "Determination of cadmium in some vegetables produced in the area near the lead and zinc smelting plant in Veles, Macedonia," *Ecol. Prot. Environ.* **4**, 35–38 (1997).

9. V. O. E. Akpambang, G. C. Ebuzeme, and J. O. Akinola, "Heavy metal contamination of topsoil around a cement," *Environmental pollutants and bioavailability* **34**(1), 12–20 (2022).

10. S. Sharifi, S. Sohrabvandi, V. Mofid, F. Javanmardi, E. Khanniri, and A. M. Mortazavi, "The assessment of lead concentration in raw milk collected from some major dairy farms in Iran and evaluation of associated health risk," *Journal of Environmental Health Science and Engineering* **20**, 181–186 (2021).

11. C. Mandal, A. Mandal, and A. Chakraborty, "The toxic effect of lead on human health," *J. auxological society* **3**, 1–11 (2022).

12. Q. Xu, Q. Qiao, Y. Gao, J. Hou, M. Hu, Y. Du, K. Zhao, and X. Li, "Gut microbiota and their role in health and metabolic disease of dairy cow," *Ruminant microflora and diseases* **8**, 1–13 (2021).

13. R. C. Gorewit, *Designing foods: animal product options in the marketplace* (Washington, D.C, National academy press, 1988).

14. N. Soltani, "Cow milk contamination with heavy metals (mercury and lead) and the possibility of heavy metals disintegration by the human intestinal bacteria," *J. Med. Microb. Diagn.* **6**, 267 (2017).

15. E. Harlia, K. N. Rahmah, and D. Suryanto, "Food safety of milk and dairy product of dairy cattle from heavy metal contamination," in *International Symposium on Food and Agro-biodiversity (ISFA)*, **102**, 1–5 (2017).

16. N. Bilandzic, M. Dokic, M. Sedak, B. Solomun, I. Varenina, Z. Knezevic, and M. Benic, "Trace element levels in raw milk from northern and southern regions of Croatia," *Food Chem.* **127**(1), 63–66 (2011).

17. M. Pirhadi, G. J. Khaniki, A. Manouchehri, and M. Bahman, "Potential harmful effects of heavy metals in milk and milk products on human health; a systematic review," *Alınteri Journal of Agriculture Sciences* **36**(1), 350–355 (2021).