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QUANTITATIVE ANALYSIS OF SELECTED TOXIC AND ESSENTIAL MINERALS IN MILK AND HAIR OF DAIRY CATTLE

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Abstract

Several essential and toxic elements were determined from cow milk and hair samples. The studied individuals (n = 10) were all females from the Romanian Spotted breed, raised through extensive farming, exclusively involving animals from local households. ICP-MS was used to determine the concentrations of Pb, Cd, Ni, Hg, Al, Zn, Cu, and Ca. Statistical analysis showed that Pb, Ni, Al, Zn, and Cu concentrations in milk and hair samples differ significantly ($p < 0.05$), all being higher in hair samples. Several strong significant correlations were observed between the analysed elements, such as the negative correlation between Ca levels in hair and Cd levels in milk ($\rho = -0.875$, $p = 0.001$) and the positive correlation between Ca and Ni concentrations in milk ($\rho = 0.855$, $p = 0.002$). The findings of this research mainly support existing knowledge regarding toxic and essential element interactions, while highlighting the importance of minimizing environmental pollution, as elements from the environment can bioaccumulate in the animals' organism and transfer through milk, and other animal-based products, to consumers.

***Key words**: cattle, essential minerals, hair, milk, toxic minerals.*

INTRODUCTION

Essential minerals play a vital role in numerous metabolic processes in dairy cattle, contributing to enzymatic activity, immune function, growth, and reproduction, thus being critical for maintaining physiological balance (Arif et al., 2024). However, when essential elements accumulate beyond physiological thresholds, they can become toxic. Additionally, heavy metals are of particular concern due to their persistence in the environment and potential to bioaccumulate in animal tissues (Ali et al., 2019). Chronic exposure to these toxic minerals can lead to adverse health effects in livestock and pose serious risks to human consumers through the food chain (Cortés et al., 2021; Jalili et al., 2021). Therefore, biomonitoring of both essential and toxic minerals is important for evaluating environmental exposure, nutritional status, and food safety. For this purpose, several essential and toxic minerals were determined from cow milk and hair samples.

MATERIALS AND METHODS

Hair and milk samples were collected from clinically healthy cows (n = 10) raised in Romania. All animals included in the study were females of the Romanian Spotted breed. The animals were divided into study groups based on their proximity to a high traffic national road (DN 64), with individuals being raised over 2 km away from the national road (n = 3) and individuals raised under 500 m of the national road (n = 7).

Hair samples were collected from clean regions of the forehead and tail hair using stainless steel scissors and milk samples were collected by manual milking. All samples were placed in urine specimen containers; hair samples were kept at room temperature and milk samples were frozen until analysis.

Sample disintegration was done by cold wet mineralization. Milk samples were thawed at room temperature. Hair and milk samples were placed in polypropylene test tubes and weighed with the analytical scale at 0.5 g. Nitric acid (5 ml) and hydrochloric acid (1 ml) were added to each sample, which were then kept at room temperature until full disintegration. Samples were diluted with ultrapure water to a total volume of 10 ml.

Inductively coupled plasma mass spectrometry (ICP-MS) was used to identify the concentrations of Pb, Cd, Ni, Hg, Al, Zn, Cu, Ca.

The obtained data was statistically processed. The Shapiro–Wilk test showed that data are not normally distributed, so non-parametric test were further used: Mann-Whitney U test and Spearman's rank correlation coefficient.

RESULTS AND DISCUSSIONS

The median concentrations of Pb, Cd, Ni, Hg, (ppb) in hair and milk samples are presented in Figure 1.

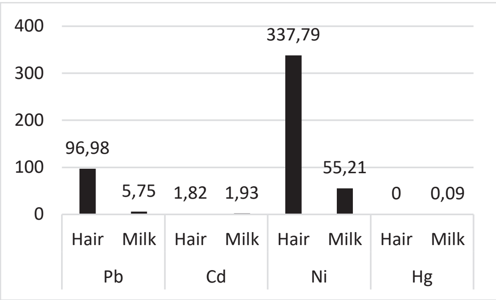

Figure 1. Median Pb, Cd, Ni, and Hg concentrations in hair and milk samples (ppb)

Statistical analysis showed that the differences were significant only for Pb and Ni concentrations ($p < 0.05$), both elements accumulating in a higher concentration in hair (96.98 ppb Pb and 337.79 ppb Ni) compared to milk (5.75 ppb Pb, 55.21 ppb Ni). Cd had similar concentrations between hair (1.82 ppb) and milk samples (1.93 ppb). Hg was detected only in milk samples (0.09 ppb).

The Commission Regulation (EU) 2023/915 on maximum levels for certain contaminants in food stipulates that the maximum allowed limit for Pb in raw milk is 20 ppb. The milk that was analysed in this study had Pb concentrations below the maximum allowed levels.

Other researchers that evaluated the concentrations of heavy metals in milk samples taken from cows raised in Romania found different results than those of the present study. Cadar et al. (2016) identified higher concentrations of Pb (15.8 ppb) and Cd (2.56 ppb). Coroian et al. (2017) also identified higher concentrations of Pb (11.53-43.22 ppb) and Cd (4.32-10.93 ppb). Grădinaru et al. (2011) identified lower concentrations of Pb (1.88-2.64 ppb) and Ni (11.17-11.91 ppb). Sager et al. (2016) also identified lower concentrations of Pb (4.6 ppb), Cd (0.99 ppb), Ni (below detection limit), and Hg (<0.1 ppb) compared to the present study.

The median concentrations of Al, Zn, Cu, Ca (ppm) in hair and milk samples are presented in Figure 2.

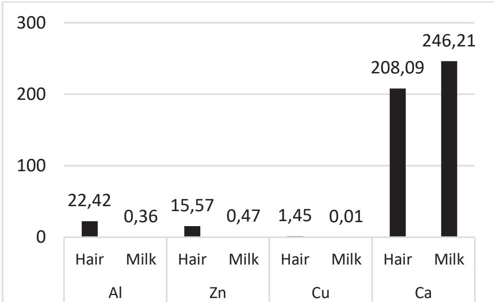

Figure 2. Median Al, Zn, Cu, and Ca concentrations in hair and milk samples (ppm)

Statistical analysis showed that the differences were significant Al, Zn, and Cu concentrations ($p < 0.05$), all elements accumulating in a higher concentration in hair (22.42 ppm Al, 15.57 ppm Zn, 1.45 ppm Cu) compared to milk (0.36 ppm Al, 0.47 ppm Zn, 0.01 ppm Cu). Ca had higher concentrations in milk (246.21 ppm) compared to hair (208.09 ppm), the differences however were not statistically significant.

Several other studies were done on cow milk samples, with results varying from those obtained in the present study. Several studies identified higher concentrations of Zn and Cu compared to the present study: Cadar et al. (2016) found 2.36 ppm Zn and 0.08 Cu ppm, Coroian et al. (2017) identified 2.26-3.86 ppm Zn and 0.10-0.42 ppm Cu, and Grădinaru et al. (2011) identified 2.07-2.74 ppm Zn and 0.25-0.31 ppm Cu. Sager et al. (2016) identified higher concentrations of Zn (2.5 ppm), Cu (0.05 ppm), and Ca (1296 ppm), while Al was below the method's detection limit.

Sizova et al. (2022) conducted a study on cow hair samples and identified higher concentrations of Zn (113-118 ppm), Cu (8.38- 9.41 ppm), and Ca (1059-2218 ppm) than those of the present study.

The median concentrations of Pb, Cd, Ni, Hg (ppb) and the median concentrations of Al, Zn, Cu, Ca (ppm) based on the proximity of the animals to the DN64 national road are presented in Figures 3 and 4, respectively.

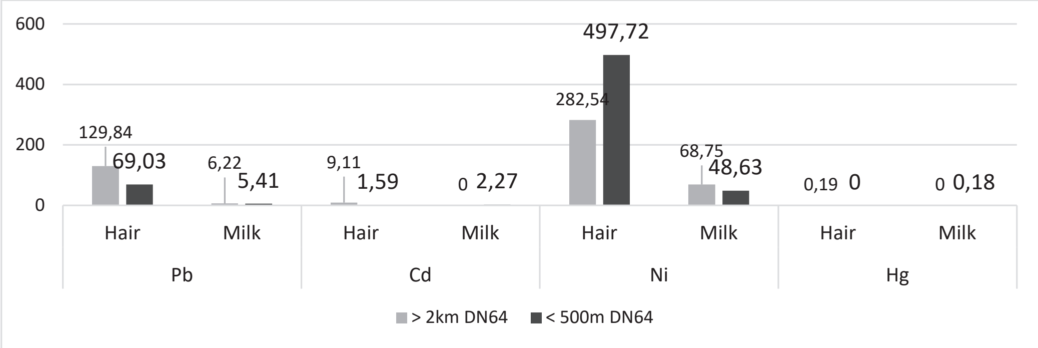

Figure 3. Median Pb, Cd, Ni, and Hg concentrations in hair and milk samples based on the proximity of the animals to the DN64 national road (ppb)

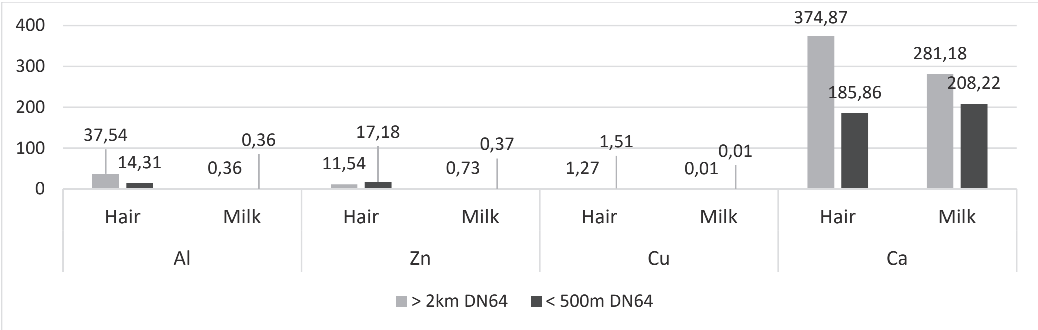

Figure 4. Median Al, Zn, Cu, and Ca concentrations in hair and milk samples based on the proximity of the animals to the DN64 national road (ppm)

Table 1. Spearman's rank correlation coefficient (ρ) for mineral elements in hair and milk samples

	Pb_Hair	Pb_Milk	Cd_Hair	Cd_Milk	Ni_Hair	Ni_Milk	Hg_Hair	Hg_Milk	Ca_Hair	Ca_Milk	Al_Hair	Al_Milk	Zn_Hair	Zn_Milk	Cu_Hair	Cu_Milk
Pb_Hair	-	0.503	0.604	-0.371	-0.358	0.624	0.588	-0.404	0.345	0.455	.891**	0.548	-0.345	0.237	-0.030	-.664*
Pb_Milk	0.503	-	0.201	0.043	-0.224	0.382	0.069	-0.156	0.030	0.358	0.248	0.597	0.091	0.353	0.212	-0.589
Cd_Hair	0.604	0.201	-	-0.544	-0.305	0.329	.705*	-0.370	0.537	-0.091	.799**	0.015	-.634*	0.067	-0.384	-0.180
Cd_Milk	-0.371	0.043	-0.544	-	0.322	-0.450	-.694*	-0.072	-.875**	-0.091	-0.547	-0.003	.657*	-0.439	.632*	0.292
Ni_Hair	-0.358	-0.224	-0.305	0.322	-	-0.164	-0.104	0.365	0.079	0.200	-0.248	-0.271	-0.042	0.055	0.176	-0.082
Ni_Milk	0.624	0.382	0.329	-0.450	-0.164	-	0.545	0.020	0.576	.855**	0.503	0.025	-0.600	.796**	-0.430	-0.589
Hg_Hair	0.588	0.069	.705*	-.694*	-0.104	0.545	-	-0.465	.683*	0.277	.683*	-0.031	-.683*	0.469	-0.372	-0.319
Hg_Milk	-0.404	-0.156	-0.370	-0.072	0.365	0.020	-0.465	-	0.260	0.156	-0.312	-0.165	-0.033	0.104	-0.371	-0.152
Ca_Hair	0.345	0.030	0.537	-.875**	0.079	0.576	.683*	0.260	-	0.321	0.539	-0.080	-.830**	0.571	-.648*	-0.410
Ca_Milk	0.455	0.358	-0.091	-0.091	0.200	.855**	0.277	0.156	0.321	-	0.248	0.074	-0.285	.754*	-0.115	-.679*
Al_Hair	.891**	0.248	.799**	-0.547	-0.248	0.503	.683*	-0.312	0.539	0.248	-	0.271	-0.503	0.176	-0.139	-0.574
Al_Milk	0.548	0.597	0.015	-0.003	-0.271	0.025	-0.031	-0.165	-0.080	0.074	0.271	-	0.197	-0.201	0.240	-0.409
Zn_Hair	-0.345	0.091	-.634*	.657*	-0.042	-0.600	-.683*	-0.033	-.830**	-0.285	-0.503	0.197	-	-0.401	.709*	0.067
Zn_Milk	0.237	0.353	0.067	-0.439	0.055	.796**	0.469	0.104	0.571	.754*	0.176	-0.201	-0.401	-	-0.237	-0.539
Cu_Hair	-0.030	0.212	-0.384	.632*	0.176	-0.430	-0.372	-0.371	-.648*	-0.115	-0.139	0.240	.709*	-0.237	-	-0.067
Cu_Milk	-.664*	-0.589	-0.180	0.292	-0.082	-0.589	-0.319	-0.152	-0.410	-.679*	-0.574	-0.409	0.067	-0.539	-0.067	-

ρ value strength of association: 0.20 - 0.39 weak; 0.40 - 0.59 moderate; 0.60 - 0.79 strong; 0.80 - 1.0 very strong
* p-value < 0.01; ** p-value < 0.001

Statistical analysis showed that the proximity to the high-traffic road significantly influenced ($p < 0.05$) the accumulation of Cd in hair and milk, Ni in milk, Hg in hair, Al in hair, Zn in hair, and Ca in hair. Most elements had higher concentrations in animals raised closer to the DN64 road, such as Cd, suggesting an exposure to Cd resulting from tire and brake pad wear.

Spearman's rank correlation coefficient was calculated for mineral elements in hair and milk samples (Table 1). Positive and negative correlations were found. Most identified correlations were weak. There were several moderate and strong correlations. There were also five very strong significant correlations, such as the negative correlation between Ca levels in hair and Cd levels in milk ($\rho = -0.875$, $p = 0.001$), indicating that higher cadmium exposure may be associated with reduced calcium accumulation in bovine tissues, and the positive correlation between Ca and Ni concentrations in milk ($\rho = 0.855$, $p = 0.002$), suggesting a possible co-variation in their excretion or regulation in the mammary gland. Other very strong significant correlations were identified between Al and Pb in hair ($\rho = 0.891$, $p = 0.001$), Al in hair and Cd in hair ($\rho = 0.799$, $p = 0.006$), and Ca in hair and Zn in hair ($\rho = -0.830$, $p = 0.003$).

CONCLUSIONS

This study highlights the importance of monitoring both essential and toxic mineral concentrations in dairy cattle as indicators of environmental exposure and potential food safety risks. Hair samples generally accumulated higher concentrations of heavy metals and trace elements compared to milk, indicating their value as effective bioindicators for long-term exposure assessment. The proximity of cattle to high-traffic areas significantly influenced the accumulation of several elements, particularly Cd. Despite variations with other studies, the identified milk Pb concentrations remained below EU regulatory limits, suggesting no immediate risk to consumers. Continuous biomonitoring remains essential for ensuring animal health and the safety of milk and dairy products entering the food chain.

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