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VOLCANIC TUFF, POTENTIAL SOURCE OF MINERALS IN DAIRY COWS FEEDING

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Abstract

The use of dietary natural zeolites in dairy cows diets increased recently, with the purpose of improving animal performance, health state, milk quality and to alleviate the adverse environmental effects. The purpose of our work was to study the effects of the dietary volcanic tuff given to dairy cows, on the feeding quality of the milk. The 100 days feeding trial used 80 Holstein Friesian dairy cows, with an average body weight of 545 kg, assigned to four groups (C, E1, E2, E3). The basal diet (C) was a single mixture of corn silage, alfalfa hay, corn, triticale, soybean meal and brewer's grains. The experimental diets included additionally three levels of volcanic tuff: 200 g/cow/day (E1); 350 g/cow/day (E2) and 500 g/cow/day (E3). Milk samples were collected in the end of the trial and assayed for the main nutrients. The results showed significantly (P<0.05) higher levels of: conjugated linoleic acid (CLA), 0.21% in group E3, compared to 0.14% total FAME in group C; copper, 0.103 mg/kg in group E3, compared to 0.065 mg/kg in group E1; iron, 1.56 mg/kg in group E3 and 1.44 ± 0.23 mg/kg in group E2, compared to 1.08 mg/kg in group C; zinc, 8.26 mg/kg in group E3, 7.64 mg/kg in group E2 and 6.11 mg/kg in group E1, compared to 3.24 mg/kg in group C. The use of up to 500 g volcanic tuff/dairy cow/day improved the feeding quality of the milk due to the significant (P<0.05) increase of CLA and trace elements: copper, iron, manganese, zinc, which are of major importance in human feeding.

Key words: *volcanic tuff, dairy cows, milk quality, minerals.*

INTRODUCTION

Due to the new alternative methods of ecological farming, the use of zeolites in agriculture, animal husbandry and environmental protection gained the attention of the scientists. The environmental concerns and the strong public demand for natural products free of toxic residues encouraged the research into prospective industrial applications in this direction. It is estimated that the zeolites will play a more important role in the agricultural practice and food safety in the near future (Eroglu et al., 2017).

Zeolites are crystalline hydrated aluminosilicates with outstanding physical and chemical properties, they loose and receive water in an inverse manner, they have adsorbent molecules which act as molecular sieves and replace the constitutive cations without structural changes. The commercial production of natural zeolites increased over the past fifty years. The Structure Commission of the International Association for Zeolites recorded over 200 zeolites, among which over 40 are natural zeolites.

The purity and physical-chemical properties of the natural zeolites, such as particle size, dimension of the crystals and the level of aggregation, as well as porosity of the individual particles can influence their efficacy. These characteristics show the access of the ingested fluids to the zeolite surface within the gastrointestinal tractus, which activates strongly its ionic exchange and adsorption properties (Papaioannou et al., 2005).

Given the properly defined chemical properties of the zeolites, the expected beneficial effects on dairy cows' health state and productivity have been confirmed (Bosi et al., 2002). Furthermore, one of the zeolites, clinoptilolite, modulates the endocrine, metabolic and antioxidant state in dairy cows, improving thus their fertility and milk yield (Valpotić et al., 2017).

Zeolites are widely used for agricultural purposes, particularly after their classification by the Food and Drug Administration (FDA) as being „non-toxic” and „safe for human consumption” (FDA, 2015). Furthermore, the Codex Alimentarius Commission (2010) mentioned the zeolites as substance authorized for the production of ecologic food and for plant protection. The European Food Safety Authority (EFSA) for the materials, enzymes, flavours and auxiliary products for food processing (CEF) approved one of the zeolites (clinoptilolite type) as being safe in feed additives (EFSA, 2013a). It also declared that zeolites used in animal feeding is safe for all animal species and has no environmental risk (EFSA, 2013b).

The use of natural zeolites in dairy cows feeding increased recently, with the purpose of improving animal performance and the milk yield (Ural et al., 2013; Ural, 2014), higher milk quality and higher milk protein (Katsoulos et al., 2006), milk fat (Dschaak et al., 2010; Cruywagen et al., 2015; Sulzberger et al., 2016), and milk minerals (Akhmetova and Lyubin, 2015), better health state (Panagiotis et al., 2016), and alleviated environmental effects. At the same time, improving milk quality by increasing the milk nutrients, particularly the milk micronutrients, is important for adequate diets, which is an increasing global challenge (IFPRI, 2016). The micronutrient deficiencies are widely spread worldwide, the most common ones being the iron, iodine, folic acid, vitamin A and zinc deficiencies (Bailey et al., 2015).

Within this context, our work studied the effects of the dietary volcanic tuff given to dairy cows on milk feeding quality.

MATERIALS AND METHODS

Animals and experimental design

The 100 days feeding trial involved 80 Holstein Friesian dairy cows, grown at the farm of S.C. ILYA AGRO S.R.L. The dairy cows, with and average body weight of 545 kg, were assigned to four groups: a control group (C) and three experimental groups (E1, E2 and E3).

The basal diet of the dairy cows was the same for all four groups. Table 1 shows the formulation of this basal diet. Unlike the control diet, the experimental formulations were supplemented with different amounts of volcanic tuff: basal diet + 200 g tuff/cow/day (E1), basal diet + 350 g tuff/cow/day (E2) and basal diet + 500 g tuff/cow/day (E3).

Table 1. Basal diet formulation

Ingredients	%
Corn silage	55.50
Alfalfa hay	10.00
Soybean meal	8.00
Corn	7.00
Triticale	5.00
Brewers grains	8.00
Molasses	1.80
Urea	1.00
Calcium carbonate	1.20
Dicalcium phosphate	1.00
Salt	0.50
Vitamin-mineral premix	1.00
Total	100

Sampling and chemical analysis

Milk samples were collected throughout the experimental period and assayed for dry matter, crude protein, crude fat, ash and minerals: calcium, phosphorus, iron, copper, manganese and zinc.

The following standardized methods were used: dry matter (DMr) was determined by the gravimetric method according to Regulation (EC) no. 152/2009 for raw materials, respectively SR EN ISO 5537: 2005 for milk, using BMT drying oven model EcoCellBlueline Comfort model (Nuremberg, Germany); the crude protein (CP) was determined by the Kjeldahl method, in accordance with Regulation (EC) 152/2009 for raw materials, respectively IDT ISO/TS 17837: 2008 for milk, using a semiautomatic system KJELTEC auto 2300 - Tecator (Sweden); the ether extractives (EE) was determined by the organic solvent extraction method, in accordance with Regulation (EC) No. 152/2009 for raw materials, respectively SR ISO 8262-1: 2009 for milk, using a SOXTEC-2055 FOSS-Tecator system (Sweden); the ash (Ash) was determined by gravimetric method, according to Regulation (EC) no. 152/2009 for raw

materials, and SR ISO 1442: 2010 for milk, using Caloris CL 1206 furnace.
For the fatty acids determination is performed an extraction of fats from milk samples, which is then subjected to a boiling saponification in reflux in a solution of acidified methanol (2% H_2SO_4 in methanol) to obtain fatty acid methyl esters, extracting them in hexane and concentrating on rotavapor. The fatty acids were determined by gas chromatography, according to standard SR CEN ISO/TS 17764 - 2: 2008, using Perkin Elmer-Clarus 500 gas chromatograph, with capillary column injection system, high polarity stationary phase (BPX70: 60 m x 0.25 mm inner diameter and 0.25 µm thick film), and high polarity cyanopril phase, which give similar resolution for different geometric isomers (THERMO TR-Fame: 120 m x 0.25 mm ID x 0.25 µm film).
The calcium (Ca) was determined by the titrimetric method, according to SR ISO 6491-1: 2006, the phosphorus (P) was determined photometrically, according to Regulation (EC) no. 152/2009, using the Jasco V-530 spectrophotometer.
Micronutrients (Fe), copper (Cu), manganese (Mn) and zinc (Zn) were determined by atomic absorption spectrometry according to Regulation (EC) No. 152/2009 for raw materials comply with SR EN 13805 for milk using an atomic absorption spectrometer with Thermo Electron flame - SOLAR M6. The apparatus is provided with a burner fed with a mixture of air + acetylene (1 l/min acetylene and 4.5-5 l/min air), corresponding to a specific optimal spraying.
Gross energy (GE) was determined by calculation, using the gross chemical analysis data and the equations developed by Burlacu et al. (2002).
The milk feed units, intestinally digestible protein allowed by the energy level of the diet (IDPE) and intestinally digestible protein allowed by the nitrogen level of the diet (IDPN), were calculated according to the equations developed by Burlacu et al. (2002).

Statistical analysis
Statistical analyses were performed using the StatView program, variance analysis (ANOVA and t test), the results being presented as mean values, the differences being considered statistically significant at $P \leq 0.05$; SEM - standard error of the means.

RESULTS AND DISCUSSIONS

Characterization of the volcanic tuff
The volcanic tuffs from Romania generally have a high level of clinoptilolite. The clinoptilolite (heulandite group) is the most common and adequate type of natural zeolite. Over 90% of the world production of zeolites is of clinoptilolite type. Currently, most marketed zeolites are of clinoptilolite type. The quality of a zeolite depends entirely on its amount of clinoptilolite, because this is the active compound within the zeolite that can make the exchange of cations.
The volcanic tuff used in our feeding trial came from the Baia Mare quarry. Table 2 shows its content of minerals and trace elements.

Table 2. Mineral and trace elements content of the volcanic tuff

Item	Volcanic tuff
DM, %	90.49
Calcium, %	1.63
Phosphorus, %	0.09
Copper, mg/kg	0.75
Iron, mg/kg	1793.18
Manganese, mg/kg	143.77
Zinc, mg/kg	21.40

Characterization of the feed ingredients
The corn silage, which had the highest contribution to the basal diet, had 1.47% protein, 0.54% fat, 8.54% fibre and 5.14 MJ gross energy/kg. The second ingredient, as proportion, was the alfalfa hay, with 17.23 % protein, 0.92 % fat, 27.86 % fibre and 15.74 MJ gross energy/kg. Soybean meal, protein feed, had 39.32% protein, 1.73% fat, 6.42% fibre and 17.06 MJ gross energy/kg. The corn had 8.24% protein, 4.97% fat, 2.26% fibre and 18.83 MJ gross energy/kg.
The highest proportion of calcium in the basal diet came from the soybean meal, 3.29%, followed by triticale, with 1.76%, and alfalfa hay, with 1.25%. The highest proportion of phosphorus in the basal diet came also from the soybean meal, 6.76% followed by triticale, with 3.85% and corn, with 0.51%. The highest proportion of copper in the basal diet came

from the soybean meal, 19.75 mg/kg, followed by the alfalfa hay, with 8.76 mg/kg, and triticale, with 4.67 mg/kg. The highest proportion of iron in the basal diet came from alfalfa hay, with 765.35 mg/kg, followed by the soybean meal, with 200.25 mg/kg, and triticale, with 55.84 mg/kg. The highest proportion of manganese in the basal diet came from alfalfa hay, with 59.70 mg/kg, followed by the soybean meal, with 35.69 mg/kg, and triticale, with 21.75 mg/kg. The highest proportion of zinc in the basal diet came from the soybean meal, 47.26 mg/kg, followed by corn, with 42.22 mg/kg and triticale, with 16.34 mg/kg. The corn silage had the lowest concentrations of minerals: 0.08% calcium, 0.07% phosphorus, 1.21 mg/kg copper, 38.05 mg/kg iron, 11.40 mg/kg manganese, and 4.56 mg/kg zinc.

Nutritive value of the basal diet

Table 3 shows nutritive value of the basal diet expressed as milk feed unite (MFU/kg DM), intestinally digestible protein allowed by nitrogen level of the diet (g IDPN/kg DM), intestinally digestible protein allowed by the energy level of the diet (g IDPE/kg DM), as calcium (g Ca/kg DM) and phosphorus (g P/kg DM).

Table 3. Nutritive value of the basal diet

Item	%	MFU		IDPN		IDPE		Ca		P	
		g/kg DM	g	g/kg DM	g	g/kg DM	g	g/kg DM	g	g/kg DM	g
Corn silage	55.5	1.02	0.57	51	28.31	59	32.75	4.2	2.33	2.5	1.39
Alfalfa hay	10	0.76	0.08	105	10.5	73	7.30	16.3	1.63	2.6	0.26
Soybean meal	8	1.4	0.11	326	26.08	174	13.92	3.7	0.30	7.2	0.58
Corn	7	1.43	0.10	96	6.72	116	8.12	0.3	0.02	2.9	0.20
Triticale	5	1.21	0.06	103	5.15	81	4.05	0.3	0.02	3.4	0.17
Brewers grains	8	1.03	0.08	294	23.52	162	12.96	2.2	0.18	5	0.40
Molasses	1.8	1.28	0.02	27	0.49	78	1.40	9.3	0.17	0.9	0.02
Urea	1	-	-	-	-	-	-	-	-	-	-
Calcium carbonate	1.2	-	-	-	-	-	-	380	4.56	-	-
Dicalcium phosphate	1	-	-	-	-	-	-	418	4.18	360	3.60
Salt	0.5	-	-	-	-	-	-	-	-	-	-
Vitamin-mineral premix	1	-	-	-	-	-	-	-	-	-	-
At 1kg basal diet			*1.02*		*100.76*		*80.50*		*13.38*		*6.61*

The nutritive value of the basal diet is expressed as: 1.02 MFU/kg DM; 100.76 g IDPN/kg DM, 80.50 g IDPE/kg DM, 13.38 g Ca/kg DM and 6.61 g P/kg DM.

Milk quality evaluation

Milk quality is important for the dairy industry and milk yield is mainly influenced by the diet (Ilic et al., 2011). The use of natural and synthetic zeolites in dairy cows diets increased recently, mainly with the purpose of improving animal performance, milk quality and the health state of the animals.

Table 4 shows milk content of the main nutrients in the milk samples collected from experimental groups, compared to the control group.

Table 4. Content of the main nutrients in the milk samples*

Item	Group C	Group E1	Group E2	Group E3	SEM	*P value*
Real dry matter, %	13.51	12.25	11.71	12.09	0.170	0.7435
Crude protein, %	2.62	3.16	2.63	2.94	0.123	0.3356
Crude fat, %	2.73^{b}	$3.54^{a,c}$	2.36^{b}	2.82	0.164	0.0252
Ash, %	0.58	0.72	0.65	0.69	0.022	0.1966

a,b,c- significant differences (P<0.05) between groups C, E1, E2

*results related to fresh sample

Table 4 data show that the dry matter content of the milk samples, the milk protein and ash were not statistically different (P>0.05) between groups. Some literature shows that the milk protein was not influenced by the zeolite (clinoptilolite) treatment (Katsoulos et al., 2006), while other studies reported higher milk protein concentrations (Dschaak et al., 2010; Tucker et al., 1994) following the dietary zeolites supplements for dairy cows.

The milk fat from group E1 (treated with 200 g tuff/cow/day) was significantly (P<0.05) higher than in the milk samples from group C (by 29.67%) and from group E2, treated with 350 g tuff/cow/day (by 50.00%).

Khachlouf et al. (2018) compiled literature data regarding the use of non-nutritional adsorbent, zeolite, on dairy cows' performance, milk quality and environmental effects. They reported that moderate levels (200-400 g zeolite/cow/day) increased milk yield, but milk fat and milk protein were not changed.

Garcia-Lopez et al. (1992) showed that 2% zeolite added to the compound feeds for dairy cows increased the milk fat and the acid-base balance. Cruywagen et al. (2015) and Sulzberger et al. (2016) studied the effect of the dietary 1-2% clinoptilolite or sodium sesquicarbonate and reported slight increases of the milk fat.

Table 5. Fatty acids concentration in the milk samples, according to the level of unsaturation (g/100 g total FAME)

Item	Group C	Group E1	Group E2	Group E3	SEM	*P value*
SFA	70.52	70.72	71.21	71.14	0.221	0.7346
MUFA	24.45	24.29	24.27	23.86	0.140	0.6299
PUFA, of which:	3.71	3.87	3.50	3.69	0.089	0.4938
CLA, %	0.14^{d}	0.17	0.17	0.21^{a}	0.009	0.0437
Ω3, %	0.30	0.33	0.33	0.34	0.014	0.8694
Ω6, %	3.27	3.37	3.00	3.14	0.071	0.2333
Ω6/Ω3, %	$10.90^{c,d}$	$10.20^{c,d}$	$9.10^{a,b}$	$9.23^{a,b}$	0.225	0.0044

FAME- total fatty acids methyl esters; SFA- saturated fatty acids; MUFA- monounsaturated fatty acids; PUFA-polyunsaturated fatty acids; UFA- total unsaturated fatty acids; CLA- conjugated linoleic acid; Ω3- omega 3 polyunsaturated fatty acids; Ω6- omega 6 polyunsaturated fatty acids; a,b,c,d- significant differences (P<0.05) from C, E1, E2, E3.

Table 5 shows that the concentration of fatty acids of the milk samples, depending on the level of saturation, was not statistically different (P>0.05) for the saturated (SFA), monounsaturated (MUFA) or polyunsaturated fatty acids (PUFA). The polyunsaturated fatty acids (PUFA) are known for their beneficial effect on consumer health, being the most valuable group, with a concentration of 3-5% (Rodriguez-Alcala et al., 2009). Our study showed that PUFA concentration in the milk samples ranged between 3.87%, in group E1, treated with 200 g tuff/cow/day and 3.50%, in group E2, treated with 350 g tuff/cow/day, values comparable with the literature reports.

The conjugated linoleic acid (CLA) is the most valuable PUFA, due to its antioxidant and anticancerogenic (anti-oncogene) properties. The presence of this acid in the diet may reduce the oxidative stress, the atherosclerosis, and can improve the blood lipid profile, shielding against the development of skin and mammary gland tumours (Shingfield et al., 2008). The milk CLA concentration is basically determined by animal feeding. The reports of D'Urso et al. (2008) show that other factors too, such as the stage of lactation, the breed and the age of the animals can influence milk CLA concentration.

The highest milk CLA concentration, 0.21%, was noticed in group E3, treated with 500 g tuff/cow/day, 50% higher than in the control group, statistically significant (P<0.05). The literature shows that dairy cows' diet supplementation with ruminal buffers will increase the acetate/propionate ratio in the rumen, increase the fat level, implicitly the fatty acids in the milk. Bougouin et al. (2018) showed that the dietary 1% sodium bicarbonate added to dairy cows' diets increased significantly (P<0.05) PUFA and CLA concentrations in the milk.

The omega 3 polyunsaturated fatty acids (Ω3) also are reputed for their positive effects on consumer health. The milk Ω3 concentration,

obtained in our study, increased proportionally with the treatment, the highest value (0.34%) being reported for group E3, treated with 500 g tuff/cow/day, 142.82% higher than for the control group.
On the other hand, the lowest milk Ω6 concentration (3.00%) was reported for group E1, 8.25% lower than for group C. Thus, Ω6/Ω3 ratio decreased in the experimental groups, the lowest value (9.10%) being reported for the experimental group E2, treated with 350 g tuff/cow/day, 16.51% lower than in the control group.

Table 6. Mineral concentration in the milk samples*

Item	Group C	Group E1	Group E2	Group E3	*SEM*	*P value*
Calcium (%)	0.11	0.11	0.12	0.12	0.003	0.0504
Phosphorus (%)	0.08	0.10	0.09	0.10	0.003	0.0787
Copper (mg/kg)	BLD	0.065[d]	0.080	0.103[b]	0.006	0.0061
Iron (mg/kg)	1.08[d,c]	1.24	1.44[a]	1.56[a]	0.070	0.0493
Manganese (mg/kg)	0.04[b,d]	0.09[a,c]	0.05[b]	0.08[a]	0.007	0.0338
Zinc (mg/kg)	3.24[b,c,d]	6.11[a,c,d]	7.64[a,b]	8.26[a,b]	0.544	<0.0001

a,b,c,d – significant differences (P<0.05) from C, E1, E2, E3; BLD- not traceable
*results related to fresh sample

Table 6 shows that the various treatments with volcanic tuff (200 g, 350 g and 500 g/cow/day) did not yield significant differences (P>0.05) in the milk calcium, with values between 0.07g%, in the experimental groups E2; E3 and 0.11g%, in the control group (C). The phosphorus concentration too, was not significantly different (P>0.05) between groups, with values of 0.08 g%, in group C and 0.10 g%, in the experimental group E3.
The milk copper concentration increased with the dietary tuff supplements, by 33.33%, in the experimental group E2, and by 83.33%, in the experimental group E3, compared to the experimental group E1, statistically significant differences (P<0.05).
Figure 1 shows this correlation very properly, according to equation y = 0.00001x + 0.0386 and coefficient $R^2 = 0.9871$.

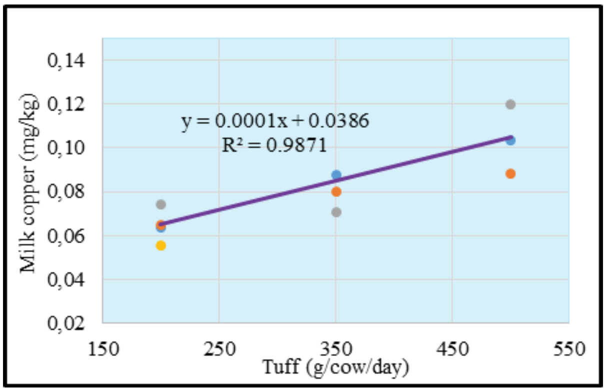

Figure 1. Correlation between milk Cu and the dietary tuff supplements

The values for copper concentration obtained in our study are lower than those reported by Akhmetova and Lyubin (2015), who used 2% and 4% (on DM basis) in dairy cows' diets, reporting 0.55 mg Cu, in the group treated with 4% zeolite and 0.52 mg Cu/kg, in the group treated with 2% zeolite.
The milk iron concentration increased proportionally with the dietary tuff, the highest value (1.56 mg), being recorded in group E3, followed by 1.44 mg, in group E2, significantly different (P<0.05) from 1.08 mg/kg, in the control group.
Figure 2 shows the correlation between the milk iron and the dietary tuff, according to equation Y = 0.001x + 1.0673 and coefficient $R^2 = 0.9894$.

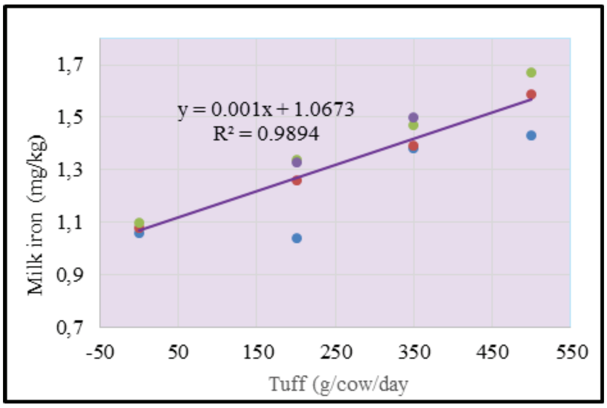

Figure 2. Correlation between milk Fe and the dietary tuff supplements

The milk manganese concentration also increased in the experimental groups, but the increase was not proportional to the amount of dietary tuff. The highest increased, by 125%, was noticed in group E1, compared to group C ($P<0.05$), followed by group E3, by 100%, also statistically significant ($P<0.05$).

Of all milk trace elements considered in our study, the milk zinc displayed the highest values, increasing proportionally with the dietary tuff amount. The highest increase, 154.93%, was noted in group E3, followed by group E2, with 135.80%, and by group E1, with 88.58%, compared to group C, the differences being statistically significant ($P<0.05$). Figure 3 shows the correlation between the milk zinc and the dietary tuff supplements, according to equation $y = 0.0096x + 3.8401$ and coefficient $R^2 = 0.8929$.

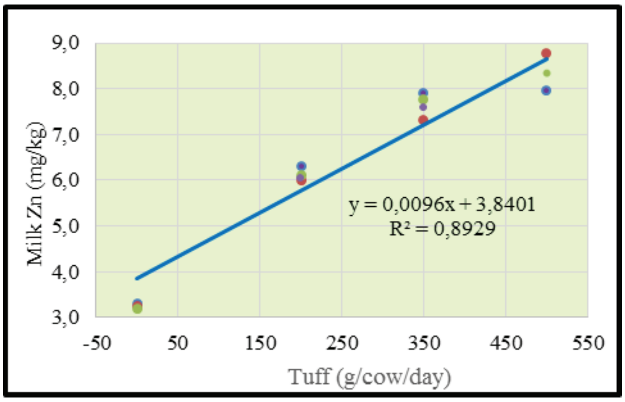

Figure 3. Correlation between milk Zn and the dietary tuff supplements

Our results are higher than those reported by Akhmetova and Lyubin (2015), who, in the study mentioned above, reported values of 5.47 mg, in the group treated with 4% zeolite and 5.37 mg, in the group treated with 2% zeolite, compared to 5.29 mg/kg, in the control group.

CONCLUSIONS

The results of this study support the fact that the use of up to 500 g tuff/cow/day improved the nutritional quality of the milk, by significantly ($P<0.05$) higher levels of trace elements: copper, iron, manganese and zinc, which are of major importance for human diets, given the worldwide efforts to control the trace elements deficiencies.

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