# EFFECTS OF USING VOLCANIC TUFF IN COWS DIETS ON THE NUTRITIONAL QUALITY OF MILK

**Margareta Olteanu[1*], Mihaela Saracila[1], Mariana Ropota[1], Raluca Paula Turcu[1], Rodica Diana Criste[1], D. Dragatoiu[2], Elena Narcisa Pogurschi[2], Monica Paula Marin[2]**

*[1]National Research-Development Institute for Animal Biology and Nutrition-IBNA-Balotesti, Ilfov, Romania*
*[2]University of Agricultural Sciences and Veterinary Medicine, Bucharest, Romania*

**Abstract**

*Natural and synthetic zeolites are widely used in animal nutrition as performance promoters, and their use also exerts a variety of favourable effects on the prevention or treatment of certain animal diseases in the farm. Natural zeolites provide the necessary macro and trace elements for animals, and stimulate their health and production (Quote Garcia- Lopez et al., 1992; Nikkhah et al., 2001; Sadeghia si Shawrangb, 2008; Dschaak et al., 2010; Deniz Alic Ural, 2014; Panagiotis et al., 2016). Thus the present paper has proposed the characterization of tuff in terms of its nutrient content and the study of the effects of its use in cows feeding on milk quality. Tuff has 90.49g% dry matter, 1.63g% calcium, 0.09g% phosphorus, 1793.18ppm iron. The raw ingredients used in the diets of dairy cows were: a mixture of barley and corn with a content of 87.52g% of dry matter, 9.61g% crude protein, 1.39g% ether extractives; corn cob + beans with 39.21% dry matter, 3.68g% crude protein, 1.36g% ether extractives; corn silage with a content of 28.71 g% dry matter, 1.47 g% crude protein, 0.54 g% ether extractives, and alfalfa hay with 88.87 g% dry matter, 17.23 g% crude protein, 0.92 g% ether extractives. Cow's milk had 13.51g% dry matter, 2.62 g% protein, 0.11g% calcium, 0.08g% phosphorus, 1.63 ppm iron.*

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

## INTRODUCTION

Zeolite is an aluminosilicate formed millions of years ago by the interaction of the hot lava poring out of volcanoes and the sea water, rich in the 4 vital nutrients for the animal body: calcium, magnesium, potassium and sodium, long known for its beneficial qualities [2], [16]. It is detoxifier, decontaminant, immunomodulator, restores the pH of the body. These qualities have been greatly improved by a special procedure that transforms the mineral into an ultra pure and micronised powder, so assuring it is very easy to assimilate. Zeolites show all the healing benefits of aluminosilicate clay at a higher level because it is crystallized and functions as a chemical coconut, but the specialists call it molecular sieve as it extracts cationic pollutants, bacteria, viruses, etc. and is eliminated within 6-8 hours after ingestion, with no side effects. For centuries, healing effects produced by clay have been used to cleanse, detoxify, relieve various diseases, and restore and refresh skin.

Nowadays, zeolites "rediscovered" by modern science, bring with them the revolutionary energy of negative ions, which we usually associate with deep rest, with the relaxing atmosphere created by the rain, mountain air, or by the ocean breeze.

Natural and synthetic zeolites have been extensively used in animal feed as promoters since 1980, with various publications demonstrating that their use also has various beneficial effects on the prevention and / or treatment of certain animal diseases. Many researchers have shown that the inclusion of zeolites in animal diets improves: the daily average gain and / or daily feed conversion of

[*]Corresponding author:
margaretaolteanu@yahoo.com
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pigs [12], [13]; calves and sheep [14] and broiler chick [5]; increases the milk production of the cows [8], [18], [19]; decreases the severity and duration of diarrhoea in calves [3], [20] and improves animal health [10], [12], [15], [11]. In vitro results also demonstrate moderate efficacy of natural clays on mycotoxin intoxication [5].

The effect of clinoptilolite inclusion in the diet [9] was investigated, either alone or in combination with intramuscular administration of selenium, in the production of antibodies to late-vaccinated dairy cows during pregnancy against enterotoxigenic Escherichia coli strains. Administration alone and in particular in combination with selenium and clinoptilolite significantly increased the antibody titers against E. coli in the hen's and calf serum and the henna colostomy.

There is evidence that zeolites can be used successfully in case of milk fever and ketosis. Milk fever and ketosis are the most common metabolic diseases in large dairy cows. In recent years, a number of experiments have been carried out to control these diseases using zeolites as feed additives [17]. The results of these experiments are very promising, but further investigation is needed to define the exact zeolite action mechanisms.

The present paper has proposed the characterization of the tuff as nutrient content and the study of the effects of its use in cow feed on milk quality.

## MATERIAL AND METHOD

The experiment was performed on a number of 20, Holstein Friesian dairy cows, weighing 450-500 kg, assigned to two groups, a control group (C) and an experimental group (E).

Table 1 Structure of the basal diet

| Raw ingredients | % |
|---|---|
| Corn silage | 55.30 |
| Mix of barley and corn | 12.00 |
| Corn beans + beans | 11.00 |
| Alfalfa hay | 10.00 |
| Soybean meal | 8.00 |
| Calcium carbonate | 1.20 |
| Dicalcium phosphate | 1.00 |
| Salt | 0.50 |
| Vitamin-mineral premix | 1.00 |

The basal diet administered to dairy cows consisted of the raw ingredients showed in Table 1. Both groups had free access to this diet. The experimental group (E) differed from control group (C) by addition of 200g tuff / head / day.

During the experiment, milk samples were collected to determine the nutrient content: dry matter, raw protein, crude fat, ash and mineral content: calcium, phosphorus, iron, manganese and zinc. For these determinations standardized methods were used as follows: dry matter (DM) was determined by the gravimetric method according to Regulation (EC) no. 152/2009 for combined feeds, respectively SR EN ISO 5537:2005 for milk, using BMT drying oven model EcoCell Blueline Comfort model (Neuremberg, Germany); the crude protein (CP) was determined by the Kjeldahl method, in accordance with Regulation (EC) 152/2009 for combined feeds, 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 feeds, 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 compound feeds, and SR ISO 1442:2010 for milk, using Caloris CL 1206 furnace.

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: 60m 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 feed 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 [4].

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

## RESULTS AND DISCUSSIONS

The tuff used in ruminant diets came from Baia Mare Quarry and had 90.49g% dry matter (DM), 1.63g% calcium (Ca), 0.09g% phosphorus (P), 1793.18ppm iron (Fe), 143.77 ppm manganese (Mn) si 21.40 ppm zinc (Zn).

The content of the main nutrients of raw materials administered to dairy cows is shown in Table 2.

As it can be seen, the highest content of crude protein (39.32%) and ether extractives (1.73%) is found in soybean meal, while of cellulose (27.86%) and of ash (9.05%) was found in alfalfa. The highest gross energy (17.06 Mj/kg) is found in the soybean meal.

Table 2 Content of the main nutrients of the raw materials

| Raw materials | DM (%) | CP (%) | EE (%) | CF (%) | Ash (%) | GE Mj / kg |
|---|---|---|---|---|---|---|
| Corn silage | 28.71 | 1.47 | 0.54 | 8.54 | 1.24 | 5.14 |
| Mix of barley and corn | 87.57 | 9.61 | 1.39 | 8.09 | 3.10 | 15.63 |
| Corn beans + beans | 39.21 | 3.68 | 1.36 | 1.46 | 0.59 | 7.21 |
| Alfalfa | 88.87 | 17.23 | 0.92 | 27.86 | 9.05 | 15.74 |
| Soybean meal | 89.00 | 39.32 | 1.73 | 6.42 | 5.78 | 17.06 |
| DM-dry matter; CP-crude protein; EE- ether extractives; CF-crude fibre; Ash-ash, GE-gross energy | | | | | | |

Table 3 Mineral content of raw materials

| Raw materials | Calcium (%) | Phosphorus (%) | Copper (mg/kg) | Iron (mg/kg) | Manganese (mg/kg) | Zinc (mg/kg) |
|---|---|---|---|---|---|---|
| Corn silage | 0.08 | 0.07 | 1.21 | 38.05 | 11.40 | 4.56 |
| Mix of barley and corn | 0.05 | 0.37 | 3.60 | 232.44 | 21.16 | 27.58 |
| Corn beans + beans | 0.01 | 0.15 | 0.48 | 18.55 | 2.54 | 8.60 |
| Alfalfa | 1.25 | 0.35 | 8.86 | 765.35 | 59.70 | 42.22 |
| Soybean meal | 3.29 | 6.76 | 19.75 | 200.25 | 35.69 | 47.26 |

Table 3 shows that the calcium content ranged between 0.05% for the barley + corn mixture and 3.29% for the soybean meal; phosphorus ranged from 0.07% in corn silage to 6.76% in soybean meal; copper ranged from 0.48 mg / kg in corn grains + grains and 19.75 mg / kg in soybean meal; iron ranged between 18.55 mg / kg in corn grains + grains and 765.35 mg / kg in alfalfa; manganese ranged between 2.54 mg / kg in corn beans and 59.70 mg / kg in soybean meal, while zinc content ranged between 4.56 mg / kg in corn silage and 47.26 mg / kg in wheat soybeans.

Analysing the data (Table 4) regarding the content of the main nutrients of the milk samples collected from the control group (C), respectively from the experimental group (E), it can be observed that the values regarding the dry matter, ether extractives and ash content do not differ (P> 0.05) statistically significant between groups. In contrast, crude protein content values varied significantly (P≤0.05) between groups, with an increase of 33.96% in experimental group (E) compared to control group (C).

Table 4 Milk samples content of the main nutrients (%)

| Nutrients | C | E | SEM | P |
|---|---|---|---|---|
| Dry matter | 13.51 ±1.11 | 13.24 ±2.09 | 0.614 | 0.0854 |
| Crude protein | 2.62[b] ±0.21 | 3.51[a] ±0.35 | 0.226 | 0.0191 |
| Ether extractives | 2.73 ±0.19 | 2.68 ±0.43 | 0.121 | 0.0835 |
| Ash | 0.58 ±0.12 | 0.71 ±0.31 | 0.088 | 0.0551 |
| a,b- significant differences (P≤0.05) compared to C and E | | | | |

There are similar results [7] regarding the effects of using a ruminal buffer containing magnesium zeolite on milk production and the increase of protein content in milk.

The basal diet consisted of 38% alfalfa hay, 19% maize silage, 14% maize grains and 30% concentrated mixture and was administered "ad libitum". The experiment was performed on 30 primiparous and multiparous Holstein cows, divided into three groups (10 cows / group). The control group received a diet without ruminal buffer, the experimental group 1 received a diet with 1.4% sodium bicarbonate and the experimental group 2 received a diet with 1.4% ruminal buffer product containing a zeolite with magnesium.

The experiment was completed after 12 weeks. Milk production was similar between the three groups (40.7 kg / day, on average) and the efficacy (4% FCM / DMI) was not affected between groups.

Milk ether extractives concentration was not different between groups, while the crude protein concentration was higher in the experimental groups 2 treated with 1.4% zeolite magnesium compared to the control group, without ruminal buffer. In contrast, other studies [8] showed that the addition of 2% zeolite to the compound feeds for dairy cows increases the percentage of milk ether extractives.

Regarding the fatty acid content of the milk samples (Table 5), SFA and monounsaturated fatty acid (MUFA) values did not differ statistically (P> 0.05) between groups, but the values of polyunsaturated fatty acids (PUFAs) decreased significantly (P≤0.05) in the experimental group (E), by 14.76%, compared to the control group (C).

Table 5 Fatty acids content of the thigh milk fat, depending on the level of saturation (g acid/100 g total fatty acids)

| Specification | C | E |
|---|---|---|
| SFA, % | 64.54 ±0.62 | 66.08 ±0.86 |
| MUFA, % | 28.87 ±0.74 | 27.88 ±0.65 |
| PUFA, % | 5.42 ±0.34 | 4.62 ±0.22 |
| Ω3, % | 0.61[b] ±0.06 | 0.72[a] ±0.02 |
| Ω6, % | 4.41[b] ±0.24 | 3.66[a] ±0.20 |
| Ω6/Ω3 | 7.20[b] ±0.32 | 5.10[a] ±0.18 |
| SFA- saturated fatty acids; MUFA- monounsaturated fatty acids; PUFA- polyunsaturated fatty acids; Ω3- omega 3 polyunsaturated fatty acids; Ω6- omega 6 polyunsaturated fatty acids; CLA- conjugated linoleic acid; a,b,c- significant differences (P≤0.05) compared to C, and E1 | | |

The values of omega-3 fatty acids (Ω3) increased significantly (P≤0.05) in the experimental group (E), by 18.03% compared to the control group (C) and the values of the omega-6 acids (Ω6) ≤0.05) in experimental group (E), with 14.76% compared to the control group (C). Thus, the values of omega-6 / omega-3 (Ω6 / Ω3) polyunsaturated fatty acids decreased significantly (P≤0.05), by 29.17% for the experimental group (E).

The values of calcium and phosphorus content (Table 6) of the milk samples collected from control group (C) and experimental group (E), respectively, did not differ (P> 0.05) statistically.

In contrast, the addition of tuff to the diets for the experimental group (E), a volcanic tuff rich in iron, manganese and zinc resulted in significant increases (P≤0.05) of these microelements: by 73.01% for iron, by 450% for manganese and by 83.64% for zinc, respectively, compared to the milk samples from the control group (C). Similar studies [1] carried out on Holstein cows, to which 2% of the natural zeolite was added to the experimental group (E1) and 4% to the experimental group (E2) have shown that the introduction of this zeolite improves the quality of milk, including higher contents of amino acids, vitamins and minerals.

Table 6 Milk samples content of minerals (%)

| Specification | C | E | SEM | P |
|---|---|---|---|---|
| Calcium (%) | 0.11 ±0.02 | 0.14 ±0.03 | 0.011 | 0.0242 |
| Phosphorus (%) | 0.08 ±0.02 | 0.13 ±0.04 | 0.016 | 0.1155 |
| Copper (mg/kg) | BLD | BLD | - | - |
| Iron (mg/kg) | 1.63[b] ±0.08 | 2.82[a] ±0.44 | 0.289 | 0.0102 |
| Manganese (mg/kg) | 0.04[b] ±0.02 | 0.22[a] ±0.18 | 0.064 | 0.0156 |
| Zinc (mg/kg) | 3.24[b] ±0.07 | 5.95[a] ±0.77 | 0.759 | 0.0573 |
| a,b- significant differences (P≤0.05) compared to C and E; BLD-below the detection limit | | | | |

## CONCLUSIONS

The introduction of 200 g volcanic tuff / head / day, with 1793.18 ppm iron, 143.77 ppm manganese and 21.40 ppm zinc resulted in improved milk quality by significant increases (P≤0.05) of protein content and of the content of these microelements.

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