

CONTENT OF ALUMINIUM, SILICON AND TITANIUM IN FEED MATERIALS OF NORTH-EASTERN SLOVENIA

SADRŽAJ ALUMINIJA, SILICIJA I TITANA U KRMIVIMA SJEVEROISTOČNE SLOVENIJE

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SUMMARY

The paper deals with the frequency of microelements and especially trace elements which appear in the soil and then in different ways migrate into forage plants. The aim of our experiment was to estimate the aluminium (Al), silicon (Si) and titanium (Ti) content in feedstuffs produced in north-eastern (NE) part of Slovenia. We analyzed eight feedstuffs using X-ray fluorescence spectrometry (K-18 compound feedstuff, hay which consists of Italian ryegrass, white clover and red clover, corn middlings, maize silage, grass silage, wheat bran, soybean cake 44 % CP, and dry beet pulp) in twenty replicates to ensure enough variability. The mean value of Al was 3.05×10^{-3} g/g DM, Si 6.06×10^{-3} g/g DM and Ti 5.22×10^{-5} g/g DM in all analysed feeds. The range between minimum and maximum value among eight feedstuffs concerning Si 2.27×10^{-2} then Al 7.93×10^{-3} and Ti 2.07×10^{-4} . This basic research in the selected samples could be important for further research on the nutritional effects of microelements (Al, Si, Ti) on animals.

Key words: Feedstuffs, aluminium (Al), silicon (Si), titanium (Ti)

INTRUCTION

Farm animals consume minerals – in field conditions – almost exclusively from forage and feedstuffs. Availability of minerals in the diet for ruminants is therefore dependent on the minerals content in the vegetative parts of plants and seeds. Mineral composition of plants also depends on the species and cultivar or variety, the soil type in which fodder plants grow, climatic conditions and stage of forage maturity (Underwood and Suttle, 1999).

Mineral composition of the feed in north-eastern Slovenia concerning the basic macroelements (calcium, phosphorus, magnesium, sodium, potassium) has been studied systematically and in practice

these data are used to calculate the rations for cattle on farms. Data on other minerals, especially the trace elements, have not been found. The minerals have been chosen for two reasons; firstly, there is little information available about concentrations of minerals in the soil and especially in the feed and secondly, the knowledge of their physiological significance is very poor.

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Aluminium as a trivalent metal cation is very common in the earth's crust and soil. In feed mixing industry it is used as a feed binder in the form of aluminium silicate, which is on the list of approved additives for use in the EU. The importance of aluminium, regardless of the scarce references in the literature is based on the principle of securing of food chain safety - from farm to table, where we expect the aluminium from the soil or animal feed to appear in a fixed proportion in animal feed.

Silicon is the second, after oxygen, the most abundant element in the earth's crust and according to geochemical classification, a lithophilic element. It appears as quartz, SiO₂, opal and in the form of amorphous and complex silica. In some plants it is associated with lignin, thereby helping to maintain the physical structure of plants. The silicon content in plants depends primarily on the composition of the soil and even the same type of plant varies significantly in the concentration of silicon in different soils.

In the earth's crust titanium occurs in the form of titanium oxide in the quantity of 1 % and in the form of various minerals such as rutilit, ilmenit and atanasit. Forage plants contain Ti in negligible quantities. The knowledge of physiological role of titanium is very poor. Titanium according to Schroeder et al. (1964) is not an essential element even if it promotes body growth in experimental mice, shortens life expectancy, increases body weight in younger animals and accumulates more in body organs of younger than older animals.

The aim of the study was to estimate the aluminium (Al), silicon (Si) and titanium (Ti) content in feedstuffs produced in north-eastern (NE) part of Slovenia.

MATERIAL AND METHODES

The analyzed samples come from a wider area of the Drava valley, bordered by the cities of Maribor, Lenart, Ptuj and Slovenska Bistrica. The surface of this area covers 360 km². Between the Alpine rock in the depth and the upper layer of humus there dominate river sand deposition layers from the Quaternary period composed of fine gray-brown particles of silicate and carbonate origin. Most precipitation in this area has been observed in August

and February, at least several decades average of rainfall for the month of August is 120 mm.

On the cattle farms feed was sampled from grassland and concentrated feed from field. We made a geographical exception in sampling in the case of soybean mill as the samples come from the area of Osijek (Croatia); soybean mill is used as a feed component and analyzed together with other feed. We investigated hay, corn silage, grass silage, wheat bran, corn middlings, dried beet pulp, a complete feed for dairy cows "K-18" and soybean mill. For each type of feed 20 individual samples were taken and analyzed.

Amounts of aluminium, silicon and titanium in the investigated feeds were analyzed by the spectroscopic X-ray method. The method is based on the fact, that atom bombarding with protons comes to an excited state and must then spontaneously revert to its original state of stable energy. They loss of energy is accompanied by the emission of electromagnetic radiation (X-ray). Since each kind of atom has a unique electronic configuration, each analyzed element will have the characteristic X-ray spectrum. If the radioactive source is strong enough then another, fluorescent X-ray will appear and can be measured. In this experiment an X-ray spectrometer with a Si (Li) detector (M 1510 Canberra) and excitation source containing Fe-55 (10 mCi) was utilized. Analysis was performed by Dr. M. Nečemer, Jožef Stefan Institute, Ljubljana. The feed samples were dried and homogenized. The fluorescence intensity read for aluminium was at 1.487 keV, for silicon 1.739 keV and for titanium 4.508 keV as reflection of anode X-rays.

The results were analyzed by using descriptive statistical methods, analyses of variance were made by ANOVA including Duncan post hoc test, and afterwards Pearson's correlation analysis was made. Statistical analysis was performed using statistical packet SPSS 17.0 for Windows (SPSS Statistics Base 17.0).

RESULTS AND DISCUSSION

Table 1 shows the results of chemical analysis of eight selected raw materials and the results of statistical data processing.

Table 1. Statistical analysis of data regarding the feed Al, Si and Ti (n = 20) content**Tablica 1. Statistička obrada podataka o sadržaju Al, Si i Ti (n=20) u krmivima**

Feed - Krma		Aluminium (g/kg DM) Aluminij (g/kg ST)	Silicon (g/kg DM) Silicij (g/kg ST)	Titanium (g/kg DM) Titan (g/kg ST)	Ash (g/kg DM) Pepeo (g/kg ST)
Hay Sijeno	\bar{x}	0.0029675 ^{ab}	0.0118830 ^e	0.0002082 ^c	103.70
	SD	0.0001964	0.0019957	0.0002924	
Corn silage Kukuruzna silaža	\bar{x}	0.0026085 ^{ab}	0.0061975 ^d	0.0000522 ^{ab}	50.00
	SD	0.0007375	0.0008777	0.0000057	
Grass silage Travna silaža	\bar{x}	0.0083597 ^c	0.0229450 ^f	0.0000963 ^b	126.46
	SD	0.0121097	0.0018557	0.0000130	
Wheat bran Pšenične posije	\bar{x}	0.0004339 ^a	0.0002021 ^a	0.0000069 ^a	53.18
	SD	0.0000135	0.0000103	0.0000002	
Corn middlings Kukuruzno krmno brašno	\bar{x}	0.0007270 ^a	0.0002329 ^a	0.0000015 ^a	14.00
	SD	0.0000442	0.0000355	0.0000002	
Dry beet pulp Suhi repini rezanci	\bar{x}	0.0018910 ^{ab}	0.0022490 ^{bc}	0.0000314 ^{ab}	70.00
	SD	0.0001685	0.0006100	0.0000017	
K-18 compound feedingstuff Krmna smjesa K-18	\bar{x}	0.0030855 ^{ab}	0.0032860 ^c	0.0000158 ^a	69.84
	SD	0.0027421	0.0046069	0.0000023	
Soybean cake (44% CP) Sojina sačma	\bar{x}	0.0043500 ^b	0.0014935 ^{ab}	0.0000050 ^a	64.83
	SD	0.0002873	0.0019847	0.0000001	

Values marked with different superscripts in the same column are significantly different from each other at the level $P < 0.05$. \bar{x} - mean, SD - standard deviation.

Vrijednosti označene različitim eksponentom u istom stupcu značajno se razlikuju jedna od druge na razini $P < 0,05$. \bar{x} - sredina, SD - standardna devijacija.

Statistical analysis of the analytical value of Al in the feedstuffs showed that the Al content in wheat bran and corn middlings significantly ($P < 0.05$) differed from the soybean cake and grass silage content. Among the K-18 feed, corn silage, hay and dried beet pulp there was no significant difference. Grass silage had a significantly ($P < 0.05$) higher concentration of Al than all other feedstuffs. In animals, aluminium is absorbed in the digestive tract, only in concentrations of 0.5 % to 2 % depending on the chemical form. This process is similar to calcium i.e. by active transport through the enterocyte cell membrane. Passive absorption (EMEA 2000) is also possible. Acidic environment in the true stomach of ruminants promotes the absorption of aluminium in

the small intestine. In animal body aluminium is transported bound to plasma transferrin, and only 20% of all aluminium in blood plasma appears in the form of various salts, especially in the form of citrate. Aluminium accumulates in the brain tissue, around the parathyroid glands and in bone tissue. Its toxicity in humans results in nervous tissue injuries while in animals it is characterized by changes in osteoporotic bones (Ganrot, 1986). The toxicity of aluminium in feed plants is recorded in 40 % of all the acidic types of soils which are agricultural by processed (Haugh, 1984; Panda et al., 2008). Adult cattle may be treated for therapeutic purposes with 30 g of aluminium hydroxide, calves and foals up to 2 g per day (EMEA, 2000).

Table 2. Pearson Correlations between Al, Si, Ti (g/kg DM) in eight feeding stuffs**Tablica 2. Linearna korelacija sadržaja mikroelemenata Al, Si, Ti (g/kg ST)**

		Aluminium Aluminij	Silicon Silicij	Titanium Titan			Aluminium Aluminij	Silicon Silicij	Titanium Titan
Aluminium Aluminij	Corr. ^a	1	-0.207	0.109	Aluminium Aluminij	Corr.	1	-0.193	-0.068
	Sig. ^b		0.382	0.647		Sig.		0.415	0.775
Silicon Silicij	Corr.		1	-0.059	Silicon Silicij	Corr.		1	-0.013
	Sig.			0.805		Sig.			0.957
Titanium Titan	Corr.			1	Titanium Titan	Corr.			1
	Sig.					Sig.			
Hay - Sijeno					Corn silage - Kukuruzna silaža				
		Aluminium Aluminij	Silicon Silicij	Titanium Titan			Aluminium Aluminij	Silicon Silicij	Titanium Titan
Aluminium Aluminij	Corr.	1	-0.246	0.215	Aluminium Aluminij	Corr.	1	0.345	-0.652**
	Sig.		0.296	0.363		Sig.		0.137	0.002
Silicon Silicij	Corr.		1	-0.331	Silicon Silicij	Corr.		1	0.177
	Sig.			0.153		Sig.			0.454
Titanium Titan	Corr.			1	Titanium Titan	Corr.			1
	Sig.					Sig.			
Grass silage - Travnja silaža					Wheat bran - Pšenične posije				
		Aluminium Aluminij	Silicon Silicij	Titanium Titan			Aluminium Aluminij	Silicon Silicij	Titanium Titan
Aluminium Aluminij	Corr.	1	-0.402	-0.118	Aluminium Aluminij	Corr.	1	0.189	-0.497*
	Sig.		0.079	0.622		Sig.		0.424	0.026
Silicon Silicij	Corr.		1	0.384	Silicon Silicij	Corr.		1	-0.081
	Sig.			0.094		Sig.			0.736
Titanium Titan	Corr.			1	Titanium Titan	Corr.			1
	Sig.					Sig.			
Corn middlings - Kukuruzno krmno brašno					Dry beet pulp - Suhi repini rezanci				
		Aluminium Aluminij	Silicon Silicij	Titanium Titan			Aluminium Aluminij	Silicon Silicij	Titanium Titan
Aluminium Aluminij	Corr.	1	-0.048	-0.239	Aluminium Aluminij	Corr.	1	-0.147	0.103
	Sig.		0.839	0.310		Sig.		0.536	0.667
Silicon Silicij	Corr.		1	0.160	Silicon Silicij	Corr.		1	-0.048
	Sig.			0.501		Sig.			0.841
Titanium Titan	Corr.			1	Titanium Titan	Corr.			1
	Sig.					Sig.			
K-18 compound feedingstuff - Krmna smjesa K-18					Soybean cake (44% CP) - Sojina sačma				

^a Correlation. ^b Significance. *Correlation is significant at the P<0.05 level. ** Correlation is significant at the P<0.01 level.

^a Korelacija. ^b Značajno. *Korelacija je značajna na P<0.05 razini. **Korelacija je značajna na P<0.01 razini.

In comparison of Si concentrations among feedstuffs a significant ($P<0.05$) difference was recorded among almost all tested forages. There were no significant differences only between corn middlings, wheat bran and soybean cake. Moreover, no significant differences were confirmed between the soybean cake and dry beet pulp, and the dry beet pulp and K-18. More Si in the feed reduces organic matter digestibility and palatability of fodder plants on the pasture. Silicates are relatively soluble in the forestomach and have a beneficial effect on rumination. Si is an essential element only for rats and chickens. Addition of Si in the quantity of 50 ppm in the feed rations facilitates the growth of animals under the experimental conditions. In addition, Si is essential for collagen formation and growth of the skeleton (van Soest, 1994). The animals in arid areas accumulate Si in urine and urinary calculi occurs frequently. Increased concentrations of silicates indicate contamination of feed with the soil.

No significant differences were observed in the concentration of Ti between corn middlings, soybean cake, wheat bran, K-18, dry beet pulp and corn silage. Sample of grass silage had a significantly ($P<0.05$) higher concentration of Ti in comparison with corn middlings, soybean cake, wheat bran and K-18. The grass silage sample was not significant by different from the sample of dry beet pulp and corn silage. Hay sample had a significantly by ($P<0.05$) higher concentration of Ti than all other samples in the analysis. Titanium is not absorbed in the gastrointestinal tract; therefore it is used as a marker for determining the digestibility of feed. Titgemeyer et al. (2001) conclude that TiO_2 can be used for nutritional purposes. Interestingly, as an indigestible indicator in the very initial trial period from 2nd to 6th day after oral application only 79.4 % of total titanium ingested occurred in faeces. But in the period from 17th to 21st day after the application it appeared in 98.3 % in faeces. According to Friest et al. (1982) TiO_2 can be used as an indicator of contamination of feed with the soil.

Table 2 shows the correlation between analyzed Al, Si and Ti in each feed.

Table 2 shows the correlation between tested elements in each raw material for cattle feed. From Table 2 a strong negative, significant correlation is apparent between Al and Ti in wheat bran ($P<0.01$),

and final by a significant ($P<0.05$) correlation of Al and Ti in dry beet pulp. There are no research results at all with which to compare these findings.

It is also obvious from these data that other investigated microelements are not in any competitive inhibition inside the analyzed feedstuffs ($P>0.05$). The European legislation concerning feed hygiene, especially undesirable substances as trace elements, laid down the maximum limits for some elements such as trace cadmium, mercury, fluorine and arsenic. However, the maximum levels for elements in feed materials intended for animal feed and discussed here, are not consolidated at all (Directive 2002/32/EC; Official Journal of EU, No. 140, 31. 5. 2002). Literature overview from last 15 years has showed no matches to compare with our findings and results.

CONCLUSIONS

Based on the available literature that deals with the issue of Al, Si and Ti in soils and occurrence in the plants compounds, and the impact of these trace elements on metabolism of farm animals we can make some basic conclusions.

1. Our results suggest a baseline study which begins to address issues of Al, Si and Ti in fodder plants for the northeastern Slovenia.
2. In the north-eastern area of Slovenia (Maribor - Ptuj - Lenart - Slovenska Bistrica) eight individual feedstuff samples contain average concentrations of Al 3.05×10^{-3} g/kg DM, Si 6.06×10^{-3} g/kg DM and Ti 5.22×10^{-5} g/kg DM.
3. Results of soybean cake analysis of Al, Si, and Ti may be associated with the origin, as shown in some cases, significantly ($P<0.05$) differ from the values of other feed components.
4. This starting research in the selected samples could be important for further research on the effects of microelements (Al, Si, Ti) on animals.

REFERENCES

1. EMEA (European Agency for the Evaluation of Medicinal Products). (2000): Aluminium distearat, Aluminium hydroxy acetate, Aluminium phosphate and Aluminium tristearate. Final summary report No. MRL/393/98, London UK, 1-4.

2. Friest, G. F., Marrow, G. S., Snow, P. A. (1982): Soil ingestion by dairy cattle. *Journal of Dairy Science* 65, 611-618.
3. Ganrot, P.O. (1986): Metabolism and possible health effects of aluminum. *Environ Health Prospect* 65, 363-441.
4. Haug, A. (1984): Molecular aspects of aluminum toxicity. *Critical Reviews in Plant Science* 1, 345-373.
5. Ma, J. F. (2000): Role of organic acids in detoxification of aluminum in higher plants. *Plant and Cell Physiology* 41, 383-390.
6. Mimmo, T., Sciortino, M., Ghizzi, M., Gianquinto, G., Gessa, C. E. (2009): The influence of aluminium availability on phosphate uptake in *Phaseolus vulgaris* L. and *Phaseolus lunatus* L. *Plant Physiology and Biochemistry* 47, 68-72.
7. Panda, S., Baluska, F., Matsumoto, H. (2009): Aluminum stress signaling in plants. *Plant Signal Behaviour* 4, 592-597.
8. Schroeder, H. A., Balassa, J. J., Vinton, W. H. (1964): Chromium, lead, cadmium, nickel and titanium in mice: effect on mortality, tumors and tissue levels. *Journal of Nutrition* 83, 239-250.
9. SPSS Statistics Base 17.0 User's Guide. SPSS Inc., 233 South Wacker Drive, 11th Floor, Chicago, IL 60606-6412. USA. ISBN-13: 978-1-56827-400-3, ISBN-10: 1-56827-400-9
10. Titgemeyer, E. C., Armendariz, C. C., Bindel, D. J., Greenwood, R. H., Loest, C. A. (2001): Evaluation of titanium dioxide as a digestibility maker for cattle. *Journal of Animal Science* 79, 1059-1063.
11. Underwood, N. J., Suttle, N. F. (1999): The mineral nutrition of livestock. 3rd. Ed. CAB International, Wallingford UK 17-20.
12. Van Soest, P. J. (1994): Nutritional ecology of the ruminant. 2nd. Ed. Cornell Univ. Press, Ithaca NY, USA, 122-131.

SAŽETAK

U članku govorimo o učestalosti mikroelemenata, posebice elemenata u tragovima koji iz tla na različite načine prelaze u krmno bilje. Cilj ovog pokusa je bio izmjeriti sadržaj aluminija (Al), silicija (Si) i titana (Ti) u krmu proizvedenoj na području sjeveroistočne Slovenije. Analizirali smo osam krmiva: kompletnu smjesu za muzne krave K-18, sijeno (talijanski ljulj, bijela i crvena djetelina), kukuruzno krmno brašno, silažu kukuruza, pšenične posije, sojinu sačmu (44% sirovih bjelančevina) i suhe repine rezance. Upotrijebili smo rendgensku fluorescentnu spektrometriju. Prosječne vrijednosti u svim krmivima za Al su bile $3,05 \times 10^{-3}$ g/g ST, Si $6,06 \times 10^{-3}$ g/g ST i Ti $5,22 \times 10^{-5}$ g/g ST. Raspon između najmanje i najveće vrijednosti za pojedine mikroelemente u svim krmivima je bio za Si $2,27 \times 10^{-2}$, Al $7,93 \times 10^{-3}$ i za Ti $2,07 \times 10^{-4}$. Ovo temeljno istraživanje odabranih uzoraka je važno za buduća istraživanja hranidbenih učinaka mikroelemenata (Al, Si, Ti) u životinja.

Ključne riječi: krmiva, aluminij, silicij, titan