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USING OF ZEOLITE TUFFS AS ENTEROSORBENTS IS IN COWS NOURISHMENT

The article deals with the experimental information due to the regularity of hard metals migration with trophic chain and loading of movable form of Cadmium, Plumbum, Mercury and Zinc by Dairy cows organisms. It was set up, that the toxical elements with different intensity migrate into organs and cows tissues. Using of zeolite meal of small grinding of Sokyrnytske field as fodder addition in dose of 0,5 gr per 1 kg of the living mass, the coefficient of bioaccumulation of Plumbum, Cadmium and Marcury movable forms is reduced accordingly to 40,9 and 44,5 % to control but accumulation coefficient of Zinc ions, on the contrary, was rised to 5,7%. Zeolite tuffs the adsorption of exo- and endotoxines, connect the toxical elements, especially hard metals, in gastro-intestinal tract and take their out of organism, that favour the increase of cows productivity and get ecologically pure milk due to the content of hard metals in the local zone of technogenic loading.

Key words: cattle, hard metals, zeolite meal, ecologically pure products.

Наведено експериментальні дані щодо закономірностей міграції важких металів трофічним ланцюгом та нагромадження рухомих форм Кадмію, Плюмбуму, Меркурію та Цинку організмом дійних корів. Встановлено, що токсичні елементи з різною інтенсивністю мігрують в органи та тканини корів. За використання цеолітового борошна дрібного помелу Сокирницького родовища як кормової добавки у дозі 0,5 г на 1 кг живої маси коефіцієнт біоакумуляції рухомих форм Плюмбуму, Кадмію та Меркурію знизився відповідно на 40,9, 33,2 та 44,5 % до контролю, а коефіцієнт акумуляції йонів Цинку, навпаки, зріс на 5,7 %. Цеолітові туфи забезпечують адсорбцію екзо- і ендотоксинів, зв'язують токсичні елементи, зокрема важкі метали, в шлунково-кишковому тракті та виводять їх за межі організму, що сприяє зростанню продуктивності корів та одержанню екологічно безпечного щодо вмісту важких металів молока в локальних зонах техногенного навантаження.

Ключові слова: велика рогата худоба, важкі метали, цеолітове борошно, екологічно безпечна продукція.

The statement of the problem and its connection with scientific and practical tasks. The ecological situation in Ukraine through non-controlled physical, chemical and biological factors of industrial enterprises and transport has created a growing threat to the health of animals and humans. Indicated factors may have a negative influence as on a whole and for individual organs, tissues and systems [1]. An important role in this process belong to heavy metals that are highly toxic , the ability to accumulate in animals and humans, causing harmful effects, even at low concentrations is reasonable cause to refer them to the priority pollutant production and environmental environment [5]. Industrial projects are able to pollute the environment for tens of kilometers. Industrial emissions of the last, in some cases, can lead to the creation of artificial local biogeochemical provinces, which are quite large areas [1].

Purpose of the work. Theoretical grounding and experimental studies of using zeolite tuff deposits of Sokyrnytsjke deposit as fodder supplement in the nutrition diet of dairy cows in order to obtain from them an ecologically safe due to the content of milk of heavy metal techno genic pollution.

Analysis of recent research and publications. A significant amount of heavy metals entering the body of animals derived from it through the gastrointestinal tract, kidney, breast (in lactating cows) and

others. It was established that most of fodders in milk is transformed Plumbum - within 6,3-10,2%, other heavy metals are transformed within 3,1-5,9% [5]. Therefore, in accordance with current biomedical and health requirements for food commodities and food products in the milk and milk products, the content of heavy metals is limited by certain regulations.

The most dangerous influence of heavy metals on the organism of young, high-productive and not adapted to the environmental conditions of the animals, which negatively affects on the immune system, metabolism, productive quality. In the prevention of heavy metal intoxication occupies an important place to balance rations for all biologically active substances and the power input to them enter sorbents. The most effective, increasing resistance of organisms to the accumulation of pollutants are natural sorbents and especially zeolite tuffs [2]. Development of scientifically and practical base on the development of dairy farming in the local zone of techno genic pollution and the supply of food to men, including environmentally safe due to the content of heavy metal refers to the actual problems of modern ecology.

Methods of Research. Scientific and Economic Research was carried out on 2 groups of clinically healthy due to infectious and invasive diseases of cows - analogies of local Ukrainian Black - Spotted Dairy cows Ltd. "Zubra", which is located in the area of technological loading of Mykolajiv mining and cement plant with 10 heads in each first - control, the second - research. Animals keeping - winter-stall. The control group had received the basic diet of the cows that supply consistent standards of dairy cows and cows of experimental group were additionally fed with forage zeolite of fine flour milling (250-1000 m) Sokyrnytsjkyj deposit in Transcarpathian region at a dose of 0,5 g per 1 kg body weight [3]. The concentration of heavy metals insoils, samples of fodder, water, milk, urine and fecal masses were investigated by spectrophotometry [6], using the mode of adsorption of air -acetylene flame in atomic adsorption spectrophotometer AA8 - 30. The obtained data are mathematically worked on by methods of variation statistics [4]. Probability of differences between the control parameters and the experimental group was assessed using the t–criteria of Student.

Experimental search. In the course of the research it was found that the content of heavy metals in soils of Ltd. "Zubra", which were at a distance of 2,0 to 10,0 km from Mykolajiv cement plant is considerably much higher than the maximum permissible concentration (MPC). Zinc concentrations in all soil samples exceeded the MPC, the maximum concentration was fixed at the level of 45,5 mg/kg, exceeding the MCL into 1,98 times. The increased content of zinc in forage crops may cause mutagenic and gona do toxicaction, accompanied by a decrease of reproductive functions and productivity of dairy cows.

Lead – one of a priority pollutant subject to priority control is a cumulative poison. Under its action the reproducible ability of heme synthesis, processes of proliferation and differentiation of cells of bone and cartilage are violated. Fluctuations of movable forms of Pb in the investigated soils were within 8,75-17,80 mg/kg, that in 1.45 - 2.96 times exceed the MPC. The content of movable forms of cadmium in soils is higher than the norm of MCL by 3-6 times. Taking into account the increased ability of cadmium to the accumulation and that its half-life in soil for more than 1000 years, become clear that the danger to the health of animals and because of animal products and people can cause it. From the large intake of cadmium, irreversible kidney damage is developing, protein synthesis and vitamin balance are disrupted. Cadmium inhibits phospho- calcium metabolism and also affects the metabolism of some trace elements, in particular, Zn, Cu, Mn, Se, etc.

Movable forms of Mercury in the investigateds oils were within 3,31-5,91 mg/kg, in 1,56-2,81excess of the MPC. Mercury, especially its organic compounds affect the central nervous system, cause embryotoxic and gonadotoxic action, showing carcinogenesis and activate lipid peroxidation. For the investigated soils its acidification is also characterized, pH ranged from 5,78 to 6,12, and it is known that with increased acidity available to plants mobile forms of heavy metals are increased and therefore their transformation in vegetative parts of forage cropsis increased.

Previously it was found that soils contaminated with heavy metals at concentrations above the MPC cause the significant cumulating of the latest in biomass of agricultural crops. Forage crops that belong to different species and familiesare characterized by different tolerance to elevated levels of movable forms

of heavy metals in soil. The green mass of clover and sugar beet tops most accumulate cadmium, corn - Lead, cereal and fodder crops - Zinc, wheat straw and sugar beet - Mercury.

For the most of agricultural crops the proportional dependence is between the level of movable forms of heavy metal ions in the soil and their accumulation by plants. In stems usually as, a rule, the content of pollutants is in 10-20 times lower than in roots. The coefficient of biological absorption of heavy metals by plants and, in particular, agricultural feed crops is often greater than one. It is known that some plants have the ability to accumulate heavy metals even at higher concentrations than their content in the soil. The accumulation of heavy metals by plants depends on the concentration of metals, pH, content of organic matter in the soil, plant age, and also from **-+96 the concentration of metal – antagonists and other reasons.

Thus, the experimental investigations have shown that biological absorption coefficient of Pb was highest in tops of sugar beet (0,98) and samples of green mass of corn silage (0,90). In roughage (straw, hay) it equaled 0,45 and 0,39, respectively. As for the green mass of alfalfa, clover and pasture, their accumulation was lower. Cadmium in all investigated samples of feed, except for the green mass alfalfa, was accumulated with the coefficient of accumulation, greater than the unit.

Factor accumulation of zinc in the investigated agricultural crops dominates unit. Cereals during the growing season can maximal accumulate Zinc (84,4 mg/kg). Zinc content in leguminous crops (green mass of alfalfa and clover) in average 13,4-17,9% was lower than the grass, which is possible due to the high content of phytic bean compounds that have the ability to inhibit the absorption of Zinc.

Fodder analysis due to the content of heavy metal in the diets of lactating cows grown in the area of the Nikolayev cement plant testifies that the average daily earnings of movable forms of pollutants in almost all samples of fodder exceeds the maximum permissible concentration (Table 1). Experimental search have shown that foods supplied 99,7% of common quantity of Plumbum; 99,0% of Cadmium, 99,8% of Mercury and 93,8% of Zinc (Table.2).

Table 1

Concentration of heavy metals in samples of ration fodder (mg/kg, M ± m, n = 10)

Indicators	Zn^{2+}	Pb^{2+}	Cd^{2+}	Hg^{2+}
Hay	67,2±5,31*	5,10±0,18	0,44±0,05	0,14±0,03
Wheat Straw	69,48±5,91*	6,03±0,20*	0,52±0,06*	0,26±0,02*
Silage maize	56,0±2,37	9,28±1,20*	0,40±0,02*	0,16±0,02*
Feed	63,4±2,88*	3,82±0,29*	0,30±0,02	0,19±0,03*
MAC **	50,0	5,0	0,3	0,1

Note: * - change indicators likely relatively MAC ($P < 0.05$); ** - according Talanova G.A., Khmelevskiy B.A., 1991.

Table 2

Depositing of heavy metals in the body of cows during research period (305 days), mg per 1 mg of animal

Indicators	Cd^{2+}	Pb^{2+}	Hg^{2+}	Zn^{2+}
Received in the organism, mg	27924,1	1868,9	779,1	25276,1
with water	270,7	5,4	1,4	263,9
%	1,0	0,3	0,2	1,1
With fodder	27653,4	1863,5	777,7	25012,2
%	99,0	99,7	99,8	98,8

Heavy metal coming in animals organism with drinking water was negligible. Comparing the total number of heavy metals coming from the feed and drinking water to those excreted animals can identify certain patterns of accumulation of these elements. Thus, under the conditions of the experiment, the highest migration and depositing activity, metal antibiotics are observed - Zinc (accumulation ratio 13,8%). Regarding the accumulation of metals, toxins, it should be noted considerable migration activity of movable forms of cadmium bioaccumulation factor which is 2,6 times higher than movable forms of

Plumbum (accumulation rate 4,9%) and 3.5 times - Mercury (accumulation factor of 3,6%) with a coefficient of accumulation of 12,5%.

Most of the heavy metals entering the body of dairy cows with fodder and water is not retained in organs and tissues, and excreted with milk, urine and stool, where heavy metals are again included in the nutrient cycle (tabl.3).

Table 3

The withdrawal of heavy metals from the body of cows for a period of 90 days of research on the background of the action of zeolite (0,5 g per 1 kg of body weight), 1 mg per animal

Performance	Control group				Experimental group			
	Pb	Cd	Hg	Zn	Pb	Cd	Hg	Zn
Taking out of the body	7836,2	482,6	221,3	66163,2	8001,0	512,3	225,3	65549,1
including milk	490,8	28,4	6,9	2315,5	216,0	22,7	3,7	2649,1
%	6,3	5,9	3,1	3,5	2,7	4,4	1,6	4.0
With excretion	971,7	54,6	62,8	3837,5	576,1	35,2	34,2	2753,1
%	12,4	11,3	28,4	5,8	7,2	6,9	15,2	4,2
with fecal masses	6373,7	399,6	151,6	60010,2	7208,9	454,4	187,4	60146,9
%	81,3	82,8	68,5	90,7	90,1	88,7	83,2	91,8
It remains in the body	403,7	68,9	8,3	10592,2	238,9	39,2	4,6	11206,3
Transformation %	4,9	12,5	3,6	13,8	2,9	7,1	2,0	14,6
± to control %	-	-	-	-	-40,9	-43,2	-44,5	+5,7

However, the amount that remains in the body of cows, which are operated in the local area of high anthropogenic load is just enough content to toxic elements exceed the maximum permitted levels. To correct the bioaccumulation of heavy metals by the organism, cows from the research group in addition to the basic diet with forage were fed with zeolite flour, enter sorbent that binds toxic elements in the gastrointestinal tract, resulting in reduced absorption and increases excretion of heavy metals from the stool with simultaneous decrease in their content in urine and milk (Bogdanov G.O. et al., 2002).In the experimental group of cows under the influence of feeding with zeolite meal as feed additive in fecal masses contents ions of Plumbum, Cadmium, Mercury and Zinc were higher, respectively 13,1, 13,7, 23,6 and 1,1% compared with the control.

Zeolites rise the adsorption of heavy metals in the gastrointestinal tract, connecting and transferring them into insoluble compounds, which together with the undigested remnants are excreted from the organism. Under the influence of enter sorbent - zeolite flour the coefficient of bioaccumulation of movable forms of Plumbum, Cadmium and Mercury has reduced respectively by 40,9 , 33,2 and 44,5% to control, but the rate of accumulation of zinc ions, by contrast, grew by 5,7%.

Table 4

Content of heavy metals in milk of experimental cows, M ± m, n = 20

Heavy metals	Control group			Experimental group		
	mg / kg	total, mg	% of fuel	mg / kg	total, mg	% of fuel
Plumbum	0,71±0,06	5,27±0,47	5,82	0,29±0,07*	2,28±0,54*	2,52
Cadmium	0,041±0,01	0,31±0,08	5,12	0,03±0,01*	0,24±0,07*	4,02
Mercury	0,01±0,002	0,08±0,01	3,16	0,005±0,001*	0,04±0,008*	1,62
Zinc	3,35±0,13	24,86±1,1	2,92	3,50±0,12	27,32±1,2	3,21

Note: MDR for Pb, Cd, Hg, Zn respectively 0.1, 0.03, 0.005 and 5.0 mg/l.

A large number of Plumbum is taken out with milk of cows from the control group (Table 4) that exceed the MRL in 7 times, Mercury – in 2 times and Cadmium - in 1,36 times. Movable forms of zinc in milk were investigated in the normal range. The transition rate of heavy metals in the milk of the control group was the highest for movable forms of Plumbum (5,82) and Cadmium (5,12), the lowest for Zinc (2,92) and moving shapes of Mercury occupy an intermediate position (3.16). In the experimental group, where zeolite tuffs were fed additionally, the excretion of heavy metals with milk, compared with the

control group was decreased (Plumbum - by 56,8% , Cadmium - by 22,0% and Mercury - by 50,0%), and the concentration Zinc in the milk of the experimental group was increased by 9,8%, which was within the maximum allowable levels (MRL).The results showed that the experimental group of cows who are fed as fodder additive zeolite flour the productivity is increased productivity by 15,1% (Table 5).

Table 5.

The effectiveness of fed zeolite flour on the productivity of cows and milk quality

Indices	Control group	Experimental group
Milk yield , kg	2565,4 ± 76,2	2952,8 ± 69,4*
Fat content ,%	3,34 ± 0,08	3,46 ± 0,01*
Milk fat , kg	85,70 ± 5,23	102,1 ± 4,8*
Protein content ,%	3,32 ± 0,02	3,42 ± 0,01*

Thus, the use of zeolite meal as fodder mineral supplement will increase the productivity of cows due to the intensity of milk, significantly improve milk quality indicators by the increased content of protein and fat, which gives reason to include zeolite flour into the category of biologically active substances.

Conclusions. Zeolite tuff as a feed supplement in the diet of feeding cows exhibit the ability to regulate the concentration of certain trace elements in the rumen, to reduce decay processes in stomach and intestine, which has a positive impact on the metabolic processes in the body as a whole. They provide the adsorption of exo-and endotoxins, bind toxic elements such as heavy metals in the gastrointestinal tract and eliminate them from the body, which contributes to increase the productivity of cows and to get ecologically safe, due to the content, heavy metals of milk in local area of techno gene loading.

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