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# Toxicological Monitoring of Toxic Chemicals in the Soil and Animal Feed in the Republic of Mari El.

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#### ABSTRACT

In the soil and animal feed in the Republic of Mari El there is a low concentration of such minerals as copper, zinc, cobalt, selenium which are essential to animals. The contamination of soil and animal feed by heavy metals is irrelevant as there are no chemical, metallurgical and petrochemical plants in the republic which are sources of soil and animal feed contamination. It has been established that 40% of the animal feed is non-toxic, 37.7% – slightly toxic, and 25.3% – toxic. Mucor, Aspergillus flavus and Penicillium pathogenic fungi have been most frequently identified.

Keywords: infestation, animal feed, soil, heavy metals, mycotoxins.

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#### INTRODUCTION

Modern civilization has a significant impact on nature. Using different elements of the environment people change the quality of it [1]. These changes are often the result of environmental pollution by industrial and household waste that has a harmful effect not only on humans but also on animals, plants and soil [2,3,4].

Environmental pollution is the change in properties of the environment occurring as a result of natural or artificial processes and leading to deterioration of the functions of the environment in relation to any biological or technological objects [5]. Substances that pollute the environment are very diverse. Depending on their nature, concentration, time of action on living organisms they can cause various adverse effects [6,7].

The results of toxicological monitoring and preventive measures developed on the basis of the data of it show that chemicals have a harmful effect on health of animals and contribute to the solution to the problems of toxicological safety [8,9,10].

The purpose of the research was to study the contamination of the soil and animal feed by heavy metals in the Republic of Mari El, as well as the analysis of the impact of mycotoxins on animal feed.

#### MATERIALS AND METHODS

The objects of the study were soils and animal feed. Feed samples were taken from farms according to GOST-17.4.4.02-84. Soil samples (20 cm) were collected from open sites at a distance of 200 m from highways.

Sanitary and mycological assessment of the animal feed in the Republic of Mari El was performed at the chemical and toxicological laboratory in the Republic Veterinary Laboratory by standard techniques.

#### RESULTS

An average phosphorus concentration in the Republic of Mari El is 15.2 mg/kg of soil, which exceeds the maximum allowable concentration by 40%. The phosphorus concentration is especially high in Volzhsky, Zvenigovsky and Medvedevsky districts –  $21.13\pm2.98$ ;  $22.13\pm2.60$  and  $25.38\pm1.20$  mg/kg of soil, respectively.

Similar data are observed in the analysis of calcium concentration. Thus, an average concentration of this element in the soil is above the maximum allowable concentration by 20 %. The calcium concentration in Yurinsky district is 3.84±2.84 mg/kg which is below the maximum allowable concentration by 61%.

The levels of such heavy metals as nickel, lead and cadmium in the soil in all the districts of the Mari El Republic do not exceed the maximum allowable concentration (Table 1). Only in some households, a slight excess of the maximum allowable concentration of lead is noted.

Districts	Lead	Nickel	Zink	Copper	Cadmium	
Volzhsky	3.21±0.07	2.88±0.02	30.55±2.23	12.21±0.82	0.18±0.007	
Gornomariysky	3.77±0.05	3.78±0.02	28.33±4.65	13.55±0.87	0.32±0.003	
Zvenigovsky	3.26±0.08	2.34±0.03	25.89±3.99	12.09±0.55	0.23±0.006	
Kilemarsky	3.66±0.03	2.12±0.01	28.30±2.98	8.76±0.23	0.22±0.009	
Kuzhenersky	3.90±0.07	5.11±0.09	33.00±4.77	10.43±0.59	0.37±0.002	
Mari-Tureksky	3.43±0.05	5.09±0.06	29.12±4.56	14.22±0.23	0.40±0.007	
Medvedevsky	4.50±0.03	4.32±0.04	29.31±3.34	9.88±0.55	0.45±0.006	
Morkinsky	4.08±0.06	3.21±0.04	34.99±8.16	10.12±0.45	0.15±0.005	
Novotoryalsky	4.48±0.09	5.20±0.08	27.77±5.23	9.65±0.28	0.32±0.009	
Orshansky	3.09±0.04	4.50±0.10	29.01±4.09	8.50±0.53	0.20±0.007	
Paranginsky	4.11±0.05	6.40±0.12	30.09±2.21	11.52±0.63	0.24±0.008	

#### Table 1: Toxic element concentration in the soil, mg/1kg

January-February

2018

RJPBCS

9(1)

**Page No. 841** 



Sernursky	3.08±0.08	6.12±0.22	36.45±7.09	8.43±0.24	0.36±0.02
Sovetsky	3.33±0.07	5.08±0.09	38.23±5.09	9.80±0.36	0.23±0.007
Yurinsky	2.75±0.06	1.43±0.03	31.45±7.21	8.80±0.43	0.08±0.005

In the Republic of Mari El there are no chemical, metallurgical and petrochemical industries which are sources of soil pollution by heavy metals. Soil pollution is mainly caused by emissions from road transport.

The analysis of zinc concentration in the soil has shown a low concentration of it in all the districts that ranges from 25.89 to 38.23 mg/kg.

The copper concentration in the soil is also below the maximum allowable concentration. Especially, it is low in Kilemarsky, Orshansky, Sernursky and Yurinsky districts which is 8.76±0.23; 8.50±0.53; 8.43±0.24 and 8.80±0.43 mg/kg, respectively.

The magnesium concentration in the soil is below the maximum allowable concentration.

The mean concentration of cobalt in the soil is  $0.85\pm0.02$  mg/kg of soil which is below the maximum allowable concentration. It should be noted that the lowest concentration of cobalt is observed in Volzhsky, Zvenigovsky, Kilemarsky, Morkinsky and Yurinsky districts where the concentration of it is  $0.89\pm0.06$ ;  $0.89\pm0.03$ ;  $0.95\pm0.05$ ;  $0.90\pm0.02$  and  $0.80\pm0.04$  mg/kg, respectively.

The mean concentration of selenium in the soil in the Republic of Mari El is 0.017 mg/kg, while the norm is 0.05 mg/kg.

The levels of iron in the soil in the Republic of Mari El are within allowable concentration (50-100 mg/kg). However, in Kilemarsky district the iron concentration exceeds the maximum allowable concentration - 127.18 $\pm$ 16.4 mg/kg of soil.

In the Republic of Mari El, there are four natural economic areas: central, northeastern, southwestern and forest-steppe. Sovetsky, Medvedevsky and Orshansky districts are in the central area. The northeastern area includes Kuzhenersky, Mari-Tureksky, Novotoryalsky, Morkinsky, Paranginsky and Sernursky districts. Zvenigovsky, Volzhsky, Kilemarsky districts and the left bank area of Gornomariysky district are in the southwestern area. The forest-steppe area includes the right bank area of Gornomariysky district.

In the central area, the iron concentration in barley exceeds the maximum allowable concentration (MAC) by 15.9%, in vetch and oat haylage by 57% and in clover silage by 25.1%, while the norm is 100 mg/kg. In the southwestern area, the iron concentration exceeds the norm in legume-grass haylage by 34.2%, in vetch and oat haylage by 51.9%, in clover silage by 33.9%. A low iron concentration is noted in barley, which is 5.9±0.01 mg/kg. In the northeastern area, the iron concentration exceeds the MAC in vetch and oat haylage by 2.5 times. In the forest-steppe area, the iron concentration exceeds the MAC in legume-grass haylage and clover silage.

In the analysis of copper concentration in the animal feed it was noted that in all the four natural economic areas there is a low copper concentration which ranges from  $4.0\pm0.006$  to  $9.0\pm0.04$  mg/kg in the central area, from  $4.21\pm0.02$  to  $10.0\pm0.01$  mg/kg in the southwest, from  $5.66\pm0.20$  to  $12.55\pm0.02$  mg/kg in the northeast and from  $4.7\pm1.12$  to  $14.9\pm3.09$  mg/kg in the forest steppe, while the norm is 30 mg/kg.

The level of manganese in wheat is  $22\pm0.02$  mg/kg in the central area,  $13.5\pm1.44$  mg/kg in the southwestern area,  $5.66\pm0.20$  mg/kg in the northeastern area. In legume-grass haylage, it is  $11.1\pm0.01$  mg/kg;  $10.4\pm1.55$  mg/kg;  $22.6\pm1.11$  mg/kg and  $45.8\pm8.12$  mg/kg, in the central, southwestern, northeastern and forest-steppe areas, respectively. In cereal straw, the manganese concentration in all the areas ranges from  $15.5\pm2.12$  to  $23.1\pm0.09$  mg/kg.

The maximum allowable concentration of zinc in animal feed should not exceed 50 mg/kg. In the central area, zink concentration in crops ranges from  $18.8\pm0.02$  to  $31.2\pm3.50$  mg/kg, the lowest zink concentration is in legume-grass and vetch and oat haylage,  $6.9\pm0.04$  mg/kg and  $5.9\pm0.04$  mg/kg, respectively. In the southwestern area, the level of zinc in wheat is  $20.1\pm3.10$  mg/kg; rye –  $16.9\pm2.32$  mg/kg, barley –

January–February 2018 RJPBCS 9(1) Page No. 842



 $30\pm4.54$  mg/kg, legume-grass haylage -  $5.67\pm0.71$  mg/kg, vetch and oat haylage -  $7.09\pm1.03$  mg/kg, clover silage -  $8.22\pm1.06$  mg/kg and cereal straw -  $5.90\pm1.09$  mg/kg. In the northeastern and forest-steppe areas, zink concentration is also low.

Cobalt concentration in the animal feed is below the maximum allowable concentration. So, in the central area the level of cobalt in crops ranges from  $0.43\pm0.002$  to  $0.60\pm0.001$  mg/kg, while the norm is 2 mg/kg. The concentrations of this mineral element in legume-grass and vetch and oat haylage, in clover silage and in cereal straw range from  $0.24\pm0.002$  to  $0.50\pm0.001$  mg/kg, while the norm is 1 mg/kg. In the southwestern area, the cobalt concentration in all the types of animal feed does not exceed  $0.40\pm0.003$  mg/kg. In the northeastern area, the level of cobalt does not exceed  $0.60\pm0.002$  mg/kg.

In the central area, the lowest concentration of selenium is observed in wheat and clover silage, where the level of it is not more than 0.02 mg/kg. The normal concentration of selenium in animal feed is considered to be not less than 0.1 mg/kg. In legume-grass, vetch and oat haylage, the levels of selenium are 0.037±0.002 mg/kg 0.049±0.003 mg/kg, respectively. In southwestern, northeastern and forest-steppe areas, the concentration of selenium in the animal feed does not exceed 0.03 mg/kg.

In the central area, the level of magnesium in wheat is  $866.1\pm18.2 \text{ mg/kg}$ , in rye  $- 664.9\pm69 \text{ mg/kg}$ , in barley  $- 975.1\pm58.9 \text{ mg/kg}$ , in legume-grass haylage  $- 866\pm43.3 \text{ mg/kg}$ , in vetch and oat haylage  $- 465.9\pm24.9 \text{ mg/kg}$ , in clover silage  $- 932.7\pm43 \text{ mg/kg}$  and in cereal straw  $- 574.9\pm45.9 \text{ mg/kg}$ . In the southwestern area, the magnesium concentration varies from  $322.9\pm44.4$  to  $1122.7\pm80.4 \text{ mg/kg}$ , in the northeastern  $- from 466.8\pm70.7$  to  $1000.5\pm87.6 \text{ mg/kg}$ , and in the forest-steppe  $- from 632\pm33.9$  to  $989.2\pm65.9 \text{ mg/kg}$ .

The levels of lead in all the animal feed and in all the districts of the Mari El Republic do not exceed the MAC which is not more than 5 mg/kg. So, in the central area the lead concentration ranges from 0.11 to $\pm 0.001$  to  $0.64\pm 0.006$  mg/kg. In the southwestern area, the lead concentration in wheat is  $0.30\pm 0.002$  mg/kg, in rye  $- 0.67\pm 0.003$  mg/kg, in barley  $- 0.21\pm 0.002$  mg/kg, in legume-grass, vetch and oat haylage and in clover silage it is not more than  $0.32\pm 0.003$  mg/kg. In the northeastern area, the highest level of lead is in clover silage  $- 0.87\pm 0.002$  mg/kg. In the forest-steppe area, the lowest lead concentration is in legume-grass haylage  $- 0.06\pm 0.002$  mg/kg.

A similar pattern is observed when analyzing cadmium concentration in the animal feed in the Mari El Republic, where it ranges from 0.03±0.004 mg/kg to 0.10±0.003 mg/kg. The MAC of it should not be more than 0.4 mg/kg.

There is no arsenic in all the animal feed in the four natural economic areas.

The analysis of the concentration of mineral elements in the animal feed in the Republic of Mari El has shown that the concentration of such minerals as copper, zinc, cobalt and selenium is low. The iron concentration in some feed exceeds the MAC. The concentration of heavy metals such as lead and cadmium does not exceed the MAC.

The study of mixed feed has shown that 27.2% is non-toxic, 45.5% – slightly toxic, 27.3% – toxic. 35.4% of grain feed is non-toxic, 41.5% – slightly toxic and 23.1% – toxic. 60% of roughage feed is non-toxic, 16% – slightly toxic and 24% – toxic.

It has been established that 40% of the animal feed is non-toxic, 37.7% – slightly toxic, and 25.3% – toxic. In 2009, 44.4% of animal feed was slightly toxic and 53.4% – toxic. That is, a decrease in the infestation of animal feed by mycotoxins occured. In our opinion, this fact is due to abnormal hot weather in the summer of 2010, when animal feed was over-dry. Low-moisture feed is an unfavorable condition for the development of fungi.

Mycological studies have shown (Table 2) that the animal feed was infested by pathogenic fungi of several genera. By the degree of infestation, micromycetes of the animal feed were in the following order according to the degree of decrease in their share in the total number of identified fungi: Mucor, Aspergillus flavus and Penicillium fungi.

January–February 2018 RJPBCS 9(1) Page No. 843



Types of animal feed	Total number of samples	Aspergillus flavus	Aspergillus niger	Mucor	Penicillium	Risopus	Althernarium	Cladosporium	Trichoderma viride
Mixed feed	150	29	2	31	25	17	5	4	-
Grain feed	150	27	3	29	25	10	6	1	1
Presscake, oil cake	20	_	_	2	_	_	2	2	-
Tankage	5	1		1	1	-	-	-	-
Hay, straw	30	4	2	2	4	2	2	-	

#### Table 2: The results of the mycological examination of the animal feed

The degree of infestation by micromycetes in different groups of animal feed, except the animal feed from oilplants has the same pattern: most of the identified fungi are Mucor, Aspergillus, Penicillium fungi, in a less degree, Risopus, Althernarium, Cladosporium, Trichoderma fungi. Oil cake is infested equally by Mucor and Althernarium fungi. Most toxicogenic fungi of the Fusarium genus are not identified during the research.

#### CONCLUSION

Thus, it can be stated that in the soil and animal feed in the Republic of Mari El there is a low concentration of such minerals as copper, zinc, cobalt, selenium which are essential to animals. The contamination of the soil and animal feed by heavy metals is irrelevant as there are no chemical, metallurgical and petrochemical plants in the republic which are sources of soil and animal feed contamination. It has been established that 40% of the animal feed is non-toxic, 37.7% – slightly toxic, and 25.3% – toxic. Mucor, Aspergillus flavus and Penicillium pathogenic fungi have been most frequently identified.

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9(1)