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INFLUENCE OF CHALKING BY DUST-LIKE OIL-SHALE ASH ON MEADOW GRASS MICROELEMENTS CONCENTRATION

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ВЛИЯНИЕ ИЗВЕСТКОВАНИЯ ПЫЛЕВИДНОЙ СЛАНЦЕВОЙ ЗОЛОЙ НА КОНЦЕНТРАЦИИ МИКРОЭЛЕМЕНТОВ В ЛУГОВЫХ ТРАВАХ

A wide application of ordinary oil-shale ash for chalking of soils in Estonia began in 1953. Since 1964, dust-like oil-shale ash from the local power-plants has been used for this purpose [1, 2].

In connection with the use of ash for chalking the concentrations of macro- and microelements (B, Cu, Mn, Mo, Co, Zn) required for mineral nutrition of plants were determined in oil-shale ash, soils and some crops [3, 4]. Scientifically grounded rates of ash application have been proposed, duration of chalking cycle has been specified, efficiency of chalking by oil-shale ash on crop capacity has been confirmed [5].

Later, by means of high-sensitivity analytical methods (INAA, XRFA, etc.) the concentrations of 43 microelements in oil-shale ash from *Baltic* power plant [6—10] and the concentrations of the elements of the first group of the Periodic Table in some Estonia's plant species were determined [11].

Since soil is the main source of microelements for plants, the behaviour of microelements in the system "soil—plants" and their accumulation in plants are of a particular interest as regards the protection of the health of people and animals. The aim of the present work was to determine the concentrations of a large group of trace elements in some meadow grass species and, on their basis, to study the influence of soil chalking by dust-like oil-shale ash.

Experimental part

As objects of the study of the chalking influence on the plant microelement composition two species of meadow grass were chosen: *Phleum pratense* and *Trifolium pratense*. Both of these accumulate microelements during one season in leaves and stalks of small volume which are wholly used as fodder.

The grass was cultivated on the lots of the Ülenurme experimental farm affiliated to the Estonian Agricultural Academy. The soddy-podzolic soil of the experimental lots is slightly loamy with the following indices of the arable layer: pH_{KCl} ~5, the mobile aluminium content 0.5 mg/100 g, the degree of base saturation 65 %, the hydrolithic acidity 3.4 Meq/100 g. The total soil chalking rate is 5.1 t $CaCO_3$/ha, but as the oil-shale ash from *Baltic* power plant with the neutralization capacity of 71 % $CaCO_3$ was used, the actual ash rate was 7.2 t/ha.

Table 1. **Mean botanical composition (%) and hay yield (h/h)**

Таблица 1. **Средний ботанический состав, %, и урожай, ц/га, сена**

Culture	Samples	
	Series C	Series I
Phleum pratense	91.6	92.7
Trifolium pratense	7.8	7.0
Different grasses	0.6	0.3
Hay	50.6	57.6

The experiment was carried out four times on the control lots and on the lots with quadruple ash rate (28.8 t/ha) in the fifth year of chalking. In spring the experimental lots were uniformly fertilized with ammonium nitrate.

The grass was cut simultaneously on all the lots. It was dried and some representative samples of the first hay (the second year of use) were taken. Let us name these samples as those of series C (from the control lots) and of series I (from the lots with chalking). In the samples, both mean botanical composition and the hay yield were determined (Table 1).

The microelement concentrations in the hay samples of meadow grass were measured with the aid of instrumental neutron activation analysis (INAA) at the Leningrad University. Analysis was carried out without any preliminary ashing of samples, the previously reported techniques were used [6, 7].

All the experimental data were treated with statistical methods. The arithmetic means for 21 microelement contents and their dispersions are listed in Table 2.

Table 2. **Content of microelements in hay samples from control (series C) and limed (series I) lots, g/t**

Таблица 2. **Содержание микроэлементов в пробах сена полевых трав с контрольных (серия C) и известкованных (серия I) участков, г/т**

Element	Series C	Series I	Change	F*
As	1.16	0.97	—0.19	0.14
Sb	0.40	0.35	—0.05	0.45
Br**	0.026	0.030	0.004	0.48
Rb	14.0	12.0	—2.0	0.86
Cs	0.22	0.17	—0.05	0.79
Ag	0.39	0.45	0.06	0.35
Au	0.015	0.028	0.013	2.03
Ba	67	55	—12	0.45
Sc	0.15	0.18	0.03	0.72
La	1.3	1.5	0.2	0.33
Sm	0.09	0.088	—0.002	0.01
Tb	0.037	0.042	0.005	0.26
Th	0.15	0.15	0.00	0.00
U	0.16	0.20	0.04	1.82
Zr	59	86	27	2.58
Hf	0.33	0.44	0.11	1.71
Ta	0.16	0.14	—0.02	0.26
Cr	4.93	4.60	—0.33	0.72
Fe	1500	1100	—400	2.25
Co	1.3	1.7	0.4	9.1
Ni	6.3	4.9	—1.4	1.89

* Actual meaning of Fisher's criterion.

** Dimension in relative unit.

To reveal statistical relations between microelements and to find out the type of hierarchical classification, the experimental data were processed using multidimensional statistical methods: main components technique (R-mode of factor analysis), paragroup technique of cluster analysis and method of dynamical groups. The set of programs "Leader" was used for the EC-1035 computer. The generalized correlation matrix for 21 elements, the diagram of graphic image of factor loading matrix, the dendrogram reflecting hierarchical classification of samples were obtained.

Discussion of results

From the geochemical point of view the elements determined in the grass samples are classified as follows: Fe, Co — biophile; Ag, Au, As, Sb — chalkophile; Ni — siderophile and Rb, Cs, Ba, Sc, La, Sm, Tb, U, Th, Zr, Hf, Ta, Cr — lithophile. The share of Ba, As, Cr, Br, Fe, Co, Ni in nutrition of plants has been established, but the functions of all the other elements are unknown [12].

In agricultural publications many of the above-mentioned elements are classified as heavy metals [13].

Since the process of chalking on the lots was carried out with the quadruple rate of ash, the quantitites of microelements induced in the soil were calculated on the basis of the data published earlier [6, 7] on the concentrations of microelements in ash (Table 3). Comparison of the introduced microelement concentrations with their mean abundances in soils [12] shows that the introduced quantities are small, forming from $n \cdot 10^{-1}$ up to $n \cdot 10^{-3}$ of their mean abundances in soils.

Table 3. **Content of microelements in series of objects**
Таблица 3. **Содержание микроэлементов в ряде объектов**

Element	Middle content, g/t		Calculated quantities of microelements, introduced into the soil with 28.8 t of ash	
	Soil [12]	Cyclonic ash [6, 7]	g/ha	g/t
As	8.7	7.43	214	0.071
Sb	0.4	0.48	14	0.005
Br	33	135	3888	1.3
Rb	80	57.5	165	0.55
Cs	3.3	2.53	73	0.024
Ag	0.33	0.15	4	0.001
Au	—	0.003	0.1	0.00003
Ba	800	205	5900	1.97
Sc	9.3	7.1	204	0.07
La	73	22.0	633	0.21
Sm	7.3	3.4	98	0.03
Tb	0.9	0.5	14	0.005
Th	9	7.4	213	0.07
U	6	5.1	14	0.05
Zr	330	104	2995	1.0
Hf	6.6	3.1	89	0.044
Ta	2.0	1.1	32	0.01
Cr	80	47	1354	0.45
Fe	$3.8 \cdot 10^4$	$3.86 \cdot 10^4$	$1.1 \cdot 10^6$	370.5
Co	9	4.9	141	0.047
Ni	33	28.5	821	0.27

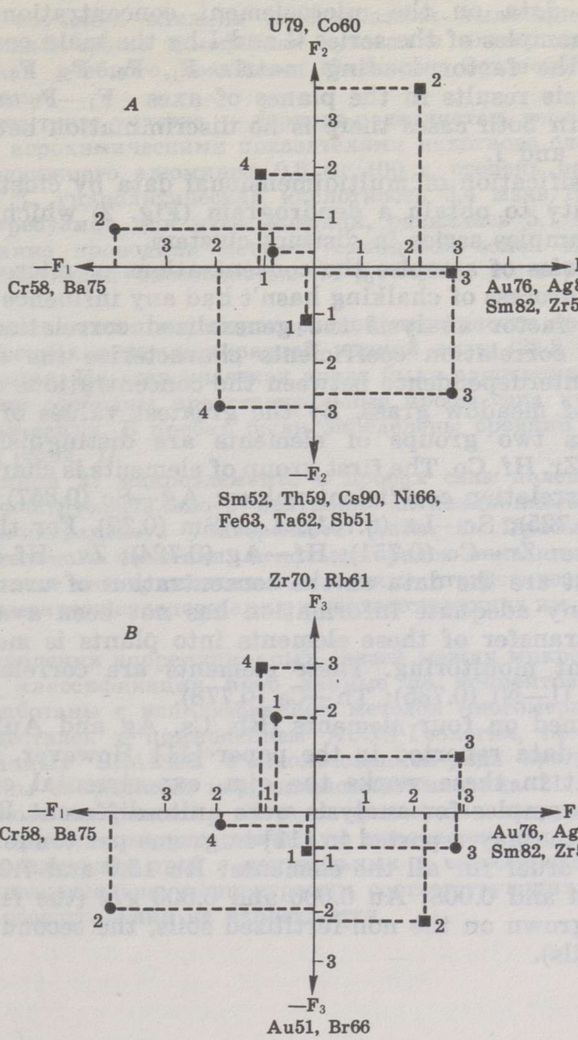

Fig. 1. Diagram of factor loading matrix F_1—F_2 (*A*) and F_1—F_3 (*B*). *1* — samples of series C, *2* — samples of series I

Рис. 1. Диаграммы факторных нагрузок F_1—F_2 (*A*) и F_1—F_3 (*B*). *1* — пробы серии C, *2* — пробы серии I

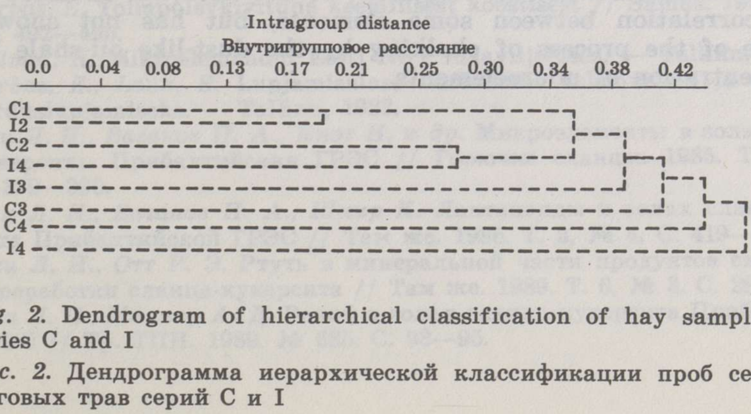

Fig. 2. Dendrogram of hierarchical classification of hay samples, series C and I

Рис. 2. Дендрограмма иерархической классификации проб сена луговых трав серий C и I

Analysis of the data on the microelement concentrations in the meadow grass hay samples of the series C and I by the main components technique yielded the factor loading matrix F_1, F_2, F_3, F_4. Graphic image of the analysis results in the planes of axes F_1—F_2 and F_1—F_3 is given in Fig. 1. In both cases there is no discrimination between the samples of series C and I.

Hierarchical classification of multidimensional data by cluster analysis gave a possibility to obtain a dendrogram (Fig. 2) which displays no unification of samples series in distinct clusters.

Hence, in both series of samples the concentrations of microelements are similar and the process of chalking hasn't had any influence on them.

On the basis of factor analysis the generalized correlation matrix was obtained. The correlation coefficients characterize the degree of mutual stochastic interdependence between the concentrations of 21 elements in the hay of meadow grass. By the greatest values of the correlation coefficients two groups of elements are distinguished: Ag, Sc, La, Sm and Ag, Zr, Hf, Co. The first group of elements is characterized by the following correlation coefficient values: Ag—Sc (0.857); Ag—La (0.899); Ag—Sm (0.725); Sc—La (0.781); La—Sm (0.72). For the second group the values are: Zr—Co (0.751); Hf—Ag (0.724); Zr—Hf (0.707).

Of special interest are the data on the concentration of uranium and thorium, because any adequate information has not been available so far. Study of the transfer of these elements into plants is meaningful for the environment monitoring. These elements are correlated with nickel and cesium: U—Ni (0.735); Th—Cs (0.778).

The results obtained on four elements (Rb, Cs, Ag and Au) may be compared with the data reported in the paper [11]. However, it should be pointed out that in these works the aim, experimental conditions and preparation of samples for analysis were quite different. Re-evaluation of the data on the hay reported in [11] in grams per tonne gave the values of the same order for all the elements: Rb 15.0 and 7.0; Cs 0.04 and 0.075; Ag 0.014 and 0.008; Au 0.006 and 0.003 g/t (the first value for meadow grass grown on the non-fertilized soils, the second for that on the fertilized soils).

Conclusions

With the use of high-sensitivity instrumental neutron activation analysis the concentrations of 21 elements in some species of meadow grass grown on the control lots and on the lots after chalking of soil have been determined. Statistical treatment of the data has revealed rather strong correlation between some elements, but has not shown any influence of the process of chalking by the dust-like oil-shale ash on the concentration of microelements.

РЕЗЮМЕ

Объектом изучения влияния известкования пылевидной сланцевой золой стали луговые травы тимофеевка луговая и клевер красный, выращенные на участках учебного хозяйства Юленурме Эстонской сельскохозяйственной академии.

Почва опытного участка — дерново-подзолистая, легкосуглинистая, со следующими агрохимическими показателями пахотного слоя: pH_{KCl} $\sim$5, содержание подвижного алюминия 0,5 мг/100 г, степень насыщенности основаниями 65 %, гидролитическая кислотность 3,4 мэкв/100 г. Полная норма извести, требуемая для известкования, равнялась 5,1 т/га $CaCO_3$. Так как известкование проводили летучей сланцевой золой Прибалтийской ГРЭС с нейтрализующей способностью 71 % $CaCO_3$, то норма золы составляла 7,2 т/га.

Опыт был заложен в четырехкратной повторности на контрольных участках и участках с четырехкратной нормой золы (28,8 т/га) на пятом году известкования. На всех участках трава была одновременно скошена и высушена, были отобраны представительные пробы сена первого укоса второго года пользования. В пробах были определены средний ботанический состав и урожай (табл. 1).

Содержания 21 микроэлемента в пробах сена полевых трав определены методом инструментального нейтронно-активационного анализа в лаборатории Ленинградского университета (табл. 2). Пробы анализировали без предварительного озоления, используя ранее описанные методики [6, 7].

Полученные экспериментальные данные статистически обработаны, средние арифметические содержания и соответствующие им дисперсии приведены в табл. 2.

Для выявления корреляционных связей между микроэлементами и иерархической классификации проб данные по концентрации микроэлементов были обработаны с использованием методов многомерной статистики. Анализ осуществлен с применением АСОИ-Геология, по системе управления базами данных “LEADER” с использованием ряда программ на ЭВМ ЕС-1035.

Получены обобщенная корреляционная матрица 21 элемента, диаграмма графического отображения матрицы факторных нагрузок (рис. 1) и дендрограмма, отражающая иерархическую классификацию проб (рис. 2). Во всех случаях разделение проб с контрольных и известкованных участков отсутствует. Следовательно, концентрации соответствующих элементов близки и влияния известкования не наблюдается.

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