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EVALUATION OF THE EFFECT OF AGRICULTURAL MELIORATION WITH THE USE OF PHOSPHOGYPSUM ON TRACE ELEMENT CONTENT IN SOILS AND VEGETATION

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INTRODUCTION

One of the main industrial wastes of the phosphorus fertilizers production is phosphogypsum ($CaSO_4 * 2H_2O+0,6\div1,0\% \ P_2O_5$). As a result of the oleum sulphate extraction process, most common in the production of phosphorus fertilizers, approximately 5 tons of phosphogypsum are precipitated per 1 ton of the ready product (P_2O_5) [1]. That gives a number of the order of 170 million tons per year if recalculated over the world's production. That is why, perhaps, the problem of phosphogypsum disposal now is already serious enough and, taking into account the ever increasing amounts of fertilizers, will become even more serious in the future. The phosphogypsum implement in agriculture as a meliorant is one of the best potential ways of its disposal. Nowadays a great variety of phosphogypsum used in acid (in conjunction with limestone materials and organic fertilizer) and alkaline (saline) soils has been developed.According to some references, the phosphogypsum implement in acid soil allows one to increase crop capacity of soya-bean, maize for silo and lucerne by 1.5-2 times [2]. Phosphogypsum implement in saline soils has the analogous effect, and the sudan grass (*corghum sudanens stapf*) capacity increases, for example, 1.5-1.9 times. However, the analysis of papers [1,2,3 and others] published in this field, shows that chemical purity of phosphogypsum had not been taken into consideration when its agrotechnical features were investigated. Practically all methods of phosphogypsum disposal are being developed without taking into account its pollution level by element-impurities of phosphate raw materials.

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ИНСТИТУТ

undertaken by the authors, showed the considerable similarity of their content (Table 1). In all cases the phosphogypsum is a concentrator of fluorine, strontium and rare-earth elements. Moreover, their concentrations exceed Clark values by 20-100 times. Taking into consideration that in the phosphogypsum macrocontent there are elements such as sulphur and calcium, the necessity of environmental consequence studies of an agrotechnical processing of such a kind becomes quite clear. The present paper is the continuation of investigations published by the authors in [4,5].

EXPERIMENTAL METHOD

The experiment with acidic (pH = 4-6) soils has been carried out in the experimental lots with soddy podzolic meadow and soddy podzolic washed (flood-plain) soils.

Soil samples were collected over the squares of the upper horizon 0 - 20 cm. From 5 to 20 samples were collected from each square. Potatoes and cabbage respectively were used as crop- indicators of trace element-pollutants. It was a one year experiment with a single introduction of different phosphogypsum doses in the upper layer of soil (0 - 20 cm) on their own, as well as in mixture with organic fertilizer. Doses introduced were of 3 and 60 ton/ha in soddy podzolic meadow soil, in the final case phosphogypsum was introduced with organic fertilizers with the total mass of mixture of 600 ton/ha. Phosphogypsum introduction doses in flood-plain soils were 10 ton/ha. Phosphogypsum implement in alkaline (pH = 7.7-8.5) soils has been done in conjunction with different methods of mechanical processing of saline and light chestnut soils.

The principal characteristic of soil processing by subsurface cultivator is the ripping of the soil from the

TABLE 1

Chemical element content in phosphogypsum, ppm (n=20)

Elem. / Samp.	F%	Na	P%	S%	Ca%	Sc	Cr	Mn	Co	Zn	As	Sr%	Y	Zr
Phosphogypsum	0.14 *)	800	0.7	15.9	18.8	1.3	28.5	30	<1	<10	<0.1	1.4	190	380
	0.07-0.26	430-2000	0.5-0.9	14.8-16.7	16.7-19.4	1.1-1.5	22-34	17-42				1.1-1.8	87-250	150-430

Elem. / Samp.	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Hf	Ta	Th	U	Pb
Phosphogypsum	540	1050	1600	360	76	30.4	5.1	3.9	0.3	<0.5	<0.5	6.0	9.8	<10
	200-915	780-1160	950-2160	240-420	52-91	19-50	3.6-7.1	2.9-5.5	0.1-0.4			2.7-11.1	7.0-12.6	

*) a - mean content.

a_1-a_2 - low and upper limits of contents.

ground, whereas three level cultivation is much more complicated : the upper humus soil horizon is turned over, and the saline and carbonate (under saline) horizons change places. That to some extent is a chemical melioration in itself. The latter method of processing especially gives the most sufficient addition to the harvest and is the most perspective in the melioration of salines. The experiment lasted for two years with a single phosphogypsum dose introduction of 10 ton/ha in the upper soil horizon in the beginning of the season. During the first year the vegetation had not been sown; during the second year the harvest of sudan grass and crops was analyzed by means of the neutron activation analysis (IBR-2, JINR, Dubna), the X-ray fluorescence analysis (GIN, Moscow) and in certain cases some methods of "wet" chemistry were used.

The process of accumulation or carrying out trace elements in soil and vegetation was evaluated by the magnitude of the concentration coefficient $K_c = C_i/C_{back}$, where C_i is an i-th sample content, C_{back} is a background sample content. C_i and C_{back} contents were calculated as averaged values over homogeneous squares with the number of samples being 12-20.

RESULTS AND DISCUSSION

Results of the analysis of background soils and vegetation samples are given in Tables 2 and 3. For soils this data demonstrates well the difference in trace element content not only in soils different in genesis (soddy podzolic and saline), but also in soils similar in genesis but with a different water regime. The difference between soddy podzolic meadow and flood-plain soils is observed in the content of practically all trace elements (excluding Ca, Zn, As and Pb), moreover, these differences reach 1.5-2 times.

TABLE 2

Chemical element content in soils (background), ppm

Element / Sample	F%	Na%	P%	S%	K%	Ca%	Sc	Cr	Fe%	Co	Zn	As	Se	Br	Rb	Sr
Soddy Podzolic (n=80)	0.02 0.01- -0.03	*) 0.65 0.54- 0.81	0.033 0.02- 0.04	0.03 0.02- 0.04	1.69 1.15- 2.14	0.71 0.44- 1.1	9.6 7.8- 11.9	62 51- 79	1.9 1.5- 2.4	11 6.7- 13	75 57- 92	7.5 4- 12	<5	8.1 5.4- 12.5	70 46- 110	146 121- 225
Soddy podzolic washed (n=20)		0.37 0.28- 0.44			1.12 0.8- 1.46	0.94 0.75- 1.15	4.7 2.9- 7.8	27 15- 40	1.7 0.8- 2.0	4.7 2.3- 7.8	72 54- 116	7.5 4- 12	<5	5.1 3.8- 7.3	42 24- 55	102 79- 126
Saline (n=12)	0.03 0.02- 0.04	1.19 1.0- 1.89	0.037 0.03- 0.04	0.03 0.025- 0.035	1.2 0.7- 1.5	1.52 1.1- 2.4	17.2 16.5- 22.6	147 132- 150	2.87 2.73- 3.2	20.7 19.5- 21.9	70.7 57- 82	7.7 5.5- 8.5	8.5 6.5- 10.9	8.8 6.9 10.6	77 70- 87	148 135- 164
Light chestnut (n=12)	0.03 0.02- 0.04	0.97 0.84- 1.1	0.03 0.02 0.04	0.09 0.03- 0.13	1.19 0.7- 1.4	1.98 1.56- 2.32	17.4 13.3- 20.4	147 120- 170	2.81 2.78- 3.2	31.5 8.1- 23.6	69.5 50- 90	7.3 5.3- 9.2	7.1 5.9- 8.3	7.4 5.0- 9.8	8.7 81- 100	153 146- 163

Element / Sample	Y	Zr	Ag	Sb	Cs	Ba	La	Ce	Sm	Eu	Yb	Lu	Hf	Ta	Pb	Th
Soddy podzolic (n=80)	30 26- 35	490 460- 550	<0.1	3.5 1.5- 7.7	2.7 1.5- 4.0	530 360- 80	34.9 23- 48	64.8 48- 81	6.0 4- 6.8	1.6 1- 2.1	3.7 1.8- 4.3	0.5 0.4- 0.8	17 14- 19	2.5 1.4- 4.7	20 12- 32	10.8 8- 13.6
Soddy podzolic washed (n=20)	24 15- 29	225 187- 280	<0.1	2.9 1- 3.6	1.7 0.6- 2.6	420 210- 665	17.5 10-21	37 18- 42	3.3 2- 4.1	1.1 0.6- 1.3	1.8 0.7- 2.8	0.3 0.1- 0.4	4.6 2-6	1.6 0.9- 1.9	25 15- 42	4.7 2- 5.8
Saline (n=12)	26 21- 29	329 311- 344	0.41 0.38- 0.43	3.8 2.9- 4.9	5.6 4.4- 7.1	617 420- 730	37.6 28- 48	83 62- 107	7.9 6.5- 10.2	3.0 2.5- 3.9	2.4 2- 3.9	0.28 0.2- 0.3	9.8 8.6- 10.9	<1	19.2 16- 22	13.6 12.8- 14.6
Light chestnut (n=12)	26 24- 30	348 330- 370	0.29 0.13- 0.39	2.6 2.1- 3.6	6.5 4.6- 9.1	635 530- 760	29.6 21- 31.9	65 53- 70	6.1 5.1- 6.7	2.3 1.9- 2.5	1.9 1.6- 2.1	0.28 0.2- 0.3	8.8 7.5- 10	<1	20.8 16- 29	12.6 11- 13.9

*) a - mean content.
a_1 - upper limit.
a_2 - low limit.

A rather weak tendency of accumulation of Ba, Br, Ca and certain REE is revealed. In potatoes the accumulation of Br and Sr is shown clearly enough.

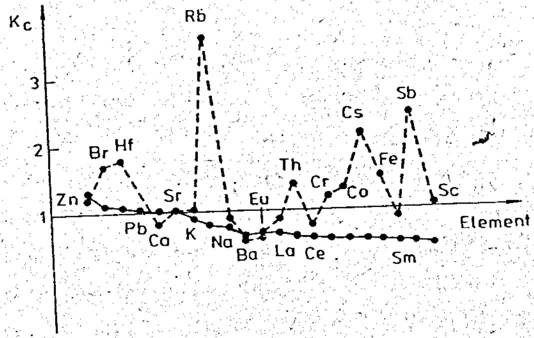

Fig.2. Distribution of chemical elements in soddy podzolic soil (washed) and in cabbage with phosphogypsum introduction dose 10 ton/ha.
______ soil
– – – cabbage.

Fig.2 shows that in soddy podzolic flood-plain soil with phosphogypsum introduction dose of 10 ton/ha, the washing out of trace elements takes place to a greater extent than their accumulation. Five trace elements only (Zn, Ba, Hf, Pb and Ca) have K_c greater than 1. The curve for cabbage in contrast demonstrates a fairly intensive concentration of Rb, Cs, Sb and to a lesser extent Br, Hf, Th, Fe. It is necessary to note, that practically for all elements, K_c for cabbage (except Ca and Ba) is either greater, or equal to K_c for soil.

At this first stage of the experiment between trace elements concentration in soils and vegetation some differences can be seen: in soils practically no accumulation of trace elements takes place (except Sr at dose of 60 ton/ha), in vegetation this accumulation is revealed relatively clearly. However, if Sr, which is introduced with phosphogypsum, and Br, which has nothing to do with phosphogypsum, are concentrated in potatoes, in cabbage no chemical element introduced by phosphogypsum is

concentrated to any noticeable degree. Curves K_c built up over results of the second year experiment on the phosphogypsum introduction in alkaline soils, present a slightly different situation of the chemical elements distribution in soil and vegetation (Fig.3 and 4).

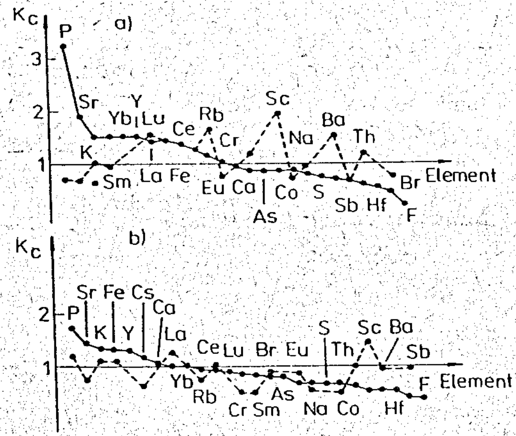

Fig.3. Distribution of chemical elements in light chestnut soil and sudan grass at phosphogypsum introduction dose 10 ton/ha.
a) light chestnut soil (ground ripping)
b) light chestnut soil (3- level cultivation)
______ light chestnut soil
– – – sudan grass.

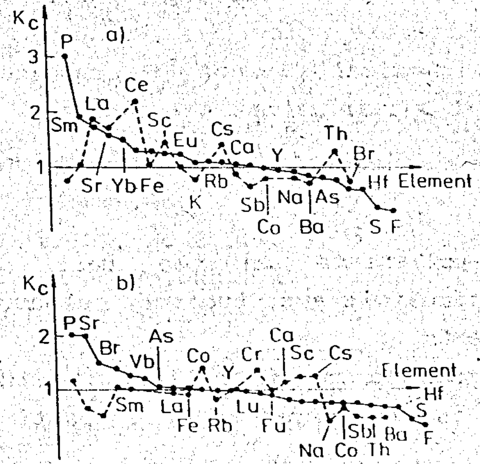

Fig.4. Distribution of chemical elements in saline and sudan grass at phosphogypsum introduction of 10 ton/ha.
a) saline (ground ripping)
b) saline (3-level cultivation)
______ saline soil
– – – sudan grass.

Firstly, clear priorities in accumulation or washing out chemical elements in soil attract one's attention. In saline as well as in light chestnut soil, which is the variety by essence of a saline one, at both types of soil processing the accumulation of phosphogypsum and to a lesser extent of Sr is observed; such elements as F, S, Hf, Br and some others are carried out.

Particular emphasis has to be placed on the sodium's tendency to be washed out from the soil which confirms the fact of lamination of salines with the introduction of phosphogypsum.

And secondly, a tendency of accumulation is revealed in the behaviour of chemical elements belonging to rare-earths as well. This tendency is more clearly shown when the soil is processed by means of ground ripping.

In conclusion it is possible to say that three level saline soils cultivation reduces to a great extent the phosphorus concentration as well as undesirable elements-impurity in salines.

As for sudan grass curves, one should say that it is difficult to discern any noticeable priorities in chemical elements accumulation. Three chemical elements - scandium, lanthanum and cerium - have $K_c > 1$ in almost all curves .

CONCLUSIONS

1. The main element-pollutants in the case of phosphogypsum implement in agriculture are fluorine, sulphur, strontium and rare-earth elements.

2. The accumulation of phosphorus in saline with the introduction of phosphogypsum is considered to be a positive factor.

3. Practically in all cases mentioned above there is a tendency of Sr and rare-earth elements to accumulate in soils.

4. The use of three level cultivation leads to a significant decrease of element-pollutants concentration in saline soils and vegetation.

5. The concentration of one or another complex of chemical elements in vegetation is determined, among other things, by the pH value of soil acidity.

6. Since our investigations have shown the real possibility of the rare-earth elements concentration in soils and vegetation, it is apparently necessary to undertake complex biogeochemical studies to reveal the extent of danger of these chemical elements for the environment.

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