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RECULTIVATION SUBSTANCE AND COMPOSTS PRODUCED FROM SEMI-COKE: THE EFFECT ON SOIL CHARACTERISTICS, THE YIELD OF FIELD CROPS AND THE ENVIRONMENT

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In the nearest years the pollution charge for semi-coke will increase almost 1.7 times, which makes the production of shale oil economically unprofitable. This urges enterprises of shale oil industry to seek intensively for possibilities for turning semi-coke less hazardous for the environment. The joint-stock company Kiviõli Chemical Industries has started to use semi-coke and sphagnum peat (volume rates 1 : 1) for producing recultivation substance. It could be applied for covering waste dumps and oil shale ash dumps, as a growth substrate in recultivation of old gravel pits and abandoned oil shale surface mines, as well as for improving soil characteristics and for increasing the yield of plants in agriculture. The current paper provides an overview of the effect of recultivation substance and the composts produced from it on the soil, the yield of field crops and the environment. It is compiled on the basis of the results of the experiments carried out at the Estonian Agricultural University in 2002.

Problems Related to Semi-Coke

One of the major problems in the production of shale oil in Estonia is related to the waste product semi-coke which presents hazard to the environment due to its high phenol and PAH (polycyclic aromatic hydrocarbons) content. At Kiviõli as much as 22 million tons of semi-coke have already been deposited, while 180–200 thousand tons are added to this amount each year [1]. The issue is actual for shale oil industry, as pursuant to the Pollution Charge Act the pollution charge for semi-coke will increase almost 1.7 times in the nearest future [2], which turns shale oil production into an unprofitable

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area of industry. This stimulates enterprises of shale oil industry to look for possibilities to turn semi-coke less harmful for the environment, on the one hand, and to find its practical applications, on the other.

A possible area of application is seen in agriculture. Owing to its high alkalinity, semi-coke would also be suitable for neutralizing soil acidity. In Estonia, patents EE03449BI [3] and EE03251BI have been acquired for processing semi-coke to produce fertilizing substances. Allegedly, application of these fertilizing substances increases the yield of field crops as well as improves the characteristics of the soil and increases its humus content. However, no reliable investigations have been conducted to date to verify these statements. As is known, the content of nutrient elements essential for plants is very low in semi-coke. Hence it is evident that the increased yield of plants cannot be associated with semi-coke itself but with the manure mixed with it, in the process of whose mineralization nutrients are released and used by plants.

The effect of the patent fertilizing substance *Viru Ramm* produced from semi-coke on soil humus content is also questionable. According to the data published in [4–6], the use of *Viru Ramm* has increased soil humus content more than the amount of organic matter present would allow. It is known too that not all carbon in organic matter is transformed into soil humus. Of the organic matter introduced into the soil (determined from carbon), a maximum of 25% is humified, while the rest is mineralized.

To obtain an objective picture about the possibilities of using semi-coke both as a component of recultivation substance and in agriculture, experimental research was undertaken at the Estonian Agriculture University (EAU) in 2001 with the aim to investigate: i) the effect of recultivation substance produced by the Kiviõli Chemical Industries on the yield of field crops and soil characteristics, as well as ii) its suitability as a growth substrate. Also, the hazard presented by recultivation substance to the environment and its effect on the quality of the yield of field crops were studied. This recultivation substance is obtained on neutralizing warm, highly alkaline semi-coke produced immediately after oil shale processing with acidic sphagnum peat at the volume ratio 1 : 1. Under the effect of the residual heat of semi-coke, its fragments disintegrate fast and the mixture of substances is homogenized. Recultivation substance differs from the patent *Viru Ramm* in the absence of manure and activating agents from its composition.

Experimental Methods

Long-Term Field Experiment with Field Crops

The field experiment consisted of a three-field (potato, spring wheat and barley) cropping system. Each crop rotation field was divided into three organic fertilizer variants:

1) No organic fertilizer.
2) Cattle manure: in the first year 40 t ha^{-1} of composted cattle manure was given to potato; in the second year the crop cultivated in the same field was spring wheat (first-year after-effect of manure); in the third year – barley (second-year after-effect of manure). Average N content in the cattle manure used in the experiment was 0.34%, P content 0.10% and K content 0.42%. Dry matter (DM) content of manure was 23.0%.
3) Recultivation substance with a composting time of almost one year (60 t ha^{-1} for potato, 40 t ha^{-1} for spring wheat and 20 t ha^{-1} for barley).

In addition, each crop rotation field was transversely divided into five mineral fertilizer treatments corresponding to the fertilizer rates used (N-0, N-40, N-80, N-120, N-160). The mineral fertilizer used for potato was the combined fertilizer Pro Magna^R 11 : 11 : 21 SG which contained, besides N, P and K, also Mg, S and microelements; the mineral fertilizer applied to cereals was Opti Crop^R NPK 21 : 8 : 12 + Mg + B. Plot size was 50 m^2 (5 × 10 m) from which the area of record subplot was 36 m^2. The plots were separated with a protection zone of 1 m. The whole experiment was performed in three replications.

The soil and recultivation substance samples were analyzed by the following methods: pH_{KCl} – ISO 10390; available P and K – Ca-lactate-extractable method; Ca, Mg and Cu–the Mehlich-3 method; humus content – the Tyurin method. The content of hazardous heavy metals Pb, and Cd both in the plant material and in the soil was determined using the method of ASS graphite furnace, and Hg was determined by the cold vapor method.

The statistical data processing of the experimental results was performed using regression and dispersion analysis.

The vegetation period of 2002 was extremely dry and warm. The amount of precipitation from May through September was, according to the data of the Eerika meteorological station, only 183 mm, while average air temperature was higher than normal. Owing to this, the yields of the crops used in the field experiment were significantly below average.

The Growth-Chamber Experiment with Grasses

The aim of the experiment was to compare the development and growth rate of grasses on fresh (1-week-old) recultivation substance based on semi-coke (treatment 1), on weathered (6-month exposure) recultivation substance (treatment 2), on a mixture of fresh recultivation substance with clay loam and sandy loam (ratio 1 : 1) (treatments 3 and 4, respectively), on pure sandy loam (treatment 5) and on clay loam (treatment 6). For this purpose, 1-dm^3 pots were filled with the above substrates and seeded with red clover or timothy (100 seeds of either plant). The pots were placed in a growth chamber with an average diurnal temperature of 20 °C. The experiment was performed in four replications and in three stages.

The Growth-Chamber Experiment with Radish

The aim of the experiment was to establish the effect of recultivation substance on the phytomass yield of radish. For this, pots were filled with the field soil, composted recultivation substance and pig manure at ten different ratios (Table 1). Phytomass was determined 35 days after the seeding of radish, for which the plants cleaned from the soil were weighed together with the leaves and the roots.

Table 1. **Pot Experiment with Radish**

Treatment number	Volume ratio, %, of field soil, recultivation substance and pig manure in growth substrate	Yield, g/pot
1	87.5 : 10 : 2.5	148.6
2	87.5 : 8.3 : 4.2	146.6
3	87.5 : 6.25 : 6.25	175
4	87.5 : 4.2 : 8.3	160.6
5	87.5 : 2.5 : 10	190
6	75.0 : 20 : 5	137.6
7	75.0 : 16.7 : 8.3	155.6
8	75.0 : 12.5 : 12.5	176.6
9	75.0 : 8.3 : 16.7	222.3
10	75.0 : 5 : 20	221.6

Results and Discussion

The Effect of Recultivation Substance on Soil Characteristics

As for mobile plant nutrients, recultivation substance contained 17.6–58.2 g Ca and 0.9–5.0 g Mg kg^{-1} DM, and only 13 mg P and almost 1,400 mg K kg^{-1} DM. As for microelements, the samples contained *ca* 30 mg B and 10 mg Mn kg^{-1} DM. Proceeding from the chemical composition of recultivation substance, there was a positive correlation between the amount of recultivation substance introduced into the soil (20, 40 and 60 t ha^{-1}) and the increase in the soil mobile Ca and Mg content which increased with increasing amounts of recultivation substance. The application of the amount of 20–60 t ha^{-1} of recultivation substance increased the content of Ca in the soil 100–950 mg kg^{-1} and the content of mobile Mg 8–54 mg kg^{-1}. As recultivation substance is poor in other plant nutrients, their content in the soil did not change significantly irrespective of the introduced amount.

The only exception was K whose content increased somewhat (*ca* 15 mg kg^{-1}) with the use of larger amounts of recultivation substance (40–60 t ha^{-1}). However, owing to its alkaline reaction, recultivation substance had an impact on soil reaction. This phenomenon was more pronounced with the application of larger amounts (40–60 t ha^{-1}) when soil pH_{KCl} increased by 0.6 units. In the case of a smaller amount (20 t ha^{-1}), soil

pH_{KCl} increased only by 0.2 units. These experimental results allow characterizing recultivation substance as a liming material suitable for neutralization of acid soils as well as for increasing soil Ca and Mg content.

The humus content of the soil of the experimental field measured in 1999 was compared with 0.2% the humus content of the soil samples taken in 2002. As an average of 15 measurements made in three replications, the use of the recultivation substance 60 t ha^{-1} increased soil humus content 0.2%, on its carbon content basis. Smaller amounts had no effect on soil humus content. Humus is a complex of organic substances with an intricate composition closely related to the soil mineral part. Humus contains on average 58% carbon and 3–8% nitrogen. As the formation of humus involves the protein of microbial origin, the nitrogen content of humus is higher than that of the initial organic remains forming it [7]. Soil humus content is determined basing on the organic carbon content of the soil, assuming that humus contains on average 58% carbon.

The quality of humus is characterized by its ratio of carbon to nitrogen. Changes in soil humus content are revealed during a longer period, because an organic substance introduced into the soil is not yet humus *per se.* Such a substance is subjected to complicated biochemical and microbiological processes in the course of which a large part of it is mineralized. As a consequence, nutrients for plants as well as energy are released. An erroneous picture of soil humus content is obtained when a large amount of organic fertilizer (or recultivation substance) is applied in autumn and soil samples from this area are taken in the following spring – in this case humification has even not started. Increase in soil humus content is not a goal in itself: organic fertilizer is given for increasing the soil nutrient pool and for improvement of the soil agrophysical and agrochemical characteristics.

Of the amount of DM present in an organic substance introduced into the soil only 8% is humified in the case of potato and 15% in the case of cereals [8]. Of the DM of the manure introduced into the soil 15–25% goes for replenishment of the soil humus pool [9]. Soil humus content is continuously changing depending on weather conditions, the plant cover on the soil, the amount and composition of dead organic matter in the soil but also on the microbiological activity of the soil. Simultaneously with formation of humus, a part of it in the soil is mineralized. This amount is larger for intertilled crops, amounting to 2.7% of the soil humus pool per year for potato; for spring cereals the respective percentage is up to 1.9 [10]. An equilibrated soil humus balance is guaranteed, e.g. by the use of cattle manure with straw in the average amount of 15 t ha^{-1} per year in a red clover and timothy-rich cropping system [11].

According to theoretical calculations, about 11 tons of organic matter are added to the soil with the use of recultivation substance 60 t ha^{-1}, of which approximately 15% can be humified. Thus the amount of formed humus can be 1.65 t ha^{-1}, which means that the humus content of a 20 cm humus layer (Dm = 1.5) would increase only by 0.055%.

The Effect of Recultivation Substance on the Yield of Field Crops

According to the results of the first year of the experiment, the effect of recultivation substance on the yield of field crops appeared to be relatively low and statistically insignificant. In 2002, the tuber yield of the potato variety *Anti* without the use of organic and mineral fertilizers was 16.7 t ha^{-1} (Table 2). With the application of manure, the yield of potato increased up to 24.2 t ha^{-1}, while the yield increase on account of manure was 7.45 t ha^{-1}. Compared with the unfertilized treatment, the use of recultivation substance (60 t ha^{-1}) resulted in a yield increase of only 1.9 t ha^{-1}. The average potato yields for the treatments in which different organic fertilizers (organic fertilizer + $N_{0–160}$) were applied showed that recultivation substance increased the potato yield by 1.6 t ha^{-1} compared with the treatments without organic fertilizer. At the same time, the average potato yield for the treatments with recultivation substance was 3.8 t lower compared with the yield obtained as a result of the influence of manure.

The yield of spring wheat in 2002 on unfertilized soil was only 0.76 t ha^{-1} (Table 3). The yield of spring wheat increased 0.58 t ha^{-1} under the after-effect of manure of the first year in the treatment without mineral fertilizer, amounting to 1.34 t ha^{-1}. The yield increase of spring wheat with the application of recultivation substance (40 t ha^{-1}) was larger (0.84 t ha^{-1}) compared with the yield increase under the after-effect of manure, while the grain yield was up to 1.60 t ha^{-1}. Although the differences between the yield of spring wheat obtained under the after-effect of manure and the yield obtained with the use of recultivation substance remain within experimental error, it is still evident that both resulted in some increase in the yield of spring wheat irrespective of the rate of mineral fertilizer (N kg ha^{-1}).

Table 2. **Influence of Recultivation Substance and Manure on the Tuber Yield of Potato against Different N Backgrounds of Mineral Fertilizer, t ha^{-1}**

N background of mineral complex fertilizer, kg ha^{-1}	Yield without any organic fertilizer	Recultivation substance 60 t ha^{-1}		Manure 40 t ha^{-1}	
		Yield	Yield increase due to recultivation substance	Yield	Yield increase due to manure
0	16.71	18.59	1.88	24.16	7.45
40	22.20	23.77	1.57	27.81	5.61
80	25.63	27.06	1.43	30.23	4.60
120	27.02	28.47	1.45	31.43	4.41
160	26.35	27.99	1.64	31.41	5.06
Average	23.58	25.18	1.59	29.01	5.43
	LSD_{05}		3.85		

Table 3. **Influence of Recultivation Substance and the After-Effect of Manure on the Grain Yield of Spring Wheat against Different N Backgrounds of Mineral Fertilizer, t ha^{-1}**

N background of mineral complex fertilizer, kg ha^{-1}	Yield without any organic fertilizer	Recultivation substance 40 t ha^{-1}		First-year after-effect of manure	
		Yield	Yield increase due to recultivation substance	Yield	Yield increase due to first-year after-effect of manure
0	0.76	1.60	0.84	1.34	0.58
40	1.84	2.12	0.28	2.32	0.48
80	2.48	2.70	0.22	2.88	0.40
120	2.69	2.93	0.24	3.01	0.32
160	2.48	2.94	0.46	2.71	0.23
Average	2.05	2.46	0.41	2.45	0.40
	LSD_{05}		0.73		

The yield of barley in the treatment without fertilization was only 1.30 t ha^{-1} in 2002 (Table 4). Under the effect of mineral fertilizers, the yield of barley at a nitrogen rate of 160 kg ha^{-1} was 3.33 t ha^{-1}. Although the use of recultivation substance (20 t ha^{-1}) against the background of no fertilizer reduced the yield of barley 0.27 t ha^{-1}, with the application of mineral fertilizer it was equal to the yield obtained as a result of the after-effect of manure. Thus, it can be concluded that recultivation substance had no effect on the yield of barley.

Table 4. **Influence of Recultivation Substance and the After-Effect of Manure on the Grain Yield of Barley against Different N Backgrounds of Mineral Fertilizer, t ha^{-1}**

N background of mineral complex fertilizer, kg ha^{-1}	Yield without any organic fertilizer	Recultivation substance 20 t ha^{-1}		Second-year after-effect of manure	
		Yield	Yield increase due to recultivation substance	Yield	Yield increase due to second-year after-effect of manure
0	1.30	1.03	–0.27	1.33	0.03
40	1.87	1.91	0.04	2.01	0.14
80	2.39	2.57	0.18	2.52	0.13
120	2.88	3.00	0.12	2.87	–0.01
160	3.33	3.20	–0.13	3.06	–0.27
Average	2.35	2.34	–0.01	2.36	0.01
	LSD_{05}		0.73		

The first results of the experiment allow to state that recultivation substance has no harmful effect on field crops, nor does it reduce their yield. At the same time, as it is a nutrient-poor organic substance, its application did not result in a significant increase in the yield of field crops, either. It is likely that the use of recultivation substance may increase the yield of field crops on light-texture acid soils where it would improve primarily the reaction of the soil but also its physical characteristic and hence the nutrition conditions for plants.

On the Suitability of Recultivation Substance as a Growth Substrate for Plants

The suitability of recultivation substance as a growth substrate for plants depended on its age, or the composting period, and nutrient content. The performed pot experiments showed that fresh recultivation substance is not a suitable growth substrate immediately after its preparation. Although seeds start to germinate in it, they do not develop into viable plants (Table 5). The phytotoxicity of freshly made recultivation substance was even revealed in a mixture with the field soil (volume ratio 1 : 1).

The number of normally developed plants that had emerged from seeds sown in it was at first considerably smaller compared with the seedings on a pure field soil. Repeated seedings on the same growth substrates demonstrated that the toxicity of recultivation substance decreases continuously and disappears with time. The first viable grass plants emerged from seedings on pure recultivation substance after two months had passed from the first seeding. The number of viable grass plants emerged from seedings on weathered recultivation substance after an exposure of six months was already close to the number of plants emerged from the seedings on a pure field soil.

Table 5. **The Effect of the Age of Recultivation Substance on Emergence of Grass Plants, %**

Treatment	Growth substrate and sowing time	Emergence of grass plants	
		Red clover	Timut
1	Fresh recultivation substance		
	First seeding 4 Feb. (7 days old substance)	0	0
	Second seeding 28 Feb. (31 days old substance)	0	0
	Third seeding 27 March (58 days old substance)	27	20
2	Recultivation substance weathered for 6 months		
	Seeding 27 March	71	56
3	Clay loam + fresh recultivation substance (1 : 1)		
	First seeding 4 Feb. (7-days-old substance)	7.6	7.3
	Second seeding 28 Feb. (31-days-old substance)	4.0	25
4	Sandy loam + fresh recultivation substance (1 : 1)		
	First seeding 4 Feb. (7-days-old substance)	9.9	8.8
	Second seeding 28 Feb. (31-days-old substance)	33.7	33.8
5	Sandy loam		
	Seeding 4 February	58.9	83.8
6	Clay loam		
	Seeding 4 February	52.9	79.4

The toxicity of fresh recultivation substance for plants is partly due to its alkaline (pH_{KCl} 9.8) reaction. For reducing and stabilizing alkalinity, recultivation substance should be let mature in humid conditions for some time after preparation to allow neutralization reaction to take place. In the present experiment where the seeding were watered daily the reaction became suitable for the growth of plants already in two weeks, while pH decreased by 2.3 units. In drier conditions, reduction in the reaction of recultivation substance can also occur during a longer period. In the case of fresh recultivation substance, its high pH is evidently not the only reason for the poor growth of plants. Even after pH had become suitable for the growth of plants, the number of plants emerged from the seedings on a mixture of recultivation substance and the soil was significantly smaller than the used seed germination.

At the same time, no viable plants emerged from the seeding on the fresh recultivation substance. It is possible that besides pH, plant growth was strongly inhibited by the presence of volatile and water-soluble low-molecular hydrocarbons (< 3 ring) present in semi-coke, whose phytotoxicity has been referred to earlier by Henner *et al.* [12]. Like in their experiment, the disappearance of the foul smell, characteristic of the substances released from recultivation substance, was associated with the emergence of viable plants in our experiment as well. All plants emerging on the recultivation substance weathered for half a year and lacked its typical foul smell appeared normal and their growth proceeded without disorders. According to Henner *et al.* [12], the foul smell is one of the major characteristics in judging the phytotoxicity of a growth substrate.

When fresh recultivation substance is used as the growth substrate, the most serious problem is its low content of plant nutrients. Due to the absence of humus and organic matter of plant origin, characteristic of the soil, nutrients are not released as a consequence of mineralization, either.

All nutrients necessary for normal plant growth should be mixed in it, or else plants should be continuously fertilized during growth. This was clearly demonstrated in the experiments with radish and grass plants. The total weight of the radish plants increased with the increasing proportion of pig manure 2.5–20% in the growth substrate (see Table 1).

The proportion of the recultivation substance in the growth substrate did not affect the total weight of the radish plants significantly. In the experiment with grass plants, plant growth stopped when the nutrient resources in the seed were exhausted, and it continued only after the application of combined fertilizer. The time point at which the nutrients, introduced in the soil with fertilizer were exhausted was clearly seen from the retarding of plant growth also after fertilization. The experiments showed that it is impossible to grow plants on recultivation substance without adding nutrients. According to the experimental results, recultivation substance can be successfully enriched with nutrients using some nutrient-rich organic residue such as sewage sediment, manure, etc. In the experiments with grass plants, the growth substrates used were, besides pure recultivation substance, also a mixture of recultivation substance and composted sewage sediment (ratio 1 : 1).

Unlike the plants that grew on pure recultivation substance, those growing on composted recultivation substance and sewage sediment did not require extra fertilization, as their total nutrient demand was covered from the nutrients released on the mineralization of composted sewage sediment. Owing to this, plant growth was continuous, without disorders resulting from nutrient deficiency, which were noted in plants growing on pure recultivation substance.

The experiments performed to date demonstrate that weathered recultivation substance enriched with plant nutrients serves as a suitable material for growth substrate for plants. Production of growth substrate from recultivation substance not only adds the value to semi-coke but also contributes to the disposing of organic residues which have so far presented a problem due to their high content of organic matter and foul smell. Owing to their different physical and chemical characteristics, recultivation substance and organic residues supplement each other, eliminating mutually their shortcomings.

The Effect of Recultivation Substance on the Environment

To find out the hazard of the recultivation substance weathered for six months to the environment, the EAU ordered an analysis from the Dutch laboratory *Analytico Milieu B.V.* for measuring the content of about 200 environmental pollutants in recultivation substance. The TerrAttest version 2.2 method was used. The analysis revealed that, compared with fresh semi-coke, the content of all pollutants in recultivation substance was essentially lower. The content of none of them exceeded the limiting value [13] established for the industrial zone in Estonia. The allowed limiting value in the living zone was exceeded in the case of *m*-cresol, and the corresponding guidance value was exceeded in the case of phenol and 4-ethyl-2,3- and 4-ethyl-3,5-dimethylphenols (Table 6).

The results indicate that the hazardous impact of semi-coke is not lasting and decreases continuously with ageing, which was also indirectly shown in the growth-chamber experiment described above. This conclusion was confirmed by the analysis of the samples taken from semi-coke dumps, according to which their content of environmental pollutants was significantly lower compared with fresh semi-coke [1]. Proceeding from the above reports it is evident that semi-coke and the recultivation substance produced from it are most hazardous for the environment immediately after production, and their content of pollutants decreases continuously.

The hazard to the environment caused by pollutants leaching from the substrates containing recultivation substance was studied in a lysimeter experiment. One lysimeter was filled with recultivation substance and the other with a mixture of recultivation substance and composted sewage sediment, and both were seeded with a mixture containing 5% *Trifolium repens*, 45% *Festuca rubra rubra,* 15% *Lolium perenne* and 35% *Poa pratensis* in spring. Both lysimeter leachates were sampled and analyzed by the method TerrAttest version 2.2 in October.

Table 6. **The Content of Pollutants in Semi-Coke, in Recultivation Substance and in a Mixture of Recultivation Substance and Composted Sewage Sediment mg kg^{-1} dw**

Pollutant	Semi-coke[1]	Recultivation substance	Mixture of recultivation substance and composted sewage sediment
Toluene	<10	<0.1	0.5*1
m+*p*-Xyleen	<10	<0.1	0.2*1
Sum (Xylene)	–	–	0.2*1
Phenol	2.1*2	1.1*1	0.32*1
o-Cresol	2.4*2	0.1	0.03
m-Cresol	15*3	1.6*2	0.20*1
p-Cresol	1.7*2	<0.01	0.17*1
2,4-Dimethylphenol	0.4*1	<0.01	<0.01
2,5-Dimethylphenol	0.9*1	0.1	0.02
2,6-Dimethylphenol	0.1*1	<0.01	<0.01
3,4-Dimethylphenol	1.5*2	0.1	0.02
o-Ethylphenol	0.3*1	<0.01	<0.01
m-Ethylphenol	2.4*2	0.3	0.007
4-Ethyl-2,3- and 4-ethyl-3,5-dimethylphenols	<0.1	0.3*1	0.1*1
Naphthalene	3.2*1	0.6	0.31
PAH 10 VROM (sum)	7.2*1	1.7	2.0
PAH 16 EPA (sum)	9.2*1	2.6	2.9

Notes: [1] The data are taken from the draft report of the joint stock company *Maves*: Dry sedimentation of semi-coke and production of recultivation substance from semi-coke, Tallinn 2001.
*1 Is equal or exceeds the guidance value of pollution in the living zone established by Regulation No. 58 of the Minister of the Environment of Estonia, 02. 07. 1999, 105, 1319 [13].
*2 Is equal or exceeds the allowed limiting value of pollution in the living zone established by the same Regulation.
*3 Is equal or exceeds the allowed limiting value of pollution in the industrial zone established by the same Regulation.

The results of tests showed low hazard compound content of leachates, none of them exceeding the allowed limit for groundwater [13] in Estonia. Only the amounts of Ba, Cd and Cu leached from recultivation substance and from the mixture of recultivation substance and composted sewage sediment exceeded the guidance value established for groundwater. Leaching of metals was more from the substrate containing composted sewage sediment (Table 7), which results from the higher metal content of sewage sediment compared with recultivation substance. The content of the other measured pollutants, including organic ones, in lysimeter water was lower than the guidance value established for groundwater in Estonia.

Table 7. **Content of Pollutants in Lysimeter Water, μg L^{-1}**

Pollutant (metal)	Lysimeter filled with recultivation substance	Lysimeter filled with mixture of recultivation substance and composted sewage sediment
Barium	260*	320*
Cadmium	0.52	1.2*
Copper	120*	120*

* Is equal or exceeds the guidance value of pollution for the living zone, established by Regulation [13].

To sum up, the obtained results allow concluding that the use of recultivation substance does not present a direct hazard to groundwater.

The Effect of Recultivation Substance on the Content of Heavy Metals in the Soil and in Plants

The traces of many heavy metals (Cu, Zn, Mo, Mn, Fe, etc.) exert a positive biological effect on plants and they are therefore named semimicro- and microelements [14]. Toxic or hazardous are Pb, Cd and Hg [15]. They can accumulate in the human organism and cause clinical intoxication [14]. Toxic heavy metals are present, in small quantities, practically in all mineral fertilizers, but also in manure and in oil shale ash used as liming material [16].

The effect of recultivation substance on the content of heavy metals in the soil and in plants was found out in a field experiment in which 20, 40 and 60 t ha^{-1} of recultivation substance were applied in the soil. Analysis of the soil samples taken six months later showed that the content of heavy metals was close to the initial level irrespective of different backgrounds of recultivation substance. The insignificant differences in soil Pb content between different experimental plots remained within experimental error and were not correlated with the amount of recultivation substance introduced into the soil (Table 8).

Table 8. **The Content of Heavy Metals in the Experimental Soil at Eerika in 2002 after the Use of Recultivation Substance**

Treatment	Pollutant, mg kg^{-1}		
	Cd	Hg	Pb
N-80 without recultivation substance	0.07	0.03	7.1
N-80 + recultivation substance, t ha^{-1}:			
20	0.07	0.05	8.7
40	0.06	0.04	8.0
60	0.06	0.04	7.4

Generalizing earlier results, it can be stated that the soil is contaminated with heavy metals only in case their content in the substance introduced into the soil is higher than their natural background is in the soil [16].

Estonian mineral soils contain on average, mg kg^{-1} DM: Pb 6–17, Cd 0.05–0.9 and Hg 0.02–0.04 [17]. In the recultivation substance used in the experiment, their content was Pb 30, Cd <0.3 and Hg <0.05 mg kg^{-1} DM. Proceeding from this, application of recultivation substance can increase only soil Pb content, as the content of the other hazardous heavy metals is close to their average content in Estonian mineral soils. Although Pb content of recultivation substance is higher than its average in Estonian soils, it is still lower than the guidance value established for the living zone [13], which means that this concentration is not hazardous for man either.

The content of heavy metals in the yield of field and garden crops is closely related to their content in the soil. When the amount of some heavy metal in the soil is large, one can also prognosticate its higher content in the yield. The plant is able to assimilate heavy metals in small quantities from the air as well. As the application of different amounts of recultivation substance in the experiment did not increase the content of heavy metals in the soil, increase in their content was not recorded in the plants in comparison with the plants which grew on pure soil, either.

The content of heavy metals remained within the allowed limit even in the grass plants which had grown on pure recultivation substance in the lysimeter experiment. Comparison of the content of heavy metals in the grass plants grown on recultivation substance and their average content in grass plants in Estonia grown on the mineral soil (Cd 0.040, Hg 0.055, Pb 0.44 mg kg^{-1}) [17] showed that their content was even lower in the first case. The possible reason for this is the alkaline reaction of recultivation substance, as plants are known to assimilate heavy metals in larger amounts on acid than on neutral soils [18]. At liming acid soils it has been noted that although liming materials increase slightly the content of heavy metals in the soil, their assimilation by plants decreases [14].

At the same time, this has been observed only in application of moderate rates of liming materials. When liming rates are high, the content of heavy metals in the yield increases. Such a relationship in the case of liming materials has been noted for Cd. It is thought to be the result of competition between Ca and Cd on the surface of soil particles [19].

Conclusions

The results of the experiments allow making the following conclusions:

1) Immediately after preparation recultivation substance is phytotoxic for plants and requires weathering in humid climatic conditions before application.
2) Owing to its high Ca and Mg content and alkality, recultivation substance is suitable for neutralizing acid soils and for increasing soil Ca and Mg content. Its effect on increasing the soil humus pool is not significant.
3) As recultivation substance is poor in certain plant nutrients, fertilizers should be added when it is used as a growth substrate.
4) To improve its plant cultivation characteristics, recultivation substance should be enriched with some nutrient-rich organic substance, for which sediment mud from water treatment plants and pig manure prove highly suitable. The mixture thus obtained can be used as growth substrate in recultivation of old pits and waste dumps.

5) The environmental hazard of recultivation substance weathered for six months is low: the content of no pollutant present in it exceeded the allowed limiting value established for the industrial zone in Estonia. Only the value of *m*-cresol exceeded the limiting value established for the living zone. The content of heavy metals in recultivation substance was close to their average value in Estonian mineral soils, only Pb being higher.
6) The content of pollutants in the leachate of recultivation substance was lower than the allowed limiting value established for groundwater in Estonia.

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