THE USE FLY ASH IN-SITU PHYTOREMEDIATION OF CRUDE OIL POLLUTED SOILS

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Abstract
The phytoremediation of lands polluted with oil products are generally applied in situ as a non-destructive technique. The process of phytoremediation participates in improving the agronomic characteristics of degraded soils. The content of petroleum products in the studied soils ranged between 70.45-120.32 g·kg⁻¹ D.M. The experimental study block consisted of in-situ variants located on land polluted by crude oil. The experimental variants were: variants of polluted soil unfertilized / fertilized with 50 t·ha⁻¹ sewage sludge. In addition, for the variants fertilized with sewage sludge an extra 50 t·ha⁻¹ fly ash originating from power plants was used. From the mixture of meadow plants used for the phytoremediation, the species Lolium spp. and Medicago spp. formed a coating plant layer on the variant fertilized with a mix of sewage sludge with fly ash, which covered up to 90% of the sown area. Effectiveness of the reduction of petroleum products in the soil was over 48% in three months time. The phytoremediation can be promoted with good results for the recovery of oil polluted soils with the use of treatments with sewage sludge and fly ash.

Introduction
The premises of the application of the method to restore damaged soils using crops, namely phytoremediation, are simple. However, as for the application any other methods, further research is needed. In this case, research is needed on the plant species in order to choose the most effective one. Additionally, the features of the polluted space, of the probable risks, of the application costs, partial and final results etc. must be defined[1-5]. Adding fertilizer to soils polluted with petroleum products is a variant of the phytoremediation technique, which is applied to increase the efficiency of biodegradation achieved by plants. The soil polluted with oil products, has an excess of carbon compounds. Nitrogen and phosphorus are often limiting factors in the process of biodegradation of hydrocarbons in polluted soils. Therefore, a balance of nutrients can reduce competition for nutrients between plants and microorganisms. Consequently, in soils polluted and fertilized, the efficiency of biodegradation of petroleum products will increase [5-6]. Flyash from fossil coal combustion in power plants are now byproducts, known mostly as waste. Fly ash have been recognized as a potential improver of the destroyed soil in that it presents minerals that contribute to plant growth. Mineral substances essential for plant growth are almost all in ionic form and have a positive impact on the physicochemical properties of damaged soil [7]. From this point of view, fly ash is considered a useful adjuvant for increasing crop production, especially in the case of the phytoremediation of damaged soils and waste dumps [8]. Discoloration of the wastewater with power plant fly ash was reported by a large number of researchers. Based on this information, the area available for the absorption of some pollutant components from the soil was studied. The studies were then extended to the
adsorption of the pollutants from the soil and reduction of their stress to the plants [9]. Finally, it should be noted that, although the technique of phytoremediation can be a cost-effective option, it requires a longer time than other alternative technologies to achieve clean soil characteristics and stability of cultures [10]. The aim of this study is to optimize the process of phytoremediation of soils polluted with petroleum products using sewage sludge as fertilizer and fly ash resulting from the burning of fossil coal in power plants.

**Experimental**

The experimental study was done on soils contaminated with petroleum products (Total Petroleum Hydrocarbon-TPH) with concentration in the range of 70.45 – 120.32 g·kg⁻¹ D.M.. The experimental block is located within the following coordinates: 46°16' 96.66" N, 21° 43' 46.1" E and 150m elevation. The experimental block includes the variants: 1). Polluted soil with petroleum products, fertilized with sewage sludge in the amount of 50t·ha⁻¹ - PN; 2). Polluted soil with petroleum products fertilized with sewage sludge in the amount of 50t·ha⁻¹, and fly ash in the amount of 50t·ha⁻¹ - PNC; Soil polluted with petroleum products - P. Sewage sludge come from the Municipal Water Treatment Station. Fly ash come from burning fossil coal in the power plant. The surface of an experimental allotment was 20m². The experimental variants are separated from each other by spaces of 1 m. For the experimental studies are selected meadow plant species on experimental variants of the polluted lands: *Lolium perenne* and *Medicago sativa*. The quantity of seeds used for sowing is of 18-20kg·ha⁻¹. Coverage of the cultivated area with different meadow plant species was established using the Braun-Blanquet abundance-dominance scale [11]. In table 1 are presented sewage sludge and fly ash characteristics.

**Results and discussion**

**The emergence stage** The first plants sprung from a mixture of seeds sown were from *Lolium perenne* species. The plants sprouted on the variant fertilized in the absence/presence of fly ash, two weeks after seeding. After the emergence, the surface covered with plants of variant PNC (fertilized with sewage sludge mixed with fly ash) was two times larger than the area of the variant fertilized in the absence of fly ash. To note that the variant of soil polluted and untreated, plants emerge 30-45 days later than those emerging on fertilized variants. Plants of the leguminous species *Medicago sativa* sprouted after two months from seeding, on the variants fertilized in the absence / presence of fly ash.

<table>
<thead>
<tr>
<th>Organic matter[+]</th>
<th>Nutrients</th>
<th>Metals content [mg·kg⁻¹ D.M.]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N[%]</td>
<td>P[%]</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>32.4 +/- 4.1</td>
<td>1.015 +/- 0.3</td>
</tr>
<tr>
<td></td>
<td>1.437 +/- 0.3</td>
<td>82.7 +/- 3.0</td>
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<tr>
<td></td>
<td>34.5 +/- 4.1</td>
<td>898.8 +/- 9.4</td>
</tr>
<tr>
<td></td>
<td>34.5 +/- 4.1</td>
<td>173.6 +/- 22.3</td>
</tr>
<tr>
<td></td>
<td>69.1 +/- 4.1</td>
<td>2450.1 +/- 134.5</td>
</tr>
<tr>
<td>Fly ash</td>
<td>0.2-2.0*</td>
<td>28.8 +/- 4.1</td>
</tr>
<tr>
<td></td>
<td>&lt; 0.05</td>
<td>65.5 +/- 4.1</td>
</tr>
<tr>
<td></td>
<td>&lt; 0.02</td>
<td>80.9 +/- 6.1</td>
</tr>
</tbody>
</table>

* coal, non bioavailable
Development stage for harvest 1. Plants of *Lolium spp.* grow exclusively in the first two months of vegetation on the experimental variants studied. *Lolium spp.* reaches 90% in the experimental variant fertilized with fly ash at the end of the 2nd month. On the variant fertilized in the absence of fly ash, the presence of *Lolium spp.* was 20% lower than when using the addition of fly ash. The culture established on the experimental variant fertilized with sewage sludge in the presence of fly ash had healthy looking plants that were heavily twinned. The culture established on the experimental variant fertilized in the absence of fly ash has had some ailing plants with yellow, necrotic leaves. On the non-fertilized variant meadow plants grow in rare clumps.

Maturity stage - harvest 1. Mowing took place two months from the emergence of plants when they reached maturity. Harvest was formed from *Lolium perenne* plants. Figure 1 shows the quantity of *Lolium spp.* harvested on the experimental variants.

![Image](image_url)

**Figure 1.** The quantity of *Lolium spp.* harvested on the experimental variants. Harvest 1

Development stage for harvest 2. After mowing, the presence of the leguminous species will gradually increase in the meadow plant culture used for phytoremediation. On the third month of vegetation, on experimental variant fertilized with sewage sludge in the presence of fly ash, the surface covered by *Medicago sativa* reached 30% of the total area covered with meadow plants. The presence of *Lolium spp.* plants will be reduced to 50% compared to the previous month. The meadow culture established on 80% of the variant experimental surface is resistant to the torrid heat and drought conditions. On the experimental variant fertilized with sewage sludge but not treated with fly ash, the surface covered with leguminous plants will reach 20% of the total cultivated area. In this case too, the leguminous species presence of the total covered area will be achieved by reducing the presence of grass plant *Lolium spp.* Figure 2 shows the vegetal layer formed on the experimental variant fertilized in the presence/absence of fly ash after mowing. It is seen from Figure 2 the healthy aspect of the culture established on the fertilized experimental variant in the presence of fly ash vs. the aspect of culture established on the experimental variant fertilized without the addition of fly ash. The meadow culture established on the experimental variant fertilized with sewage sludge in the absence of fly ash has had some ailing plants with yellow leaves. In addition emerged in the meadow culture clumps of plants that have dried after harvesting.
The aspect of the culture established on a) the fertilized experimental variant in the presence of fly ash, b) the experimental variant fertilized without the addition of fly ash.

Conclusions
The advantages of using as amendment fly ash from thermal power plants in the process of phytoremediation with meadow grass plants are that they resulted in: 1. Emergence of plants 30-45 days earlier than the fertilized experimental variant not treated with fly ash; 2. The forming of a rich vegetal layer with healthy plants even from the first stages of development; 3. *Lolium spp.* culture presence was 20% higher than culture in the absence of the addition of fly ash; 4. Increase the yields by 14.2%; 5. Presence of leguminous plants with 10-15% more vs. presence of leguminous the experimental variant not treated with fly ash; 6. Maintaining of the vegetation under conditions of a summer characterized by low rainfall and very high long time heat.

References