Some Aspects of the Phytoremediation upon a Haplic Luvosoil under Control Polluted with Crude Oil, from Oradea, Romania

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Abstract. The paper presents the results of the researches carried out at the Agricultural Research Station Oradea, Bihor County, between 1994 and 2002, regarding millet and wheat yields from a haplic luvosoil polluted under control with oil brought from the exploitation site at Suplacu de Barcău.

Phytoremediation is a recent technology that is used to stabilize or remove wastes from soils, groundwater or other medium by using living plants.

The experimental device was made out of micro parcels of 1 m², set up in a randomized manner, in a Latin square, polluted with a concentration of: 0, 1, 3, 5 and 10 % (0, 3, 9, 15, and 30 l/m²), oil in the ploughed layer, in four repetitions.

The experience was than cultivated with in the first three years with millet (1993-1995), a plant that is considered to be resistant to pollution, and than until 2002 with spring wheat. The tendency of relative yields of polluted plots show that in the time of research period of ten years, the pollutant was phyto degraded, without any ameliorative measures.

For the plot variants polluted with different concentration of crude oil, between the relative yields and time of research period was established second degree polynomial correlations, distinct and very significant statistically.

The shape of the curves indicates the fact that after a minimum of relative yields, registered in the first or the second year of research period these increases continuously in time, until the finish of the experiment.

The intensity of soil pollution, in the last year of research period, using the yield losses, in the plots with 1 % oil concentration is unpolluted, in the plots with 3 % oil concentration is weakly polluted, in the variant plots with 5 % oil concentration is moderate polluted and respectively in the plots with 10 % oil concentration is yet strong polluted.

The time of phytodegradation, evaluated with help of equations, through the condition for relative yields to be 95 %, when the soil pollution characterization became unpolluted results that: on the 1 % variant the soil became unpolluted after 5,4 years, on the 3 % after 7,8 years, on the 5 % variant after 9,6 years, and on the 10 % variant the soil became unpolluted after 10,8 years.

Keywords: phytoremediation, haplic luvosoil, oil pollution, oil biodegradation, biodegradation time.

INTRODUCTION

Plants are used to remove metals through three mechanisms: phytoextraction, rhizofiltration, and phytostabilization. At sites contaminated with organic contaminants,
plants are used for remediation of organic wastes in several ways: phytodegradation, rhizodegradation, and phytovolatilization. (Lan, 2004)

In conditions of Bihor County, the extraction, processing and transport of oil products took place at the Plants in Suplacu de Barcău, Marghita and Oradea, today belonging to OMV. S.C. Petrolsub S.A Refinery Suplacu de Barcău is nowadays in preservation. The soil is thus affected by historical pollution on a surface of about 200 ha, and measures for ecological reconstruction are needed. (Sabău et al. 2002)

For the conditions in Western Romania Colibaş et al, 1995 publish some researches regarding millet (hay) yield losses in the first year of controlled pollution with oil.

Later Şandor Maria et al. (2007) Şandor and Sabău (2007) and Sabău et al. (2009) publish the results of yields, of some parcels polluted under control, at the experimental field from the Agricultural Research Station Oradea, and some correlations between yields and oil concentrations.

Researches carried out by Toti et al. (2003) regarding the effects of oil pollution on the agricultural land affected by pollution at the oil extraction sites in the Southern part of the country have established that the life of the plants is affected at a relatively small pollution of 1 kg/m² (0,3 %) oil residue. The authors consider that at 1,5-3,0 kg/m² (0,5-1,0 %) concentration, pollution is moderate, between 3-15 kg/m² pollution is strong, and between 15-30 kg/m² pollution is very strong, the plants seeds no longer germinate, and at over 30 kg/m² pollution is excessive.

The researches makes by Siciliano et al. (2003), have demonstrated that phytoremediation systems, respective cultivated plants increase the microbiological potential of rhizosphere soil by altering the functional composition of the microbial community. This change in composition was linked to specific functional genotypes with relevance to petroleum hydrocarbon degradation.

**MATERIALS AND METHODS**

The researches carried out in Oradea had the objective of establishing the effects that controlled pollution with oil residue from Suplacu de Barcău had on agricultural crops and on the biodegradation time, without any ameliorative measures.

The oil supply at Suplacu de Barcău is at relatively small depth (30 – 40 m), in a layer of pontian sands, with high content of asphaltines.

Almost half of the soil polluted in Romania (49,397 %) is a luvisols, and that the soil polluted at Suplacu de Barcău is a luvisol, the experience was set up at on the haplic luvisol at the Agricultural Research and Development Station in Oradea.

The experimental field set up in 1993 is made out of micro plots of 1 m², set up in a Latin square, randomized, with 4 repetitions, polluted with oil from Suplacu de Barcău with 0, 3, 9, 15 and 30 l/m², thus having concentrations of 0 (unpolluted witness), 1, 3, 5 and 10 %.

The field was cultivated in the first three years (1993 - 1995) with millet (hay), a plant that has a very high tolerance to pollution, and than for the next 7 years with spring wheat, Speranţa breed.

By analyzing the agricultural millet and wheat yields we can conclude that the values of the yields from the polluted plots increase in time without having to apply ameliorative measures. They become proportionally insignificant in time, in direct proportion with amount of oil residue that was applied. This proves that the biodegradation of oil residue through phytoremediation was taking place in the soil.
Starting from this observation this paper wants to evaluate the influence of time on the process of oil residue biodegradation, through phytoremediation, by using the hay millet and spring wheat relative productions from the studied period.

RESULTS AND DISCUSSION

Taking in consideration that the experimental field was cultivated, in the research period, with two different plants, millet and spring wheat, we are considered to express the yields of parcels under control polluted with different concentration of crude oil, in percents (%), reported to the yield of control parcel, unpolluted with crude oil.

The average relative yields (%) evolution in the research period have an increasing tendency it registered a minimum of this in the fourth year of cultivation, 1996 the first year in that it is cultivated the spring wheat. (Fig. 1)

![Fig. 1. Evolution of the average relative yields (%) in the experimental period (1993-2002)](image)

The tendency of average relative yields of polluted plots show that in the time of research period of ten years, the pollutant was phytodegraded, without any ameliorative measures.

The fact that the average relative yields are strongly reduced after the first three years of cultivated millet sows that the millet offer more good conditions than spring wheat for the development of microbial community in soil ryzosphere, especially the genotypes implicated in oil phytodegradation.

When the plot of experimental field we are polluted under control with crude oil, the intensity indications of soil pollution, after Toti et al. 2003 was taking in consideration. After the first year of research, the characterization of soil pollution intensity, after Florea and Munteanu, 2000, with the help of Institute for Pedology and Agrochemistry Research (ICPA) Bucharest methodology was near the same (Tab. 1).
Intensity of soil pollution with crude oil in the first year of research

<table>
<thead>
<tr>
<th>Crude oil concentration (%)</th>
<th>Crude oil administrated (kg/m²)</th>
<th>Intensity of soil pollution in the first year of research after Toti et al. 2003</th>
<th>Intensity of soil pollution in the first year of research after Florea and Munteanu, 2000 ICPA methodology</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Characterization</td>
<td>Relative Yields (%)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>unpolluted</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>moderate pollution</td>
<td>80,68</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>strong pollution</td>
<td>68,75</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>very strong pollution</td>
<td>65,31</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>excessive pollution</td>
<td>36,36</td>
</tr>
</tbody>
</table>

It registered differences at the last two variants where the characterization after the quantity of oil administrated are very strong and excessive polluted in comparison with characterization after the yield losses registered in the first year of experiment, that are strong and very strong polluted.

The time influence on soil phytoremediation can be demonstrated through the 3D correlation with the two factors interaction, between the average relative yields (RY) of the two cultivated plants and oil concentrations (C) and respectively the years of experiment (T). This spatial correlation is very significant, the correlation coefficient is $R = 0,9086395$ (Fig.2).

The surface of graphic representation of relative yields sows that these it reduced inverse proportionally with the oil concentration and grow in direct link with the passing of years. The interaction between the two factors, concentration and time, expressed by the coefficient of the $C \times T$ term is important, about + 0,386986.

For each concentration of crude oil the link between average relative yields and time can be expressed by a polynomial equation of second degree (Tab.2).

The evolution of relative yields from research period described by second degree polynomial equation have a minimum at a certain period after under control soil pollution. This period ($T_{\text{min}}$) can be calculated through the cancellation of the first derivation of second degree polynomial equations.

Thus, the minimum of average relative yields, for control variant (unpolluted) it obtains after the fourth year from experiment start. ($T_{\text{min}} = 4,2$ years) In the case of plots under control polluted with different concentrations of crude oil, the minimum of average relative yields it registered in advance given the control variant. If for the plot with 1 % oil concentration, the minimum is registered at 3,66 years for the variant with maximum of oil concentration of 10 % this is registered still the first year of research period.

The minimum relative yields ($R_{\text{Ymin}}$) that are obtained for $T_{\text{min}}$, from the ten years of research period are included between 94,51 %, for control variant and respectively 30,89 % for variant with maximum of pollutant concentration 10 %.

The characterization of soil pollution using the yield losses (%) that corresponding to minimum relative yields (after Florea and Munteanu, 2000) show that after 3,66 years the variant with 1 % concentration of crude oil, the soil became from the initial characterization moderate polluted to weakly polluted. The other polluted variant characterization remains the same, for 3 and 5 % oil concentration strong polluted and respectively for 10 % oil concentration very strong polluted. This means for the variant with minimum of oil concentration (1 %) that in the first four years of period it registered the phytodegradation of pollutant.
Fig. 2 The 3D correlation Relative Yields (%) - the oil Concentrations (%) and Time (years)

\[ RY = 100.88996 - 12.210026 C + 0.525824 C^2 - 3.037680 T + 0.361727 T^2 + 0.386986 CT. \]

Tab. 2

The minimum average relative yields in research period

<table>
<thead>
<tr>
<th>Oil concentration C (%)</th>
<th>The first derivate of relative yields function ( RY' = 2cT - b = 0 )</th>
<th>( T_{\text{min}} ) (years)</th>
<th>( RY_{\text{min}} ) (%)</th>
<th>Yield Losses (%)</th>
<th>The soil pollution characterization (after Florea and Munteanu, 2000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( 0.723454T = 3.03768 )</td>
<td>4.20</td>
<td>94.51</td>
<td>-</td>
<td>unpolluted</td>
</tr>
<tr>
<td>1</td>
<td>( 0.723454T = 2.650694 )</td>
<td>3.66</td>
<td>84.34</td>
<td>9.17</td>
<td>weakly polluted</td>
</tr>
<tr>
<td>3</td>
<td>( 0.723454T = 1.876722 )</td>
<td>2.59</td>
<td>66.41</td>
<td>28.10</td>
<td>strong polluted</td>
</tr>
<tr>
<td>5</td>
<td>( 0.723454T = 1.102735 )</td>
<td>1.52</td>
<td>52.14</td>
<td>42.37</td>
<td>strong polluted</td>
</tr>
<tr>
<td>10</td>
<td>( 0.723454T = -0.832181 )</td>
<td>-1.15</td>
<td>30.89</td>
<td>63.62</td>
<td>very strong polluted</td>
</tr>
</tbody>
</table>

The different period at that it registered the minimum of average relative yields, for the plots polluted with different concentrations of oil can be explained through the reduction of microbial community of genotypes implicated in oil biodegradation and the reduction of their activity, in inverse proportion with the size of oil concentration.

If we take in consideration the relative yields of the four plot variants, in case of control plot the evolution of that in the period of research is linear and horizontal (\( RY = 100 \% \)) In the case of polluted variants the correlations established are polynomial second degree. (Fig.3)
The coefficient correlations of this polynomial equations shows that the link between relative yields and time are distinct significant statistically, for the variants polluted with 1 and 3 % crude oil concentrations and respectively very significant statistically for the variants with the high concentrations of pollutant (5 and 10 %) administrated. (Tab. 3)

The different intensity of link between relative yields and time, for the variant polluted with different concentrations of oil shows the different behavior of variants polluted with small concentration (1 and 3 %) in comparison by the variants polluted with high concentration of oil (5 and 10 %).

The shape of the polynomial curves indicates the fact that after a minimum of relative yields, registered in the first or the second year of research period these increases continuously in time, until the finish of the experiment.

After ten years of research, the simulated relative yields are over 100 %, the yield of control plot, for the variant polluted with 1 % (101,10 %) and between 92,64 % and 72,59 % for the others one variants polluted.

If we interpret the intensity of soil pollution, using the yield losses in the last year of research period, with the help of ICPA methodology, in the plots with 1 % oil concentration the soil is unpolluted, in the plots with 3 % oil concentration the soil is weakly polluted, in the variant plots with 5 % oil concentration is moderate polluted and respectively in the plots with 10 % oil concentration is yet strong polluted.

Through the comparison of soil pollution characterization in the first year of experiment (Tab. 1) by the characterization of pollution in the last year of research period (Tab.3) we can to observe that on the variant with 1 % oil concentration the soil became from moderate polluted to unpolluted and on the variant with 3 % oil concentration from strong polluted to weakly polluted, without any melioration works.
The evolution in time of relative yields

<table>
<thead>
<tr>
<th>Oil concentration C (%)</th>
<th>The second degree equation RY=a+bT+cT²</th>
<th>Correlation coefficient R</th>
<th>The relative yield for the last year RY(T=10)</th>
<th>The yield losses due to pollution 100-RY(T=10)</th>
<th>The characterization of pollution in the last year</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>RY=100,0000 + 0,0000 T</td>
<td>0,0000</td>
<td>100,00</td>
<td>-</td>
<td>unpolluted</td>
</tr>
<tr>
<td>1</td>
<td>RY=81,6690-1,1193 T + 0,3062 T²</td>
<td>0,4327**</td>
<td>101,10</td>
<td>+ 1,10</td>
<td>unpolluted</td>
</tr>
<tr>
<td>3</td>
<td>RY=68,2230-2,8654 T + 0,5307 T²</td>
<td>0,4549**</td>
<td>92,64</td>
<td>- 7,36</td>
<td>weakly polluted</td>
</tr>
<tr>
<td>5</td>
<td>RY=54,0790-3,0950 T + 0,6193 T²</td>
<td>0,6295***</td>
<td>85,06</td>
<td>- 14,94</td>
<td>moderate polluted</td>
</tr>
<tr>
<td>10</td>
<td>RY=37,8480-1,6342 T + 0,5408 T²</td>
<td>0,6949***</td>
<td>72,59</td>
<td>- 27,41</td>
<td>strong polluted</td>
</tr>
</tbody>
</table>

Therefore, in these two cases of the pollution with small quantity of pollutant, in ten years was phytodegraded nearly all oil from the soil, two steps of pollution characterization being covered.

In the case of the last two variants, with the big quantity of oil, 5 and 10 % concentrations was covered only one step of pollution characterization, from strong polluted and respectively very strong polluted these became moderate polluted and respectively strong polluted.

If we calculated the time of phytodegradation with help of equations, through the condition for relative yields to be 95 %, when the soil pollution characterization became unpolluted results that: on the 1 % variant the soil became unpolluted after 5,4 years, on the 3 % after 7,8 years, on the 5 % variant after 9,6 years, and on the 10 % variant the soil became unpolluted after 10,8 years.

CONCLUSIONS

The phytoremediation, a new method can be used for biodegradation of soil polluted with oil when the pollutant is located on the surface of profile, in the ploughed horizon or in ryzosphere zone.

The time influence on soil phytoremediation can be demonstrated through the 3D correlation with the two factors interaction, between the average relative yields (RY) of the two cultivated plants and oil concentrations (C) and respectively the years of experiment (T). This spatial correlation is very significant, the correlation coefficient is R = 0,9086395. The interaction between the two factors, concentration and time, expressed by the coefficient of the C x T term is important, about + 0,386986.

The different intensity of link between relative yields and time, for the variant polluted with different concentrations of oil shows the different behavior of variants polluted with small concentration (1 and 3 %) in comparison by the variants polluted with high concentration of oil (5 and 10 %).

The shape of the polynomial curves indicates the fact that after a minimum of relative yields, registered in the first or the second year of research period these increases continuously in time, until the finish of the experiment.

The minimum of relative yields, for the plots polluted with different concentrations of oil can be explained through the reduction of microbial community of genotypes implicated in
oil biodegradation and the reduction of their activity, in inverse proportion with the size of oil concentration.

The times of phytodegradation estimated with help of equations, through the condition for relative yields to be 95 %, when the soil pollution characterization became unpolluted are: on the 1 % variant the soil became unpolluted after 5,4 years, on the 3 % after 7,8 years, on the 5 % variant after 9,6 years, and on the 10 % variant the soil became unpolluted after 10,8 years.

REFERENCES