THE INFLUENCE OF THE FERTILIZATION SYSTEMS ON PRODUCTION IN THE LAST YEARS OF AGROCHEMICAL IMPROVEMENT OF A CRUDE OIL POLLUTED SOIL

Sabău Nicu Cornel*, Şandor Maria**

*University of Oradea, Faculty of Environmental Protection, 26 Gen. Magheru St., 410048 Oradea, Romania, e-mail: nsabau@uoradea.ro
**Agricultural Research and Development Station Oradea, 5 Calea Aradului St., Oradea, Romania, e-mail: scdaoradea@yahoo.com

Abstract

Among the many methods used for remediation of soils contaminated with oil residues, the stimulated biodegradation method on field is one of the most used because it is environmentally friendly and it has low costs compared to other methods.

The objective of our research is bioremediation of a haplic luvisol, on the experimental field from Research and Development Station Oradea, under control polluted with crude oil brought from Suplacu de Barcău, Bihor county, at a concentration of 3 % per the arable layer by cultivating millet and spring wheat and the stimulation of biodegradation by applying systems of organic and mineral fertilization.

Achieved average yields of spring wheat, in the last seven years of experiment varied within very large limits and yield differences were significant statistically for organic fertilized variants and without statistical significance for the variants fertilized with complex fertilizers.

Variance analysis method for multiple comparisons, using Duncan test demonstrated that the small doses of complex fertilizers (NPK) without the administration of manure (M) do not have statistically significant yield increases, and when applying high doses of complex fertilizers in association with manure (NPK x M) they have statistically significant effect.

The best results were obtained for the variant polluted, which were given 150 t / ha manure and the highest dose tested of complex fertilizers ($N_{300}P_{240}K_{210}$) the growth of production in comparison with no fertilization variant being of 97.7%.

The second degree polynomial correlations established for annual production and time, distinct significant statistically for the variations without the stimulation of biodegradation and significant statistically for the variations with stimulated biodegradation, using maximum quantities of manure and complex fertilizers shows that bioremediation period extends up to eight years.

Key words: soil pollution, crude oil, haplic luvisoil, fertilizing systems, biodegradation, bioremediation;

INTRODUCTION

Worldwide, of the marine and terrestrial environment oil pollution represents in the last decade one of the largest environmental disasters due to their very serious consequences.

Hydrocarbons represented by crude oil, natural gas and natural oil residues are the organic compounds in that are predominant hydrogen and carbon.

Soil pollution with oil products in Romania is caused by the extraction, transportation, manufacturing and retail sale, of which the largest share has the pollution with crude oil in the extraction fields. (Iliaş et al, 2009)

Contaminated surface with petroleum products shall be estimated at about 50 000 ha of which, in 2009, crude oil and salt water pollution from extraction occupies 2654 ha.

After the data from 2009, only in Bacău, Covasna, Gorj, Prahova and Timiş counties, soil pollution covers 751 ha polluted with oil products. (ANPM, 2009, http://www.anpm.ro/upload/16102_5%20SOL%202009.pdf)

In the western part of Romania, areas affected by historical pollution with crude oil is about 250 ha, being located in extraction fields from Suplacu de Barcău, Marghita and Oradea. (Sabău, 2007)

Soil pollution by crude oil is very complex because it is often associated with pollution of the soil with salt water, because crude oil contains over 17 thousand complex organic substances, including heavy metals, of whom predominant is the organic carbon that can reach about 85 %.

Effects of soil pollution with crude oil still occur at concentrations of only 1% agricultural production of crops, incur losses due to unbalance ratio organic carbon/nitrogen C/N. (Toti et al, 2003, Voiculescu et al, 2006)

The creation of a crude oil film on the surface of the soil profile disturbs the gas exchange between the soil atmosphere and the terrestrial atmosphere, thereby increasing the CO_2 concentration in the soil air, which hinder the germination of seeds and leads to the reduction of aerobic microorganisms' activity in the soil.

At the same time, the toxic effects of soil pollution with crude oil, sometimes underestimated, are directly dependent on crude oil characteristics and the physical, chemical and biological soil properties, it often acting as a selective filter of the pollutant fractions that tends to seep into the groundwater.

Between the various technologies used today to improve the cultivated soil, polluted with crude oil, the bioremediation of organic pollutants in the field is often the most used method because it is environmentally friendly and due to the low costs. (Onifade et al, 2007; Bijay et al, 2012)

Bioremediation technology is the biodegradation of pollutants in the soil, the decomposition of pollutants, especially organic, using enzymes produced by living organisms, particularly plants grown, bacteria and fungi from soil. (Atlas, 1981; Muthuswamy et al, 2008; Wang et al, 2012)

Due to the fact that in bioremediation of agricultural soils, the pollutant concentration decreases with time under natural conditions, bioremediation produced by crops and microorganisms, it was called natural attenuation. (Wiedemeier et al, 1999; Margesin et Schinner, 2001; Marques Alvarez et al, 2011)

Given that the natural attenuation period of the waste oil in the soil is great, it is enhanced the process of biodegradation by creating optimal conditions for soil microorganisms, through the cultivation of tolerant plants, (phytoremediation) inoculation of specialized microorganisms (bioaugmentation) soil aerating trough deep loosening, acidity correction and the balancing of the organic carbon/nitrogen C/N ratio. (Onifade et al, 2007; Glick, 2010; Marques Alvarez et al, 2011)

For the biodegradation of hydrocarbons in soil, using selected strains of bacteria, isolated from indigenous microflora of polluted soil are referred to in the scientific literature the genera: *Achromobacter, Arthrobacter, Acinetobacter, Bacillus, Flavobacterium, Novocardia, Pseudomonas, Xanthomonas, etc.* (Cocuț et al, 2008; Fagaraşi, 2011; Potra et al, 2012)

Taking in consideration that to the biodegradation of hydrocarbons in the soil, the involved bacteria use the organic carbon for the food, which is passed throughout the cellular mass in a proportion of one-third and the two-third remained are converted to carbon dioxide, one of the important factors for stimulating their activity is to balance carbon/nitrogen/phosphorus C/N/P report.

This ratio is controlled by the administration of organic or mineral fertilizers, in amounts which depend on the necessary bacterial mass and the concentration of hydrocarbons, the optimum specified by the specialty literature being 300/10/1. (Fan et Tafuri, 1998)

The first research on the effects of under control pollution on a soil with crude oil, brought from Suplacu de Barcău and their agrochemical improvement were placed on a haplic luvsol from the Research and Development Station Oradea by Maria Şandor in 1993, and the first partial results were published Colibaş Iuliu in 1995. (Colibaş et al, 1995; Şandor, 2011)

The objective of this paper is to study the influence of mineral and organic fertilization system on spring wheat yields achieved for the past seven years of agrochemical improvement on a soil, under control polluted with crude oil, from Oradea, Bihor County.

MATERIAL AND METHOD

Experimental field from the Research and Development Station Oradea, is composed of two experiments, one to assess the effect of under control crude oil pollution in various doses on agricultural production and evaluation of natural attenuation and second, to agrochemical improve of controlled crude oil polluted soil in concentration of 3 % on arable layer (enhancing natural attenuation) with different doses of organic (manure) and mineral (NPK, complex fertilizers) fertilizers.

Experiment on agrochemical improving of under control polluted soil, with crude oil is of type 2 x 4 x 4 with three factors, with subdivided plots placed randomly in four replications, with an area of 1 m^2.

The three factors studied are: the factor A, with two graduations a1, the control and a2, polluted soil with crude oil, in concentration of 3 % (9 l/m^2) on plowed horizon; the factor B, organic fertilization with manure: b0 - 0 t / ha, b1 - 50 t/ha, b2 - 100 t/ha and b3 - 150 t/ha manure; the factor C, mineral fertilization with complex fertilizers in doses of: c_0 – $N_0P_0K_0$ kg/ha; c_1 - $N_{100}P_{80}K_{70}$ kg/ha; c_2 – $N_{200}P_{160}K_{140}$ kg/ha; c_3 – $N_{300}P_{240}K_{210}$ kg/ha.

Soil type of the experimental field is haplic luvosol, characterized by colloidal clay content (< 0.002 mm) greater than 40 %, moderately acidic reaction (pH = 5.5) and low contents in humus and nutrients on plowed horizon.

Unlike other hydrocarbon characteristics exploited in Romania, crude oil from Suplacu de Barcău is characterized by the high percentage of hard fractions, prevalent being oils, 40.1 % and asphaltine, 35.3 %, while the light fractions, naphtha and kerosene were represented each of a rate by 1.3 %. (Sabău et al, 2011)

From soil samples collected from a polluted land at the Suplacu de Barcău were isolated 12 strains of bacteria of the genus: *Acinetobacter, Bacillus* (three strains), *Burkholderia* and the species *Pseudomonas putida, Pseudomonas fluorescens, Burkholderia cepacia, Burkholderia gladioli* (two strains), *Enterobacter clocae* (two strains) and 12 fungal strains of the genus: *Aspergillus* (five strains), *Acremonium, Crysosporium, Mortierella,* (two strains) *Paecylomice* and two strains of *Penicillium.* (Fagaraşi, 2011)

Observations from the two experiments were conducted in the period 1993-2002, of which in the first three years, have been cultivated with millet and in the past seven years with spring wheat, Speranța variety.

RESULTS AND DISSCUSIONS

The average yields of spring wheat cultivated plots in seven years to enhancing bioremediation in under control polluted soil with 3 % crude oil, using mineral and organic fertilization showed very wide variations, from 11.58 and 11.63 q/ha for polluted variants without fertilizer management and between 16.26 and 16.48 on unpolluted variants, fertilized with maximal doses of complex fertilizers $N_{300}P_{240}K_{210}$ and respectively, manure, 150 t/ha. (Sabău et Şandor, 2013)

Analysis of variance of average production, using the ANOVA method and analysis of statistical significance of differences in production using tests Fischer (F) and Student's (t) showed that the applied doses of mineral fertilization did not produce yield differences, statistically significant nor in polluted variants nor in the unpolluted, because the annual production values were considered to be seven repetitions.

This can be explained by the variability of the production of the seven years considered repetitions, taking into account that for the variance analysis annual yields, using the same method, the dose effects of complex fertilizer on production differences produce stronger statistical significance than the quantities of manure tested, in most years studied.

The large differences between annual production made by the studied variants can be explained by the trifactorial linear correlation, very significant statistically, established between experimentation time, T (years) manure quantities, M (t/ha: 100) and doses of complex fertilizers C (100 x NPK) and respectively the production of spring wheat Y. (Table 1.)

Table 1.

Trifactorial linear correlations of spring wheat yields Y (q / ha) and time T (years), amounts of manure M (t ha: 100) and doses of complex fertilizers C (NPK x 100)

Cod	Variants	Equation	Correlation report R^2	Statistical significance
a_0	Unpolluted (Control)	Y = 43.86893 - 4.60195 T + 2.246893 M/100 + 1.079929 C x100	0.881006	***
a_1	Polluted 3 %	Y = 39.97525 - 4.04242 T + 3.077696 M/100 + 1.279027 Cx100	0.849198	***

Looking for the form equations of unpolluted (R^2 = 0.881006) and under control polluted variants (R^2 = 0.849198) it is noted that the most important influence on the production has the time T, followed by the quantities of manure M and complex fertilizer doses C.

The influence of the experiment duration T is negative, the stronger in the case of the unpolluted variants, the coefficient for this variable, a1 = 4.60195, it is greater than for the polluted variants (a1 = 4.04242) it indicating that in both cases the yields of wheat be reduced annually. This reduction is explained by applying monoculture a long period of seven years.

If for variance analysis is used multiple comparisons method (Duncan test) is emphasized that the variant with the highest statistical significance of differences in production is the version with maximum quantities of manure and maximum doses of complex fertilizer administered on unpolluted plot followed by the variant with the same treatment of polluted plot. (Table 2.)

Given that the production differences of group noted with the letter e no has statistical significance in comparison with the variant polluted without treatments (a1b0c0), we believe that the production differences of d group are significant statistically, the c group is distinct significant and respectively a and b groups are very significant statistically.

Table 2.

Multiple comparisons of spring wheat average yields from agrochemical melioration of polluted soil with crude oil, Oradea field, Bihor County (Duncan test)

Nr. crt.	Variants	The Yields (q/ha)	Yield Differences (q/ha)	Yield Differences (%)	Signification	
1.	$a_0b_3c_3$	17.47	8.78	201.04		a
2.	$a_1b_3c_3$	17.18	8.49	197.70		b
3.	$a_0b_2c_3$	17.00	8.31	195.63		b
4.	$a_0b_3c_2$	16.94	8.25	194.94		b
5.	$a_0b_2c_2$	16.78	8.09	193.10		b
6.	$a_1b_3c_2$	16.78	8.09	193.10		b
7.	$a_1b_2c_2$	16.28	7.59	187.34		c
8.	$a_0b_3c_1$	16.23	7.54	186.77		c
9.	$a_1b_2c_3$	16.02	7.33	184.35		d
10.	$a_1b_1c_1$	15.79	7.10	181.70		d
11.	$a_0b_1c_3$	15.62	6.93	179.75		d
12.	$a_0b_1c_2$	15.39	6.70	177.10		d
13.	$a_0b_2c_1$	15.37	6.68	176.87		d
14.	$a_0b_3c_0$	15.29	6.60	175.95		d
15.	$a_1b_1c_3$	15.13	6.44	174.11		d
16.	$a_0b_0c_3$	14.95	6.26	172.04		d
17.	$a_1b_2c_1$	14.73	6.04	169.51		d
18.	$a_0b_0c_2$	14.50	5.81	166.86		d
19.	$a_1b_3c_0$	14.46	5.77	166.40		d
20.	$a_1b_1c_2$	14.21	5.52	163.52		e
21.	$a_0b_2c_0$	14.04	5.35	161.66		e
22.	$a_0b_1c_1$	13.94	5.25	160.41		e
23.	$a_1b_0c_2$	13.21	4.52	152.01		e
24.	$a_1b_0c_3$	13.11	4.42	150.86		e
25.	$a_1b_2c_0$	12.91	4.22	148.56		e
26.	$a_0b_0c_1$	12.77	4.08	146.95		e
27.	$a_0b_1c_0$	12.41	3.72	142.81		e
28.	$a_1b_1c_1$	12.23	3.54	140.75		e
29.	$a_1b_0c_1$	11.32	2.63	130.26		e
30.	$a_0b_0c_0$	10.68	1.99	122.90		e
31.	$a_1b_0c_0$	10.46	1.77	120.37		e
32.		8.69	-	100.00		-

Thus, in the group of variants with differences in average yields without statistical significance prevailing polluted variants (a1) that have not received manure (b0) and the quantities were small (b1) or medium (b2) and the variants of mineral fertilizers. (c0 - c3).

Differences in average production in recent years of improvement are distinct significantly in unpolluted variant, for the maximum quantity of manure (b3 = 150 t/ha) and for the lowest dose of complex fertilizers (c1 = $N_{100}P_{80}K_{70}$ and in the case of the polluted variant, for average doses of organic and mineral fertilizers. (b2 = 100 t/ha, c2 = $N_{200}P_{160}K_{140}$)

Among variants under control polluted by 3 % crude oil, notes with very significant production differences, the ones who have received the maximum quantity of manure (150 t/ha) in combination with medium and high doses of complex fertilizers. ($N_{200}P_{160}K_{140}$ şi $N_{300}P_{240}K_{210}$)

For analyze the evolution of annual average production of the last seven years of agrochemical improve (T years) were studied correlations between these productions on unpolluted and polluted variants, without application of organic and mineral fertilizers (a0b0c0 and a1b0c0) and the obtained productions on the variants in who were applied the biggest quantity of manure and the biggest doses of complex fertilizer. (a0b3c3 and a1b3c3) Were established correlative links, polynomial of degree two, of the type $Y = a2\ T^2 + a1\ T + a_0$, significant and distinct significant statistically. (Figure 1.)

It may be noted that in both variants, unpolluted (R^2 = 0.9303) and polluted (R^2 = 0.9790), without fertilization, the correlation report indicates a distinct significant link, while the variants fertilized with the largest quantity of manure (150 t/ha) and doses of complex fertilizers ($N_{300}P_{240}K_{210}$) correlative links are only significant statistically (R^2 = 0.8164 and R^2 = 0.87590)

The fact that for the polluted variants, the correlation report is higher than for the unpolluted variants, suggest a stronger influence of the applied fertilizer system on the average annual production obtained and thus a positive influence on the biodegradation of the crude oil in the soil.

Form of curves show that in all cases exists a tendency to reduce the level of spring wheat yields, trend explained by long cultivation of spring wheat.

If we compare the slope of the obtained curves in without treatment variants, it is noted that somewhat lower slope is on the variant polluted, and this can be explained by the crude oil phytoremediation, under the rhizosphere influence around the roots of wheat.

In case of application the mineral and organic fertilization systems, the tend to reduce the production on polluted version is higher than in unpolluted version, but the shape of the curve has a minimum point in eighth year, followed by an upward trend, which could be interpreted as the total biodegradation point of crude oil in the soil. This supposition is confirmed by the differences in average yields, significant statistically, negative in the fifth year and respectively positive in the last year of improvement.

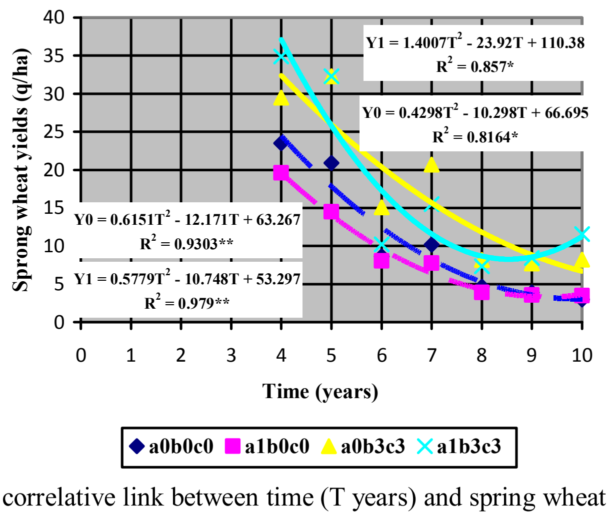

Figure 1. The correlative link between time (T years) and spring wheat yields (q/ha)

Therefore reconstruction of under control polluted soils with crude oil brought from Suplacu de Barcău, by cultivation in field and application of an organic fertilizer system with large quantity of manure (150 t/ha) and a mineral fertilization system with high doses of complex fertilizers ($N_{300}P_{240}K_{210}$) is possible, but do require a long period of time.

CONCLUSIONS

Achieved average yields of spring wheat, grown in the last seven years, in the experimental field of enhancing the bioremediation of soil under control contaminated with crude oil from Oradea, showed very wide variations, from 11.58 to 16.48 q/ha.

Linear correlations with three factors, established for variants unpolluted and polluted, very significant statistically, showing that the trend is the reduce production, the time has the greatest influence in shaping annual productions, in comparison of organic and mineral fertilizer system, the trend is due to the application of monoculture.

Analysis of differences in average production achieved by studied variants made by the multiple comparisons method (Duncan) showed that the doses of complex fertilizers used to enhancing oil biodegradation have statistical significance, especially for the variants where the effect of these is conjugated with the effect of manure quantities administered.

The polynomial quadratic curves of correlations established between annual production and time, for unpolluted and polluted variants, without fertilization or with maximum doses of manure and complex fertilizer, distinct significant and respectively significant statistically, in the case of polluted variants show a minimum after the eighth year, suggesting length of enhancing biodegradation process on field.

The bioremediation method of contaminated with oil residue soils, by cultivation of the field is one of the most used because it is environmentally friendly and cost efficient, but its disadvantage consists in long period of the biodegradation process.

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