

THE ROLE OF ORGANIC MATTER IN THE BIODEGRADATION PROCES OF CRUDE OIL FROM THE SOIL

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Abstract

The paper presents the partial results of researches regarding the agrochemical melioration of soils under control polluted by petroleum residues that took place at the Agricultural and Research and Development Station in Oradea, Bihor County. The researches have like objective the study of organic matter influence on millet-hay yields, in the time of melioration process of a soil under control polluted with crude oil.

The experimental device was made out of 1 m² microparcels, spread out in subdivided parcels, in four repetitions, having tree factors: A - the pollution by crude oil from Suplacu de Barcău, B – the mineral fertilization, and C – the organic fertilization.

The experience was set out on a haplic luvisol in the year 1993 and the soil was cultivated with millet in the first 3 years and with spring wheat in the last 7 years of research.

The role of organic matter added in the biodegradation of petroleum residue is to balance the nitrogen content from the C/N ratio and to inoculate the microorganisms implicated in the biodegradation process.

Key words: biodegradation, crude oil, haplic luvisol, organic fertilization, mineral fertilization.

INTRODUCTION

In Romania a surface over 50 thousands ha are affected by the overflows of crude oil and salty water from oil extraction fields. (Voiculescu et al, 2006) Oil extraction, processing and transport in Bihor took place at the sites in Suplacu de Barcău, Marghita and Oradea, which have become nowadays stations for OMV and Petrolsub SA Suplacu de Barcău Refinery, today in conservation. Following these activities, the soil is affected by historical pollution on a surface of about 250 ha, and is need of measurements of ecological rehabilitation. (Sabău et al, 2002)

At sites contaminated with organic contaminants, plants are used for remediation of organic wastes in several ways: phytodegradation (biodegradation), rhizodegradation, and phytovolatilization. (Dzhura, et al, 2008; Gerhardt, et al, 2009; Lan, 2004)

In the same time, plants are used to remove metals from polluted soil through three mechanisms: phytoextraction, rhizofiltration, and phytostabilization. (Garbisu, end Alkorta, 2001) In Romania, for bioremediation of sites with lead contaminated, the phytoremediation techniques were used. (Ichim, et al, 2010)

Phytoremediation technologies are recognized as cost-effective methods, as environmentally friendly, as simple and sustainable technique and its technical and economic advantages over conventional approaches. (Flatham and Lanza, 1998)

As an adjunct to various phytoremediation strategies and as part of an effort to make this technology more efficacious, was explored the possibility of using various soil bacteria together with plants. (Glick, 2010) This technology can be more efficacious through bioaugmentation, which means the addition of specialized microorganisms. (Purohit H., 2006)

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. (Siciliano et al, 2003)

In the case of soils polluted with hydrocarbons petroleum, the microorganisms from the kind *Pseudomonas* presents the bigger adaptability. (Cocuț et al, 2008)

Microbe-assisted phytoremediation, including rhizoremediation, appears to be particularly effective for removal and/or degradation of organic contaminants from soils, particularly when used in conjunction with appropriate agronomic techniques. Inorganic nutrient, amendments may stimulate plant and microbial growth, and clipping aboveground biomass might stimulate root turnover, which has been associated with increases in soil microbial populations. (Olson et al, 2008)

The research carried out in the south of Romania (Toti et al., 2003) concerning the melioration of agricultural lands polluted by crude oil from extraction fields, have provided that the plant's average life expectation diminished after a pollution of 1 kg/m² (0,3 %) oil residue in the ploughed layer.

For the conditions from Western Romania, Colibaș et al., 1995 published the first partial results of researches regarding yield losses in millet, after the first year of controlled pollution with different doses of crude oil, from Suplacu de Barcău on the haplic luvisoil from Agricultural Research and Development Station Oradea.

Later, Șandor et al, 2007; Sabău et al, 2009, publish the results of yields, of some parcels polluted under control, at the experimental field from the Agricultural Research and Development Station Oradea and some correlations between yields and crude oil concentrations. It sows that under the influence of cultivated plants the crude oil concentration decreases in time, without any sort of agropedomeliorative measures.

The researches carried out in Oradea have like objective the study of organic matter influence on millet-hay yields, in the time of melioration

process of a soil under control polluted with crude oil, from Suplacu de Barcău, Bihor County.

MATERIAL AND METHOD

Taking in consideration that on Romanian territory, from the surface which are affected by pollution with petroleum residue and salty water, near a half (49,4 %) is occupied by luvisols and the type soil preponderantly polluted with crude oil at Suplacu de Barcău is also luvosoil, the experience carried out at Agricultural Research and Development Station Oradea, was placed also on a haplic luvosoil.

The soil reaction is acid in the ploughed A horizon, then slightly acid. The soil content in humus medium and it is well provided with mobile potassium and phosphorus. (Colibaş et al, 2000)

The experiment looking “The agrochemical melioration of polluted by petroleum residue of soils” is an experiment having three factors, the type $2 \times 4 \times 4$, with microparcels of 1 m^2 , set out randomized, in four repetitions after the system of subdivided parcels. (Săulescu and Săulescu, 1967)

The studied factors are:

The factor A: Pollution by crude oil: a_1 – control unpolluted; a_2 – polluted by crude oil, in concentration of 3 % (9 l/m^2) on ploughed layer;

The factor B: Organic fertilizer: b_0 – 0 t/ha manure; b_1 – 50 t/ha manure; b_2 – 100 t/ha manure; b_3 – 150 t/ha manure;

The factor C: Mineral fertilizer: c_0 – $\text{N}_0\text{P}_0\text{K}_0$ kg/ha; c_1 – $\text{N}_{100}\text{P}_{80}\text{K}_{70}$ kg/ha; c_2 – $\text{N}_{200}\text{P}_{160}\text{K}_{140}$ kg/ha; c_3 – $\text{N}_{300}\text{P}_{240}\text{K}_{210}$ kg/ha;

The experimental device was carried out in 1993, at the same time with the experiment looking the study of different doses of petroleum residue effect on yields, being cultivated in the first three years with millet and then in the next seven years with spring wheat, Speranța breed.

RESULTS AND DISCUSSIONS

Soil pollution with oil residue is a very complex phenomenon, which involves knowing the chemical nature and concentration of the pollutive agent and the soil conditions.

The crude oil from Suplacu de Barcău, Bihor County, in comparison with the other crude oil from Romania is characterized by the predominance of the heavy fractions. (Table 1.)

The percent of gross fractions are: 40,1 % for oils, 35,3 % from asphaltine and 22,0 % for diesel oil, while the percent of light fractions are: 1,3 % for gasoline and kerosene.

Table 1

Some characteristics of crude oil from Suplacu de Barcău

Nr. crt.	The characteristic	Measure	The value
1.	Gasoline	%	1,3
2.	Kerosene	%	1,3
3.	Diesel oil	%	22,0
4.	Oils	%	40,1
5.	Asphaltine	%	35,3
6.	Sulphur	%	0,222

In the conditions of the major presence of gross fractions in the crude oil, the infiltration in the controlled pollution on the topsoil is more reduced.

The crude oil from the top of soil profile makes up a film of oil that hinders the soil respiration and being hydrocarbons (organic carbon) determines the increasing of the organic carbon-nitrogen ratio (C/N).

In the same time the soil is polluted with the heavy metals from the pollutant. The crude oil from Suplacu de Barcău contents big concentrations of cadmium of 483 ppm, iron of 186 ppm and nickel of 40,5 ppm. (Table 2.)

Table 2

Heavy metals content of crude oil from Suplacu de Barcău

Nr. crt.	The heavy metal	Measure	The value
1.	Cadmium	ppm	483,0
2.	Iron	ppm	186,0
3.	Nickel	ppm	40,5
4.	Copper	ppm	1,1

The melioration of polluted soils with petroleum residue must to have in consideration the equilibrium between organic carbon and nitrogen, in the C/N ratio and for that it uses the administration of fertilizers with nitrogen.

For the stimulation of the crude oil biodegradation, in our experiment was added mineral fertilizers (complex fertilizer: $N_0P_0K_0$, $N_{100}P_{80}K_{70}$, $N_{200}P_{160}K_{140}$, $N_{300}P_{240}K_{210}$ kg/ha) and organic fertilizer (manure: 0, 50, 100, 150 to/ha)

In the first three years of the experiment (1993-1995) the doses of fertilizers administrated on the not polluted and polluted with 3 % crude oil variants are determinate mullet hay yields between 30,3 q/ha on the polluted variant, without any fertilizer administrated ($a_2b_0c_0$) and 54,0 q/ha on the not polluted variant and with maximum doses of mineral and organic fertilizers ($a_1b_3c_3$). (Table 3.)

Using the Duncan test, for the multiple comparisons of the yield losses, given of the variant with maximum yield ($a_1b_3c_3$) was established

that the yield losses of millet, bigger for the polluted variants and smaller for the not polluted variants are significantly statistical.

Table 3

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

Nr. crt.	Variant	The Yield (q/ha)	The yield losses (q/ha)	Signification	
1.	a1b3c3	54,0	-]	a
2.	a1b3c2	53,1	0,9		a
3.	a1b3c1	49,6	4,4]	ab
4.	a1b2c3	49,5	4,5		ab
5.	a1b2c2	48,6	5,4]	b
6.	a2b3c3	48,0	6,0		b
7.	a1b1c3	47,2	6,8]	bc
8.	a1b0c3	45,8	8,2		bc
9.	a2b2c3	45,7	8,3		bc
10.	a1b1c2	45,6	8,4]	c
11.	a1b2c1	45,5	8,5		c
12.	a2b1c3	44,6	9,4		c
13.	a2b3c2	44,4	9,6		c
14.	a1b3c0	43,8	10,2]	cd
15.	a2b2c2	43,2	10,8		cd
16.	a1b0c2	43,1	10,9		cd
17.	a2b3c1	42,7	11,3		cd
18.	a2b0c3	42,5	11,5		cd
19.	a2b1c2	41,6	12,4]	d
20.	a1b2c0	40,6	13,4		d
21.	a1b1c1	40,2	13,8		d
22.	a2b2c1	39,7	14,3		d
23.	a1b0c1	39,4	14,6		d
24.	a2b0c2	39,3	14,7		d
25.	a1b1c0	37,8	16,2]	de
26.	a2b3c0	37,7	16,3		de
27.	a2b1c1	37,6	16,4		de
28.	a2b2c0	36,5	17,5		de
29.	a1b0c0	34,7	19,3		de
30.	a2b1c0	34,4	19,6]	e
31.	a2b0c1	34,3	19,7		e
32.	a2b0c0	30,3	23,7		e

The influence of the fertilizer systems, organic fertilizer (X_1) and mineral fertilizer (X_2), on the millet-hay average yields (Y), in conditions of soils not polluted and polluted with 3 % crude oil, was described by spatial second degree polynomial equations. These correlations are very significant statistically; the correlation coefficients are 0,9830 in the case of the not polluted soil and respectively 0,9906 in the case of the polluted soil.

If we analyze the influence of the organic fertilizers on the average millet hay yields, the correlative links for the not polluted and respectively polluted with 3 % crude oil variants are deducted second degree polynomial equations. (Figure 1.)

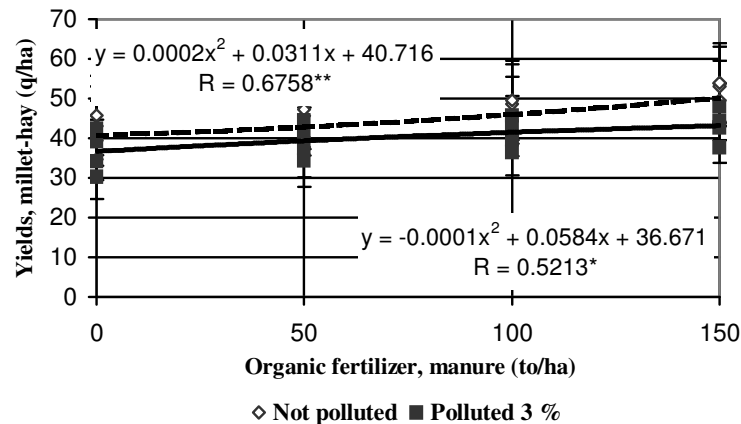


Fig. 1. The links between the quantity of manure administrated and the average yields of millet hay (1993-1995).

These correlation equations are distinct significant statistically ($R = 0,6758$) in the first case and only significant statistically in the second case ($R = 0,5213$). They show that in the case of polluted soil the importance of the added organic matter is more reduced than in the case of not polluted soil.

If we analyze the influence of manure quantities administrated on the average millet hay yields, at the different agricultural backgrounds, definite by the different doses of mineral fertilizer ($N_0P_0K_0$, $N_{100}P_{80}K_{70}$, $N_{200}P_{160}K_{140}$, $N_{300}P_{240}K_{210}$) we can establish the same polynomial second degree correlations. These correlations are distinct significant statistically. (Figure 2.)

In spite of the fact that the manure represents organic matter, and in the polluted with crude oil soils this unbalances the C/N ratio, the more closely link between the manure quantities and average yields were established in the case of the agricultural background without mineral fertilizer ($N_0P_0K_0$) when the correlation coefficient is about 0,9990.

The reduction of correlation coefficient values in function of the increasing of mineral fertilizer doses shows that the importance of nitrogen from the administrated manure is reduced.

The correlative links remain distinct significant statistically at the big doses of mineral fertilizer, because the organic fertilizer administrated

inoculates in the polluted soil the microorganisms implicated in the biodegradation process.

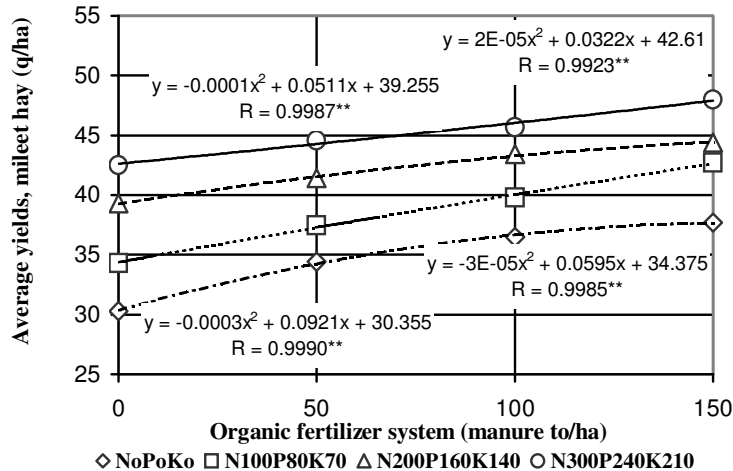


Fig. 2. The influence of manure quantities administrated on the polluted variants (3 % crude oil) at the different agricultural background of mineral fertilizers on the average millet hay yields

CONCLUSIONS

In the case of polluted with 3 % concentration of crude oil soil the importance of the added organic matter at the different agricultural background of mineral fertilizers is more reduced than in the case of not polluted soil.

The manure quantities administrated in the case of the agricultural background without mineral fertilizer (N₀P₀K₀) are more importance, because they represent the main source of nitrogen, than in the case of the agricultural background with mineral fertilization, when those inoculates in the polluted soil the microorganisms implicated in the biodegradation process.

REFERENCES

1. Cocuț Dana-Camelia, Diaconu Mariana, Cojocaru C., Macoveanu M., 2008, Studiu privind biodegradabilitatea unor produse petroliere folosind unele tulpini microbiene, Universitatea de Științe Agricole și Medicină Veterinară, Lucrări Științifice, vol 51, seria Agronomie, Iași;
2. Colibaș I., Colibaș Maria, Șandor Maria, 1995, Măsuri de ameliorare a solurilor poluate cu rezidii petroliere, Cum să cultivăm pământul în zona centrală din vestul țării, Stațiunea de Cercetări Agrozootehnice Oradea
3. Colibaș I., Colibaș Maria, Tirpe Gh, 2000, Solurile brune luvice, caracterizare și ameliorare, Ed. Mirton Timișoara;

4. Dzhura N., Romanyuk O., Oshchapovsky I., Tsvilynyuk O., Terek O., Turovsky A., Zaikov G., 2008, Using plants for recultivation of oil-polluted soils, *J. of Environmental Protection and Ecology* 9 (1);
5. Flatham P.E., Lanza G.R., 1998, Phytoremediation: Current views on an emerging green technology, *Journal of Soil Contamination*, Vol. 7, no. 4, pp. 415-432;
6. Garbisu C., Alkorta I., 2001, Phytoextraction: a cost-effective plant-based technology for the removal of metals from the environment, *Bioresource Technology* 77, pp 229 – 236;
7. Gerhardt K.E., Huang X.D., Glick B.R., Greenberg B.M., 2009, Phytoremediation and rhizoremediation of organic soil contaminants: Potential and challenges, *Plant Science*, Vol. 176, Issue 1, pages 20-30;
8. Glick B.R., 2010, Using soil bacteria to facilitate phytoremediation, *Biotechnology Advanced*, Vol 28, Issue 3, pp 367-374;
9. Ichim M., Vișan A., Enache R., 2010, Phytoremediation of lead contaminated soils, 3rd International Symposium of Biotechnology, Bucharest.
10. Lan J.K., 2004, Recent developments of phytoremediation, *Journal of Geological Hazards and Environmental Preservation*, vol 15, no 1, pp 46-51;
11. Olson P.E., Castro A., Joern M., Duteau N.M., Pilson-Smits E., Reardon K.F., 2008, Effects of Agronomic Practices on Phytoremediation of an Aged PAH-Contaminated Soil, *Journal of Environmental Quality*, Vol. 37, pp 1439-1446;
12. Purohit H., 2006, Impact of bioaugmentation with a consortium of bacteria on the remediation of wastewater-containing hydrocarbons, *Journal Environmental Science and Pollution Research*, publisher Springer, Berlin/Heidelberg;
13. Sabău N.C., Domuța C., Berchez O., 2002, *Geneza Degradarea și Poluarea Solului, Partea a II-a Degradarea și Poluarea Solului*, Ed. Univ. din Oradea, 282, 240-242.
14. Sabău N. C., Șandor Maria, Domuța C., Brejea R., Domuța Cr., 2009, The estimation of degraded oil with the maximum of spring wheat yields on a preluvoil from Oradea, Romania. International Symposia "Risk Factors for Environment and Food Safety" & „Natural Resources and Sustainable Development” 6-7 november, *Analele Universității din Oradea, Fascicula Protecția Mediului*.
15. Săulescu N.A., Săulescu N.N., 1967, *Câmpul de experiență*, Editura Agro-Silvică București;
16. Siciliano S.D., Germida J.J., Banks K., Greer Ch.W., 2003, Changes in microbial community composition and function during a Polyaromatic Hydrocarbon phytoremediation field trial, *American Society for Microbiology, Applied and Environmental Microbiology*, vol 69, No 1, pp. 483-489;
17. Șandor Maria, Sabău N.C., Domuța C., Domuța Cr., Brejea R., 2007 The influence of soil pollution on agricultural crops, *Joint International Conference on Long-term Experiments Agricultural Research and Natural Resources*, Debrecen-Nyirlugos, 31May-1June, 608,304-311,
18. Toti Mh., Dumitru Mh., Rovenă Voiculescu Anca, Mihalache Mh., Mihalache Gabi, Constantinescu Carolina, 2003, *Metodologia de biodegradare a solurilor poluate cu țitei, cu ajutorul microorganismelor specifice selecționate din microflora autohtonă*, Edit. GNP Minischool, 164,
19. Voiculescu Anca-Rovenă, Dumitru Mh., Toti Mh., 2006, *Decontaminarea solurilor poluate cu compuși organici*, Editura SITECH Craiova.