NATURAL ATTENUATION FACTOR IN ENHANCING NATURAL ATTENUATION OF CRUDE OIL ON A CONTROLLED POLLUTED HAPLIC LUVISOL IN ORADEA, ROMANIA

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Abstract

The biodegradation is the process used for the degradation of the pollutants from environment or for the reduction of their toxicity, through the usage of the living organisms, microorganisms and plants (phytoremediation), these acting through many mechanisms: phytoextraction, phytostabilization, rhizofiltation, phytodegradation and phytovolatilization.

The natural attenuation is a process more complex than biodegradation, having a larger meaning, the reduction of the contaminants concentration being realized, moreover through the physical-chemical mechanisms, which can immobilize or decrease the pollutant concentration from environment (advection, dispersion, dilution, diffusion, volatilization, sorbtion/desorbtion, ion exchanges, abiotic complexing, etc.).

It was defined the concept of enhancement of the natural attenuation, that refers to the measures taken for the initiation or intensification of the process of natural attenuation with the aim of the faster decrease of the pollutant concentration from environment. For the screening of the pollutants natural attenuation it is recommended the using of Natural Attenuation Factor (NAF), which provides information regarding the speed of the process development.

The aim of this paper is the estimation of the Natural Attenuation Factor (NAF) of the crude oil from Suplacu de Barcău, under the conditions of the controlled polluted soil and different measures of Enhancing Natural Attenuation (ENA) through the administration of fertilizers, (manure, complex fertilizer and combinations of them) from the experimental field Oradea.

Natural Attenuation Factor (NAF) has got values between 0,56 %/year, in the Natural Attenuation (NA) process of variants polluted with 3 % crude oil and 0,90 %/year for the Enhancing Natural Attenuation (ENA) process through organic and complex fertilization (manure x NPK).

Key words: soil pollution, biodegradation, natural attenuation factor, fertilizing system.

INTRODUCTION

The main sources of soil pollution by hydrocarbons of different kinds are as follows: extractive industry, manufacturing, transport and refueling of vehicles.

For the Romania's conditions one considers that the main source of pollution is the extraction fields where the crude oil, waste oil and salt water spills caused historical pollution of nearly 50,000 hectares of land. In the west of the country, i.e. Bihor County, one inventoried an area surfacing roughly 200 hectares of land contaminated with oil residues within the oil extraction fields from Suplacu de Barcau, Marghita and Oradea near the Petrolsub refinery from Suplacu of Barcău (Sabău et al., 2011).

Crude oil, waste oil and salt water, as soon as they reach the soil surface by means of spilling over or reaching the bed of the soil profile, by rising via underground broken pipes, are subject to transportation processes (advection, diffusion and dispersion), and retention on the solid particles surface (adsorption, precipitated by ion exchanges or abiotic complexation) with the risk of underground water pollution (Baliga et al., 2010).

These processes are accompanied by a reduction in pollutant concentration due to a possible volatilization, dilution or to their physical, chemical or biological degradation. The process by which the living organisms, microorganisms and plants degrade soil and groundwater pollutants is known as biodegradation.

Although this essential function of soil i.e. organic matter biodegradation has been known for hundreds of years and is being attributed to the microorganisms living in soil, in the early '90s, the decomposition capacity of soil and water pollutants was called "in situ" rehabilitation (Vidali, 2001).

Bioremediation of soils contaminated with organic contaminants which are intrinsically produced under natural conditions, without operating engineering technology, is called natural bioremediation. This natural bioremediation of soil polluted with organic contaminants is carried-out not only by the action of soil microorganisms (i.e. bacteria, fungi, etc.), but also by cultivated plants that are playing an important role and their action is called phytoremediation (Dzhura et al., 2008).

Plants cultivated on contaminated land act to reduce the concentration of pollutants in the soil in several ways as follows: phytostabilisation, phytoextraction, rhizodegradation and phytovolatilisation (Gerhardt et al., 2009).

Nowadays the concept of bioremediation, including phytoremediation, widely used in natural, intrinsic, "in situ" decontamination of contaminated soil and water is replaced with the notion of natural attenuation (NA) which is a broader concept than the biodegradation term due to the fact that, in order to reduce the concentration of soil contaminants, there are other environmental related physicochemical processes (i.e. advection, dispersion, dilution, diffusion, volatilization, sorbtion/desorbtion, ion exchange, abiotic complexation, etc.) that can immobilize or destroy contaminants (Wiedemeier et al., 1999).

Natural attenuation (NA) has been very diversely defined, but the most complete definition can be considered the Environment Organization Symposium from Bavaria's held in the city of Augsburg, i.e. "a set of physical, chemical and biological processes occurring in soil and aquifers without human intervention". On this occasion it was noted that, depending on the environmental conditions of the contaminated site, these processes act differently to reduce the mass, toxicity, mobility, volume and concentration of contaminants in soil and aquifers (Weber, 2003).

Natural attenuation (NA) has been accepted as modern remedy technology for the polluted sites, first of those polluted with organic contaminants and then moving on the sites polluted with heavy metals due to its low implementation cost. The implementation of natural attenuation for the intrinsic bioremediation of soils and waters contaminated sites involves screening the contaminated sites (Brady et al., 1999) to understand soil characteristics (porosity, hydraulic conductivity, adsorption capacity, etc.) and pollutant characteristics (concentration, composition, viscosity, etc.) and Monitored Natural Attenuation (MNA) to establish Natural Attenuation Factor (NAF) required for mathematical simulation of pollutants outage evolution in time (Alboiu et al., 2011).

Natural Attenuation Factor (NAF) is:

$$NAF = HDF + SF + R_{inv} + BF;$$

Where:

HDF – Hydrologic Dilution Factor;

SF – Sorbtion Factor;

R_{inv} – Irreversible Uptake;

BF – Biodegradation/Chemical Transformation Factor.

Natural attenuation (NA) using bioremediation becomes more effective when bio-augmentation activity (selection and inoculation of microorganisms in the rhizosphere) is combined with agronomic practices designed to stimulate the activity of microorganisms and plant vegetative mass growth (Glick, 2010).

In order to stimulate biodegradation processes in soils polluted with hydrocarbons the recommended agronomic practices are as follows: correcting soil acidity by application of amendments, organic and mineral nutrients for correcting the carbon/nitrogen (C/N) ratio and boosting vegetative mass and soil aeration by soil deep loosening work (Kovacs, 2012).

If comparison is made with *natural attenuation* (NA) the bioremediation correspondence by applying engineering measures to stimulate the reduction of the concentration of pollutants in soil one was defined the *Enhancing Natural Attenuation* (ENA) notion (Onifade, 2007).

In Romania research was performed on bioremediation of soils polluted with crude oil in western area i.e. the city of Oradea, being evaluated the effects of oil pollution on agricultural crops; as for the conditions in the southern Romania, where oil pollution is accompanied by salted water pollution, bioremediation was set by using microorganisms selected indigene microflora (Toti, 2003).

This paper aims that, starting from the outcome from the first three years of field research in Oradea experimental field (1993-1995), Bihor county, and since an unpolluted soil is considered the soil with an oil concentration less than 1 % oil and production losses of less than 5 % as compared to a neighboring uncontaminated plot (Florea, Munteanu, 2000), to set the values of the Natural Attenuation Factor (NAF) for both the *Natural Attenuation* (NA) variants and *Enhancing Natural Attenuation* (ENA) surveyed.

MATERIAL AND METHOD

The reason for which, The Experimental Field of controlled pollution with crude oil, brought from Suplacu de Barcău, Bihor County was mounted on a land at Research and Development Station Oradea is that almost a half of the soils so polluted in Romania are Luvosoils (49,4 %) the site being occupied by a haplic luvisoil.

The haplic luvosoil from Experimental Field has moderate acid reaction (pH = 5.51), low content by humus and total nitrogen on the plowed horizon and high content of colloidal clay (< 0.02 mm) in Bt argic horizon, of almost 40 %.

The crude oil from Suplacu de Barcău, in comparison with the other deposits from Romania is characterized by the predominance of the heavy fractions, the percent of gross fractions being: 40.1 % for oils, 35.3 % for asphaltine and 22.0 % for diesel, while the percent of lighter fractions are: 1.3 % for gasoline and kerosene.

The Experimental Field was installed in 1993 consisting of two experiments, the first to assess the effects of different concentrations of crude oil on crop plants, during Natural Attenuation (without any ameliorative measures) and second to Enhancing Natural Attenuation through the application of organic and mineral fertilization systems.

The first experiment consists of micro parcels of 1 m^2, located in the Latin square, randomized in four repetitions, under controlled polluted by crude oil with 0, 3, 9, 15 and 30 l/m^2, leading to the following crude oil concentrations reported in thick 20 cm plowed horizon: 0 (unpolluted control), 1, 3, 5 and 10 %.

The second experiment is the type 2 x 4 x 4, with three factors, after the system of subdivided parcels of 1 m^2, randomized, set out in four repetitions. The studied factors are:

Factor A: Crude oil pollution: a_1 – unpolluted control; a_2 - polluted by crude oil, in concentration of 3 % (9 l/m^2) on plowed layer;

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;

Factor C: Mineral fertilizer: 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;

Experimental Field was cultivated in the first three years with millet and then in the next seven years with spring wheat, Speranța variety.

RESULTS AND DISSCUSIONS

In order to achieve objectives, evaluating of natural attenuation factor (NAF) in natural attenuation (NA) and enhance natural attenuation (ENA) processes, of controlled contaminated parcels with the crude oil concentration of 3 % per ploughed layer we analyzed the evolution of millet-hay yields, in the first three years of research conducted in the experimentally field in Oradea, Romania.

For all variants investigated, millet-hay yields were lower in the first year of research, they ranging between 12.1 q/ha for natural attenuation (NA) and 20.4 q/ha for the cumulative effect of manure quantities and mineral fertilizers doses administered. In this year, the mineral fertilization (NPK) and the combination of mineral and organic fertilization achieved increases of percentage yields by + 6.1 % and + 15.8 % respectively (Table 1).

Table 1

Average yields of millet-hay registered in the first three years of researches in the experimental field from Oradea, Romania

Variant Code	1993			1994			1995		
	q/ha	%	Percentage differences	q/ha	%	Percentage differences	q/ha	%	Percentage differences
UC	17.6	100.0	-	44.2	100.0	-	40.7	100.0	-
NA	12.1	68.7	-31.3	25.5	57.7	-42.3	30.7	75.4	-24.6
OF	17.6	100.0	0	40.1	90.7	- 9.3	46.2	113.6	+13.6
MF	18.2	106.1	+6.1	41.8	94.5	-5.5	49.3	121.2	+21.2
OMF	20.4	115.8	+15.8	42.6	96.4	-3.6	54.0	132.7	+32.7

Note: UC - Unpolluted control; NA - Natural attenuation; OF - Organic fertilizer (manure); MF - Mineral fertilizer (NPK); OMF - Organic and mineral fertilizer (manure x NPK).

Millet-hay crops grow over in the next two years, becoming larger than twice of the first year yields. Percentage yield differences reported at control unpolluted variant of natural attenuation variant (NA) shows that they are negative in all years studied, ranging between -24.6 % and -42.3 %. It can also be noted that in the second year, the percentage differences of yields are negative for all variants studied, and then, in the last year 1995, they become positive (from +13.6 to +32.7 %) less for natural attenuation (NA) variant.

If in the conditions of controlled experiments, conducted in green house, obtained yields during natural attenuation processes are less affected by weather conditions, which can be controlled, in terms of field experiments, annual climatic conditions, induce vary widely of yields.

Thus, in the three years period of observation were established second degree polynomial correlations between rainfall of the vegetation season and yields of studied variants, that are statistically significant for natural attenuation, organic fertilization and mineral fertilization alternatives and only distinct significant in the case of the cumulative effect of organic and mineral fertilization (Fig. 1).

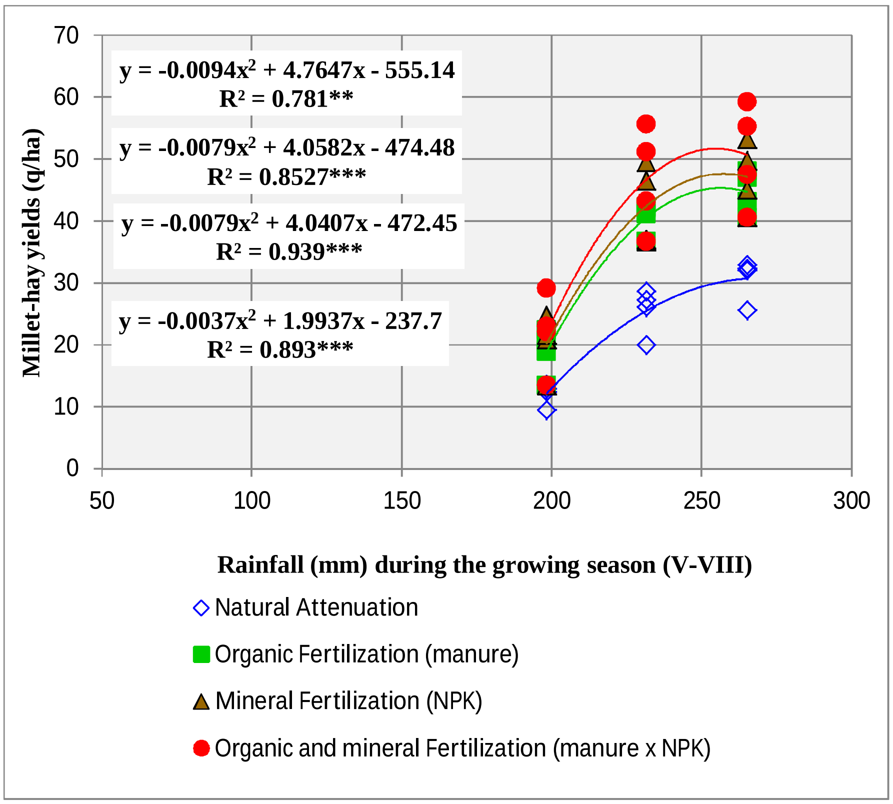

Fig. 1. Influence of rainfall (mm) during the growing season (months V-VIII) on millet-hay yields (q/ha)

Correlative links established between average temperatures in the growing season and yields of millet-hay, during the observations are also second degree polynomial type, very and distinct statistically significant (Fig. 2).

Form of regression curves so derived show that for all variants analyzed, the yields increase with increasing rainfall, recorded a peak between 250 and 300 mm and they are reduced with increasing average temperatures, realizing their maximum in the range 17-18 °C.

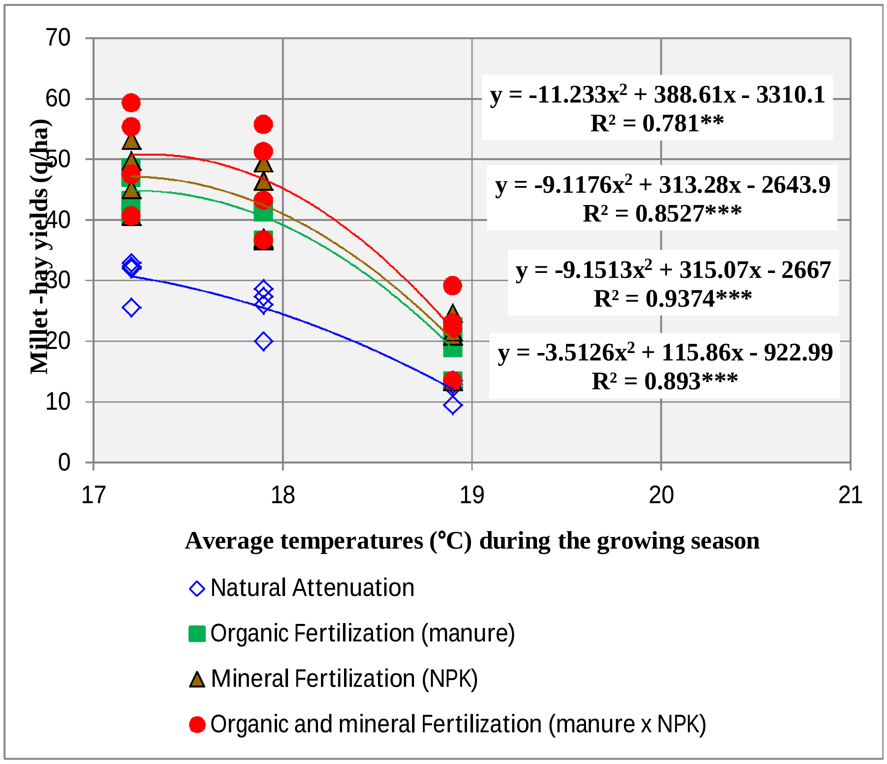

Fig. 2. Influence of average temperatures (°C) during the growing season (months V-VIII) on millet-hay yields (q/ha)

If we analyze the evolution of yield differences between variants of natural attenuation and enhanced natural attenuation studied and unpolluted control variant, expressed in percent, during the three years of observations can also establish a second-degree polynomial correlations (Fig. 3).

These correlative links are statistically significant, less natural enhancing attenuation alternative, using organic and mineral fertilizer (OMF) for which the correlation coefficient R^2 = 0.577 is very close to the value of the limit significance, R^2 = 0.58 (Table 2).

Since legal regulations in Romania established the border between unpolluted and one weak polluted soil by yield losses percentage, more smaller than 5 % in comparison with unpolluted witness, from the above second degree equations we can set the time that they fall below this limit. These time periods are higher in NA variant, of 3.59 years and lower of 2.23 years in OMF variant.

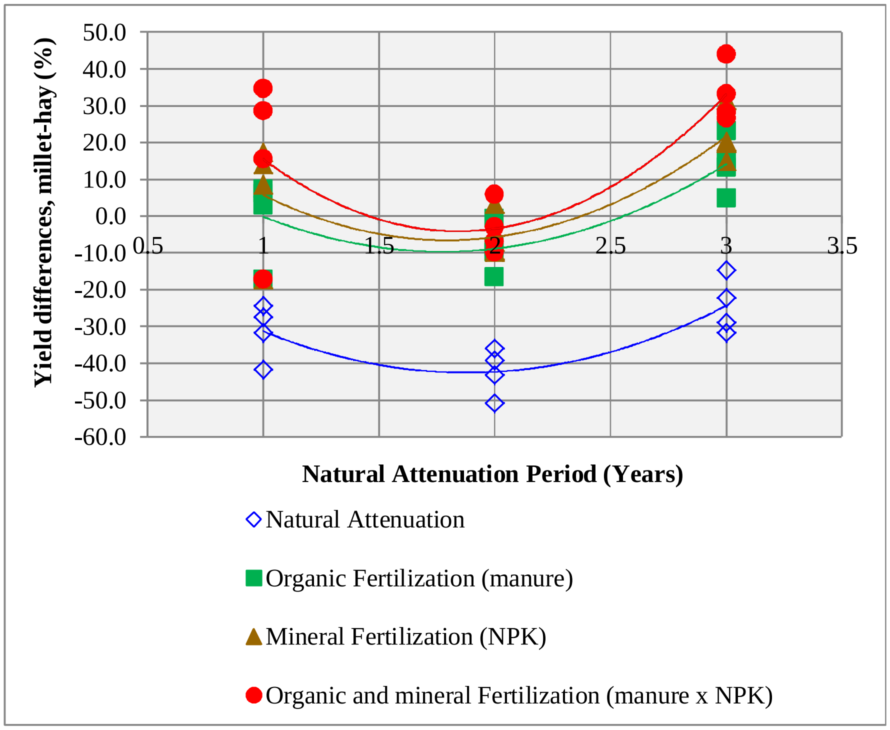

Fig. 3. Influence of natural attenuation period (years) on the yield differences in millet-hay (%)

Table 2

Calculation of Natural Attenuation Factor (NAF)

Variant Code	Regression equations	Correlation coefficient R^2	Statistical signifi-cance	Natural attenuation period (Years)	Natural Attenuation Factor NAF (%/year)	±
NA	$Y=14.49\ X^2-54.488\ X+8.6745$	0.5844	*	3.59	0.56	-
OF	$Y=15{,}803\ X^2-56.083\ X+40.105$	0.6085	*	2.56	0.78	+0.22
MF	$Y=19.337\ X^2-69.377\ X+55.71$	0.611	*	2.37	0.84	+0.38
OMF	$Y=27.636\ X^2-101.77\ X+89.6$	0.5777	-	2.23	0.90	+0.44

Note: NA – Natural attenuation 3 % concentration of crude oil; OF – Organic Fertilization with manure; MF – Mineral fertilizer with complex fertilizers (NPK); OMF – Organic and Mineral Fertilization with different quantities of manure and different complex fertilizers (manure x NPK).

The same legal regulations, in the case petroleum hydrocarbon the limit concentration which a soil is considered unpolluted is 100 mg/kg dry soil, or 1%. Thus, in such time periods established, initial concentration of 3 % crude oil has been reduced by natural attenuation to less than 1 %.

For experimental field conditions, Natural Attenuation Factor (NAF) or reduction average speed of crude oil concentration, from 3 % to 1 %, (%/year) is between 0.56 %/year on Natural Attenuation (NA) option and 0.90 %/year on enhance natural attenuation process by organic (manure) and mineral (NPK complex fertilizers) fertilizer (MOF).

The use of soil fertilization systems in the Enhancing Natural Attenuation (ENA) process, Natural Attenuation Factor (NAF) values increases, compared to Natural Attenuation (NA) by 0.22 %/year for organic fertilizer OF (manure), 0.38 %/year for mineral fertilizer MF (NPK) and 0.44 %/year for organic and mineral fertilization OMF (manure x NPK).

CONCLUSIONS

Hay yields of millet, made in studied variants from the experimental field, Oradea were lower than production by the unpolluted witness (-31.3 to 0,0%) in the first year (1993) and for the third year (1995) they are higher for all variants of Enhancing Natural Attenuation (ENA) increasing from + 13.6 % to + 32.7%, less Natural Attenuation (NA) option (-24.6 %).

Yields during Natural Attenuation (NA) and Enhance Natural Attenuation processes varies greatly from year to year, influenced by the climatic conditions of the years recorded, rainfall and average temperatures during the growing season.

Natural Attenuation Factor, (NAF) determined through established correlations between yield differences (%) and observation period (years) has values between 0.56 % of crude oil/year on Natural Attenuation (NA) variant and from 0.78 to 0.90 % of crude oil/year on Enhance Natural Attenuation (ENA) variants, using different fertilization systems.

Organic Fertilizer (OF) with varying amounts of manure increases the value of Natural Attenuation Factor (NAF) in comparison to Natural Attenuation of 0.22 %/year, Mineral Fertilization (MF) with different doses of complex fertilizers with + 0.38 %/year, and their cumulative effect (OMF) produces an increase of 0.44 %/year.

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