# BIODEGRADATION FACTOR OF THE CRUDE OIL IN SOIL UNDER THE CONDITIONS OF THE NATURAL ATTENUATION OF THE CONTROLLED POLLUTED SOIL IN ORADEA

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***Abstract***

*The Natural Attenuation (NA) of the pollutants in the environment, involves beside the natural biodegradability also the physical-chemical processes that immobilize and decrease the pollutants concentration. The main feature of this process is the Natural Attenuation Factor (NAF) that provides information regarding the speed of the process development, including in its composition the Biodegradability Factor/ Chemical Transformation Factor (BF) of the pollutants. The Natural Attenuation Factor is used for mathematic simulation of the process in subsoil regarding the evolution of the pollutants' concentration, by using specialized software.*

*The aim of this work is the estimation of the Biodegradability Factor (BF) of the crude oil from Suplacu de Barcău, under the conditions of the controlled polluted soil with different crude oil concentrations from the experimental field of Oradea.*

*The values of the Biodegradability Factor (BF), established under the conditions of the experimental field of Oradea (1993-2002) are higher in the first three years when the polluted parcels were cultivated with millet (0,3 - 2,52 %/year) than in the last seven years when the parcels were cultivated with spring wheat (0,22 - 1,07 %/year).The highest values of the Biodegradability Factor are obtained for the variants with the maximal concentrations of the pollutant (10 % crude oil on ploughed layer).*

**Key words:** biodegradability, natural attenuation, monitoring of natural attenuation, biodegradability factor.

## INTRODUCTION

The natural attenuation of the pollutants in the soil and groundwater is a relative new concept, although it was known since a long time the soil capacity to transform the organic matter from the animals and vegetal rests into products that can be reused in the natural cycles. These processes were actually the only mean of remediation of the soil and of the aquifers before the development of the modern technologies used in the processes of the ecological restoration of today. (Madsen E.L., 1998)

The first researches regarding the natural attenuation began in the United States of America in the first half of the '90s, but the natural attenuation was used at the remediation of contaminated sites even before the appearance of the first scientific works on this theme.

The Committee on Intrinsic Remediation, The Water Science and Technology Board, The Board on Radioactive Waste Management, The

Commission on Geosciences Environment and Resources, 2000 reminds about the pollution of the Coast Guard Base of Traverse City, Michigan in the year 1969 with 95m$^3$ aviation fuel. The pollution was highlighted only in the year 1980 when it was highlighted the BTEX-presence (Benzene – Toluen – Etilbenzene - Xilen) in the groundwater in the region. The later researches performed in this region highlighted the fact that after the pollution source was eliminated, the natural attenuation was effective and led to the successful rehabilitation of the site.

In the early '90s the self-cleaning phenomenon of the environment was attributed to the microorganisms that have the capacity to discompose the pollutants in the water and soil and it was named bio-rehabilitation in situ (Wiedermeier, et al. 1995)

In this way it is done the difference between the decomposition process of the degradable material, named bio-degradation and the technologies, used for the bio-degradation of the pollutants in the environment, named bio-remediation (Alexander M., 1994).

Vidali M., 2001, places the bio-rehabilitation in the category of the biotechnologies and defines it as being a process in that the living organisms, microorganisms and plants are used for the degradation of the contaminants in the environment or for their transformation in less toxic forms.

Regarding the Bioremediation it is made the difference between the natural, intrinsic bioremediation and engineering bioremediation that uses engineering technologies to simulate the activity of the microorganisms and to increase the biodegradation rate of the contaminants.

On the basis of the observations regarding the natural remediation of the polluted sites, the notion of biodegradation was extended being replaced by the notion of Natural Attenuation (NA) that includes also the natural physic-chemical processes that can immobilize or destroy the contaminants. Thus because of the simplicity, efficiency and reduced costs it got that the natural attenuation (NA) to be accepted as a method of remedy of the polluted sites, first for the sites contaminated with hydrocarbons and second for that contaminated with chlorinated solvents, heavy metals, pesticides, radionuclides, etc. (Wiedermeier, et al. 1999)

The definition of the natural attenuation (NA) as natural, intrinsic remediation of the pollutants is very diversified.

The easiest definition, given by ASTM (American Society for Testing and Materials) says that “The natural attenuation is a potential remedy for the contaminants, that reduces quantitatively the concentration of the pollutants from the environment in order to protect the human health and environment”.

The Agency for Environment Protection from USA defines the natural attenuation as being an assembly of processes that includes: biodegradability, dispersion, dilution, absorption, volatilization, radioactive degradation and the chemical or biologic stabilization, transformation or destruction of the contaminants.

The Department of the American Army, implied in the attenuation processes of the pollutants, especially hydrocarbons, defines this mechanism as being a reduction of the contaminants concentration in the environment through biological processes (aerobic and anaerobic degradation, absorption by vegetables and animals), physical phenomena (advection, dispersion, diffusion, volatilization, sorption/desorption) and chemical reactions (ions changes, complexion, abiotic transformation).

In Europe the definition given to Natural Attenuation (NA) at the symposium of the Environment Organization of Bavaria land in Augsburg presents that this is "*an assembly of physical, chemical and biological processes that take place in soil and aquifers without the human intervention"*. It was mentioned the fact that depending on the environmental conditions on the contaminated site, these processes action in different proportions for the reduction of the mass, toxicity, mobility, volume and concentration of the contaminants in soil and aquifers. (Weber, 2003)

In our country, the notion of Natural Attenuation (NA) being relatively new was defined in the Decision no. 1403/26.11.2007 on the restoration of the soil, subsoil and terrestrial ecosystems that have been affected through natural attenuation. Thus this Decision defines the concept of the Natural Attenuation through an assembly of conditions and geologic, physic and chemical phenomena that produce in time the neutralization or the decrease of the concentrations of pollutants in the geologic environment (National Agency for Environment Protection, ANPM, 2011).

Baliga et al, 2010, improves the definition of the Natural Attenuation of Weber 2003, mentioning the complexity of the mechanisms that are produced underground, without human intervention.

All guides regarding the application of the Natural Attenuation mention the necessity of the screening of the contaminated sites and the necessity of the monitoring of the process of Natural Attenuation.

The screening of the contaminated sites refers to the identification of the local natural conditions and to the quantification of the possibilities of the pollutants natural attenuation. Brady, et al., 1999 recommends for the screening of the polluted sited the evaluation of the Natural Attenuation Factor NAF:

$$NAF = HDF + SF + R_{inv} + BF; \qquad [1.]$$

where:

NAF - Natural Attenuation Factor;

HDF - Hydrologic Dilution Factor;

SF - Sorbtion Factor;

$R_{inv}$ - Irreversible Uptake;

BF - Biodegradation/Chemical Transformation Factor;

The monitoring of the Natural Attenuation, MNA (Monitored Natural Attenuation), refers to the controlling on long term of the natural attenuation processes in order to point out the reduction processes of the contaminants both quantitatively and also qualitatively and to describe their efficiency. The degradation and transport processes take place by itself, without human intervention, they are only monitored and observed. (Wiedermeier, et al. 1995)

The importance of the monitoring of the Natural Attenuation can be pointed out by the example of the airbase from Vandenberg, California, where the soil was contaminated with 2,16 $m^3$ fuel as consequence of the cracking of a tank from the alimentation station. After the monitoring of the natural attenuation of the contaminated site it was pointed out the fact that BTEX (Benzene –Toluen – Etilbenzene – Xilen) is stationary indicating the biodegradability, while in the case of BTBE (Metil - Terbutil - Eter) the plume is in expansion indicating that the natural attenuation is not sufficient (Durrand, et al., 1999).

The observations done at the monitoring of the natural attenuation (MNA) can be used for mathematical modeling of the process of Natural Attenuation (NA) with the aim of the prognosis of the evolution of pollutant plume and of the degradation and retention processes of the pollutants in soil and aquifer.

For the mathematical modeling of the flow and transport processes through soil and aquifers regarding the prognosis of the evolution of the pollutant plume it is use the software PMWin (Processing Modflow for Windows) and for the modeling of the equilibrium thermodynamic reactions that characterize the degradation and retention of the pollutants it is used the software FreeqC. (Chiang and Kinzelbach, 2005; Parkhurst and Appelo, 1999)

One of the most important characteristics necessary for the prognosis of the evolution in time of the concentration in the pollutant plume is the Natural Attenuation Factor (NAF) that can be obtained for different scenarios simulated using the program FreeqC or can be experimentally determined under the laboratory or field conditions.

For the advantages of the natural attenuation, highlighted in the researches done in USA and for the existence in Europe of numerous polluted sites, the European Commission admits to financing in the year 2001 the Project CORONA (**C**onfidence in f**OR**ecasting **O**f **N**atural **A**ttenuation), at that take part Universities and Research Centers from Great Britain, Germany, Switzerland, Denmark, Holland, Italy and Czech Republic, having as aim the confidence increase in the possibilities of the prognoses of the Natural Attenuation (Lerner, et al, 2005)

Germany made researches regarding the controlled natural retention and degradation of the pollutants for the rehabilitation of the groundwater within the national program KORA (**KO**ntrollierter natürlicher **R**ückhalt und **A**bbau von Schadstoffen bei der Sanierung kontaminierter Grundwässer und Böden), that comprehends 8 subprojects, each of them following another type of pollutants. (ITVA, 2003)

The researches done in our country focused especially on the crude oil biodegradation in the contaminated soils in the west of the country, using the phytoremediation (Colibaş et al, 1995; Sabău and Şandor, 2006; Şandor Maria, et al, 2007) and the bioremediation of the soils polluted with crude oil and salt waters in the south of the country. (Toti et al, 2003)

## MATERIAL AND METHOD

The researches carried out in Oradea had as an objective the study the natural attenuation (NA) of crude oil from Suplacu de Barcău, used for controlled pollution of soil, on the ploughed layer.

The experimental field was set up in 1993 and is made out of micro parcels of 1 $m^2$, set up in latin square, randomized in three repetitions, polluted under control by crude oil, with 0, 3, 9, 15 and 30 $l/m^2$, thus having the following concentrations: 0 in the ploughed layer (unpolluted witness), 1, 3, 5 and 10 %.

The field was cultivated with millet in the first three years (1993 – 1995), a plant that has an increased tolerance to pollution and then for the next seven years (1996 - 2002) with spring wheat, Speranța breed.

The objective of this paper is to estimate the biodegradation factor (BF) of the crude oil from Suplacu de Barcău, in the conditions of under control polluted soil by different concentrations from Oradea (Romania), experimental field.

The biodegradation factor (BF) is interpreted in this paper by the speed, rapidity of crude oil degradation and it is express by the quantity of pollutant one-self degraded in the time of one year.

## RESULTS AND DISSCUSIONS

In the conditions of polluted soils, the difference between a polluted soil and an unpolluted soil can be realized by the losses of yields, in comparison with the yields of unpolluted parcels. Florea and Munteanu, 2000 consider that the limit between the unpolluted and polluted soils is the yield losses of 5 %.

In the first three years, (1993-1995) when the polluted parcels was cultivated with millet, the yield losses in comparison with unpolluted parcels was between 6,9 % and 67,8 %, smaller for 1 % crude oil concentration and bigger for the maximum of crude oil concentration of 10 %.

Between the yield losses of millet hay and the time from under control pollution was established correlation links, the type of these are polynomial second degree. The statistical signification of these is between very near statistical significance ($R^2$=0,5754) in the case of 1 % crude oil pollution and very significant ($R^2$=0,9628) for the 10 % concentration of the pollutant. (Fig.1.)

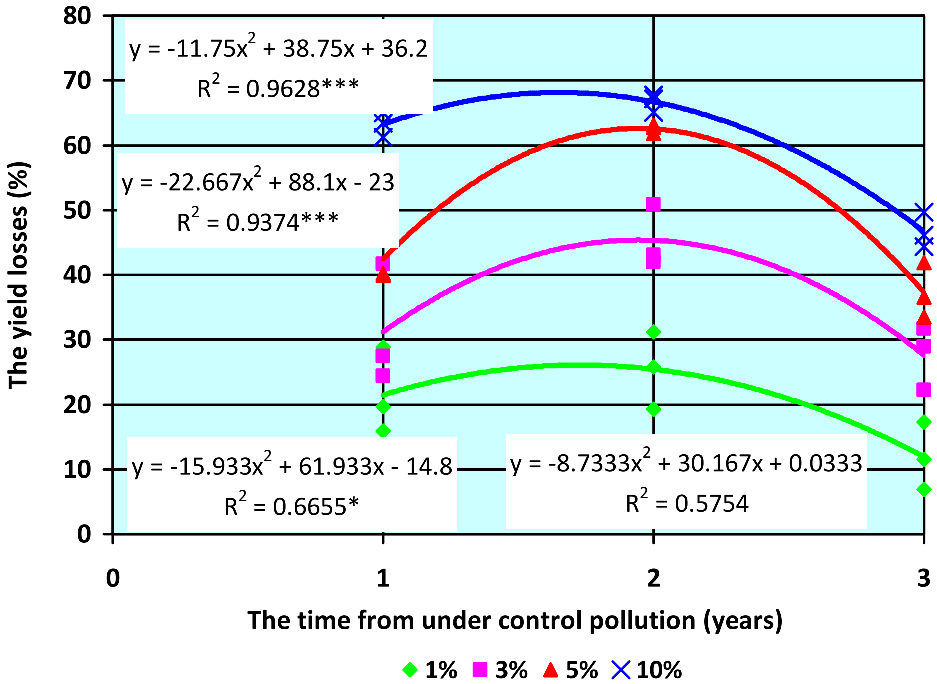


Fig.1. The links between the yield losses of the parcels under control polluted by 1, 3, 5, and 10 % crude oil and the time of experiment.

The time evolution of yield losses of millet hay, for all variant of crude oil concentrations was registered in the second year of the experiment, afterwards, in the third year the yield losses are registered the minimum values.

If we consider that the soil became unpolluted when the yield losses come under 5 % and we put this condition in the established equations result the time of crude oil biodegradation, in years. (Table 1.)

Table 1.
The estimation of biodegradation factor (BF) after the yield losses of millet (1993-1995)

| Initial concentration of crude oil (%) | The condition equations | The time of biodegradation (years) | The average biodegradation factor, BF (%/year) |
|---|---|---|---|
| 1 | $-8,733\ X^2 + 30,167\ X - 4,9667 = 0$ | 3,28 | 0,30 |
| 3 | $-15,933\ X^2 + 61,933\ X - 19,8 = 0$ | 3,54 | 0,85 |
| 5 | $-22,667\ X^2 + 88,1\ X - 28,0 = 0$ | 3,54 | 1,41 |
| 10 | $-11,75\ X^2 + 38,75\ X + 31,2 = 0$ | 3,97 | 2,52 |

In the hypostasis that all quantity of crude oil administrated was degraded, when the yield losses of millet hay became 5 %, the time of biodegradation is between 3,28 years for 1 % initial concentration and 3,97 years for 10 % concentration of crude oil.

The values of average biodegradation factor (BF) increase from 0,3 %/year (1 % crude oil initial concentration) to 2,52 %/year (10 % initial concentration) these show the good tolerance of millet for the crude oil contaminated soils.

In the next seven years, the experiment was cultivated with spring wheat and the trend of yield losses is of decrease from the four year to the ten year, from all pollutant concentrations studied. The yield losses of spring wheat became fewer than 5 % in the eight year, from 1 % crude oil concentration and in the ninth year, from the 3 % crude oil concentration.

The links between the yield losses in spring wheat and the time established in the last seven years of experiment are linear, with different statistical significances. (Table 2.)

Table 2.
The estimation of biodegradation factor (BF) in function of spring wheat yield losses (1996 – 2002)

| Initial concentration of crude oil (%) | The linear equation | Statistical significance $R^2$ | The time of biodegra-dation (years) | The average biodegradation factor, BF (%/year) |
|---|---|---|---|---|
| 1 | $Y = -6,0192\ X + 50,083$ | 0,4785 | 7,49 | 0,22 |
| 3 | $Y = -6,4909\ X + 70,347$ | 0,4956* | 10,07 | 0,42 |
| 5 | $Y = -7,1025\ X + 86,684$ | 0,7641*** | 11,50 | 0,59 |
| 10 | $Y = -7,8762\ X + 102,48$ | 0,8226*** | 12,38 | 1,07 |

If in the first three years the values of biodegradation factor are 0,3-2,52 %/year they reduced in the last seven year, being from 0,22 %/year for

1 % concentration to 1,07 %/year for the maximum concentration of crude oil. In spite of the fact that the experiment was cultivated in ten years by two different plants, can be estimated the biodegradation factor (BF) because the yield losses are express, in both cases in the same measure unit, percent.

The links between yield losses in millet-hay and spring wheat and respectively the time of bioremediation are polynomial second degree, very significant, from statistical point of view, less in the variant with 1 % crude oil concentration, when she is near of statistical significance. (Table 3.)

Table 3.

The biodegradation factor (BF) of crude oil from soil

| Initial concentration of crude oil (%) | The polynomial second degree equation | Statistical significance $R^2$ | The time of biodegradation (years) | The average biodegradation factor, BF (%/year) |
|---|---|---|---|---|
| 1 | $Y = -0.863X^2 + 5.5615X + 11.914$ | 0.3942 | 7.51 | 0.13 |
| 3 | $Y = -0.9809X^2 + 7.1076X + 25.215$ | 0.5681*** | 9.43 | 0.32 |
| 5 | $Y = -0.7875X^2 + 4.9096X + 42.917$ | 0.5979*** | 10.72 | 0.47 |
| 10 | $Y = -0.71X^2 + 3.2193X + 59.89$ | 0.6653*** | 11.35 | 0.88 |

Taking in consideration the hypostasis that all pollutant was biodegraded wen the yield losses lower below 5 %, the estimated times of biodegradation are between 7,51 years, for 1 % pollutant concentration and 11.35 years for the maximum of pollutant administrated, 10 %.

The biodegradation factor (BF) estimated in the ten years period is between 0.13 %/year for 1 % pollutant concentration and 0.88 %/year for maximum concentration of contaminant in soil, the values being smaller than the values obtained for millet-hay and spring wheat.

Analyzing the values of biodegradation factor it can say that in the first three years these are more great, the intensity of biodegradation process being higher than in the last seven years.

The values of biodegradation factor (BF) are influenced by the initial concentration of pollutant, these increasing with the growth of the pollutant administrated.

**CONCLUSIONS**

The natural attenuation of the pollutants is a relative new concept, although it was known since a long time the soil capacity to transform the organic matter from the animals and vegetal rests into products that can be reused in the natural cycles.

On the basis of the observations regarding the natural remediation of the polluted sites, the notion of biodegradation was extended being replaced by the notion of Natural Attenuation (NA) that includes also the natural physic-chemical processes that can immobilize or destroy the contaminants.

The main feature of this process is the Natural Attenuation Factor (NAF) that provides information regarding the speed of the process development, including in its composition the Biodegradability Factor/ Chemical Transformation Factor (BF) of the pollutants. The Natural Attenuation Factor is used for mathematic simulation of the process in subsoil regarding the evolution of the pollutants' concentration, by using specialized software.

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