

## RESEARCH REGARDING THE EVOLUTION OF AN OIL POLLUTED SOIL AT SUPLACU DE BARCAU

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### **Abstract**

*Study the time evolution of a soil polluted with oil and oil products was performed on a 15-year period, 1997-2013, it is monitored evolution of the main physical and chemical polluted land every 5 years (1997, 2002, 2007, 2013) compared to a control ground, unpolluted. Both experiences were located on the same type of soil, human intervention is excluded. After indicator values in the study quantifying the polluted soil with control values can be seen that the trophic properties of the soil was polluted after 15 years, they were slightly higher than the control soil, being comparable with a medium soil fertility.*

**Key words:** soil, polluting, correlation, comparison, evolution

### **INTRODUCTION**

Study the time evolution of a soil polluted with oil and oil waste was pursued for a period of 15 years, 1997-2013, the unit taxonomic soil was the soil type albic luvisols being monitored main physico-chemical soil: structure, the bulk density, the content of organic carbon in the humus content, the ratio C / N.

For the study was chosen an area of land dilapidated oil installations located outside fronts of underground fuel, located in the SE structure Suplacu of boats, homogeneous in terms of topography, vegetation and unity taxonomic soil, not Brotherhood canvas is covered, do not benefit from additional intake of rain water in nature, due to leakages recorded on the slopes and not within the scope of the human factor, thus excluding all factors that could influence the accuracy of the results.

### **MATERIAL AND METHODS**

Sampling of soil to perform the set of physicochemical analyzes in 1997 in the opening two soil profiles, soil polluted and unpolluted soil, the latter constituting itself as profile witness in interpreting the results. Physico-chemical complete control on all sections were made only in 1997. In the years 2002, 2007 and 2012 has followed the evolution of time and changes in qualitative and quantitative indicators: structure, bulk density, organic carbon content, humus content, C / N, the polluted soil. Analyses were

performed on samples taken from 0-20 cm depth or 20-24 cm, 0-24 cm depth. It is considered the maximum depth of penetration of oil into the soil.

## RESULTS AND DISCUSSION

Tables No.1 and No.2. They are presented physicochemical properties and hydro indicators for polluted soil and soil used as a control since 197

Table 1.  
*The physicochemical properties of soil and hydro indicators witness, 1977*

Horizons	Ao	AE	Ea	Bt	C
Depth(cm)	0 - 20	20 - 34	34 - 60	60 - 120	120 - 145
Coarse sand (2 to 0,2 mm) %	6,2	9,5	13,2	3,8	1,2
Fine sand (0,2 to 0,02 mm) %	48,3	47,8	43,4	36,9	32,1
Dust (0,02 to 0,002 mm) %	13,6	14,3	24,9	25,6	23,8
Clay (dust 0,002 mm) %	30,9	29,4	18,5	33,7	42,9
Texture	LN	LN	SG	TT	TT
In water ph	5,42	5,28	4,9	5,7	6,4
Organic carbon %	1,27	0,66	0,23	-	-
Humus %	2,20	1,34	0,40	-	-
Total nitrogen %	0,26	0,12	0,08	-	-
C/N ratio	4,9	5,5	2,9	-	-
<b>INDICATORS HYDRO</b>					
Apparent density (mass density) g/cm <sup>3</sup>	1,42	1,46	1,52	-	-
The density (specific gravity) g/cm <sup>3</sup>	2,7	2,7	2,72	-	-
The coefficient of wilting%	10,48	11,04	-	-	-
water capacity field %	24	23,7	-	-	-
Water capacity useful %	13,52	12,6	-	-	-
Total porosity %	47,4	46	-	-	-
Total capacity water%	33,45	31,3	-	-	-

*General aspects of control soil:* medium developed herbaceous vegetation, soil is not affected by pollution, ground water table is at depths of 2m.

Interpretation of results of laboratory analyzes to control soil: sandy loam texture soil on 0-34 cm depth, coarse sandy clay loam in the depth of 34-60 cm and 60-145 cm depth on clay., Grainy soil structure is poorly developed in depth 0-20 cm (Ao), the depth of 20-34 cm poorly made (AE) without the depth of 34-60 cm structure (Ea), prismatic depth of 60-120 cm (Bt) and nonspecific below ground reaction 0-120 cm depth acidic to slightly acidic and under 120 cm., organic carbon content is low, very low humus content, total nitrogen content is very low density (mass density) and hydro indicators show normal values soil type albic luvisols

Table 2.

*The physicochemical properties and indicators for polluted soil hydro 1977*

Horizons	Ao	AE <sub>1</sub>	AE <sub>2</sub>	Ea	Bt	C
Depts(cm)	0 - 20	20 - 24	24-34	34 - 60	60 - 120	120 - 145
Coarse sand (2 to 0,2 mm) %	6,2	9,5	9,5	13,2	3,8	1,2
Fine sand (0,2 to 0,02 mm) %	48,3	47,8	47,8	43,4	36,9	32,1
Dust (0,02 to 0,002 mm) %	13,6	14,3	14,3	24,9	25,6	23,8
Clay (dust 0,002 mm) %	30,9	29,4	29,4	18,5	33,7	42,9
Texture	LN	LN	LN	SG	TT	TT
In water ph	5,1	5,2	5,28	4,9	5,7	6,4
Organic carbon%	8,78	7,63	0,66	0,23	-	-
Humus %	-	-	1,34	0,40	-	-
Total nitrogen%	0,26	0,24	0,12	0,08	-	-
C/N ratio	33,76	31,79	5,5	2,9	-	-
<b>INDICATORS HYDRO</b>						
Apparent density(mass density) g/cm <sup>3</sup>	1,64	1,59	1,46	1,52	-	-
The densaity (specific gravity) g/cm <sup>3</sup>	2,7	2,7	2,7	2,72	-	-
The coefficient of wilting %	10,48	11,4	11,04	-	-	-
water capacity field %	23	23	23,7	-	-	-
Water capacity useful %	12,52	11,96	12,6	-	-	-
Total porosity %	39,26	41,12	46,00	-	-	-
Total capacity water%	23,93	25,86	31,30	-	-	-

*Interpretation of test results and observations to the polluted soil*

Comments made the pitch to the polluted soil

The soil surface is flat, with no external drainage soil surface is flat, devoid of external drainage, grass vegetation is sparse or missing due to pollution accented aspect muddy wetting sharp, high toughness in natural conditions of low humidity, strong smell hydrocarbons.

The soil has high cohesiveness wet, dry, wet plastic, solid and tough in dry, wet tack, high toughness, uncertain passage between Ao horizon and AE thickness of 24 cm infiltration of pollutants.

Interpreting laboratory results from the polluted soil: sandy loam texture soil on 0-34 cm depth, coarse sandy clay loam in the depth of 34-60 cm and 60-145 cm depth on clay. Soil structure no depth 0- 60 cm, depth 60-120 cm prismatic structure and nonspecific below 120 cm., slightly acid pH on 0-120 cm depth, and weak acid below 120 cm., organic carbon levels are elevated in Ao horizons and AE1 on 0-24 cm depth, indicating pollution of organic substances, nitrogen content is very low, C / N ratio of 33.76 to 31.79 respectively Ao horizon horizon AE1 indicates the presence of pollutants in the soil of nature Organic density (mass density) has high values Ao and AE1, due to compaction degree high and compactness accommodated the presence of the pollutant indicators hydro have values different from those of the control sample in the horizons Ao and AE1, due to the compactness of high horizons affected by pollution.

In Fig. no. 1, 2, 3, are shown graphically indicators organic carbon, total nitrogen percentage and C / N, soil polluted soil compared with control values for 1997.

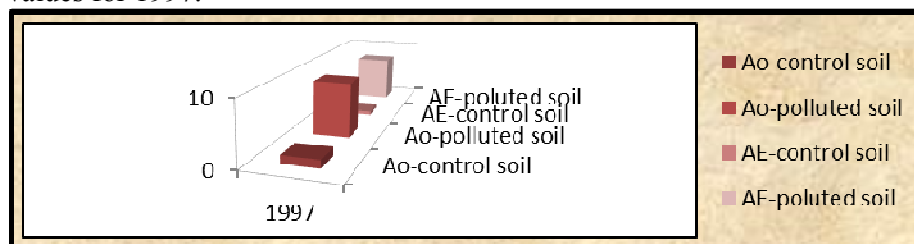


Fig. 1. Comparative values of organic carbon between soil and soil pollution control (1997)

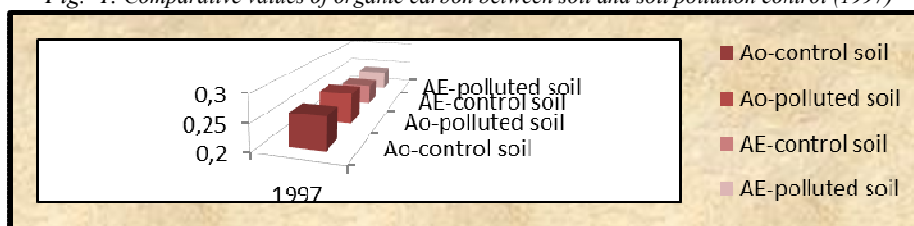


Fig. 2. Comparative values of the percentage of nitrogen in polluted soil and ground control (1997)

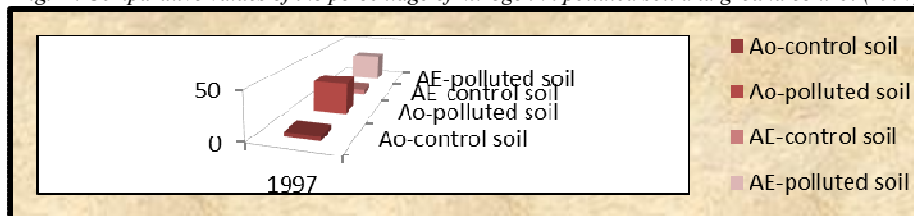


Fig. 3. Comparative values of C / N ratio between the polluted soil and ground control (1997)

### Analytical results from 2002

The result of field observations: the soil surface are visible phenotypic characteristics of soil polluted with oil, there is the presence of a shallow installation herbaceous vegetation consisting of Gramineae and muscle

In Table. 3. presentation of this result physicochemical analyzes carried out after 5 years from the date of commencement of the trial.

Table 3.

*The result of physical and chemical analyzes conducted in 2002 in polluted soil*

Horizons	Ao	AE <sub>1</sub>
Depts(cm)	0 - 20	20 - 24
Structure	early stages of forming the structure of grain	
In water ph	5,4	5,2
Organic carbon %	6,62	6,84
Humus %	-	-
Total nitrogen	0,37	0,31
C / N ratio	17,89	22,06
Apparent density	1,52	1,52

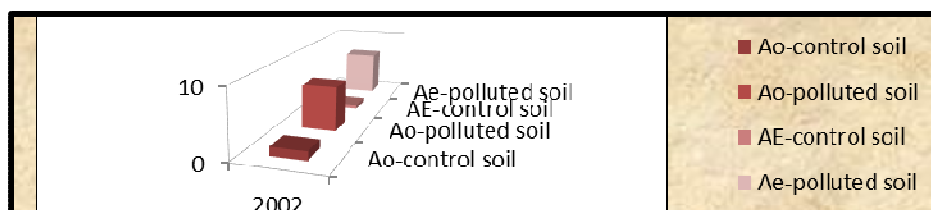


Fig. 4. Comparative values of organic carbon between soil and soil pollution control (2002)

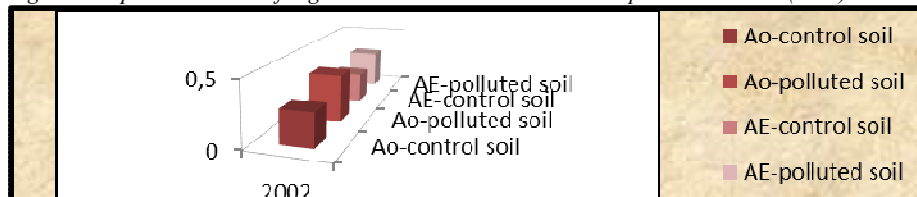


Fig. 5. Comparative values between the percentage of total nitrogen and soil polluted soil control (2002)

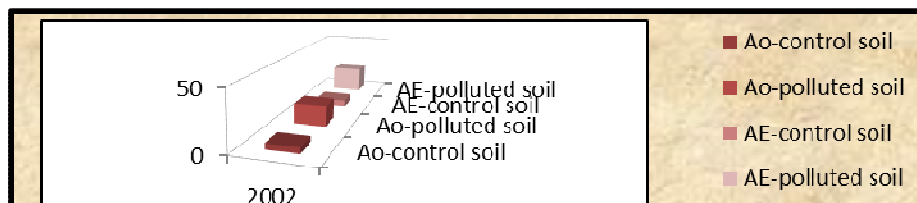


Fig. 6. Comparative values of C / N ratio between the polluted soil and ground control (2002)

Interpretation of results from laboratory and field observations: actual acid value increased by 0.3 units in Ao indicator values decreased organic carbon in Ao horizon from 8.78 to 6.62 and from 7.63 to the AE1 6.84, total nitrogen percentage increased to 0.11 units Ao horizon (from 0.26 at 37) and the unit AE1 0.07 (from 0.24 to 0.31) values C / N ratio decreased significantly from 33.76 to 17.89 in Ao and from 31.79 to 22.06 in AE1, bulk density values decreased in value in both horizons del,52

#### **Analytical results from 2007**

The result of field observations: indicate the presence of vegetation grassy meadow coagulated, composed of species of Gramineae, no signals oil pollution of the soil surface soil, structure formed, grainy weak - medium developed at the top and underdeveloped between 15-24 cm deep.

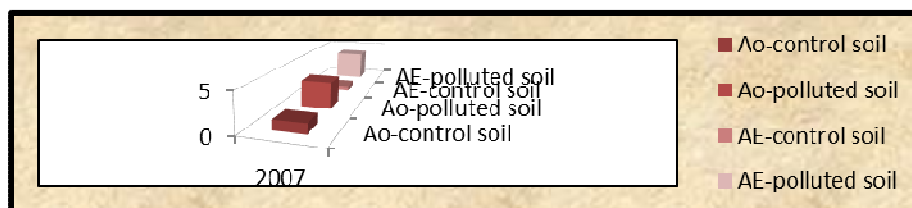
In Table. 4 comprise the result of physical and chemical analyzes carried out to the polluted soil, after a period of 10 years from the start of the study.

Table 4.

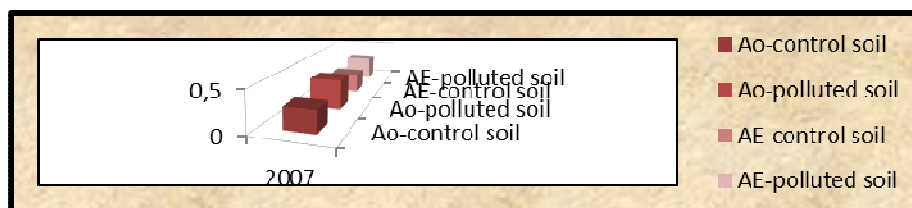
*The result of physical and chemical analyzes carried out to the polluted soil in 2007*

Horizons	Ao	AE <sub>1</sub>
Depts(cm)	0 - 20	20 - 24
Structure	Poorly structure - medium developed	
In water ph	5,9	5,4
Organic carbon %	3,46	3,92
Humus %	-	-
Total nitrogen	0,37	0,31
C / N ratio	10,17	12,64
Apparent density	1,44	1,5

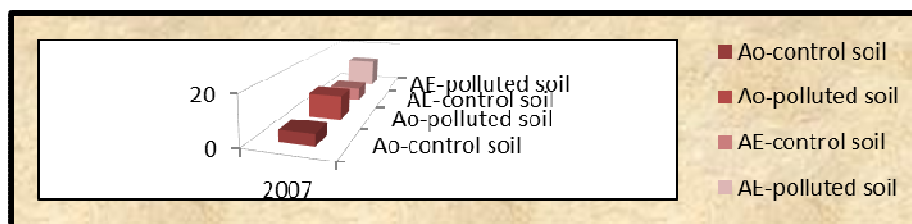
In Fig. no. 7, 8, 9, indicators are presented graphically organic carbon, total nitrogen percentage and C / N, soil polluted soil compared with control values for 2007.



*Fig. 7. Comparative values of organic carbon between soil and soil pollution control (2007)*



*Fig. 8. comparative values of the percentage of total nitrogen, from polluted soil and ground control (2007)*



*Fig.9. Comparative values of C / N ratio between the polluted soil and ground control (2007)*

Interpretation of results from laboratory and field observations: actual acid value increased by 0.5 units in Ao, and 0.2 in the horizon AE<sub>1</sub>, the percentage of organic carbon fell sharply compared with 1997, from 8.78 to

Ao horizon 3.46 and from 7.63 to 3.92 in AE1, the percentage of total nitrogen remained constant at the 2002 level,  $C / N \approx$  record lows being 1/3 of the values of 1997, values bulk density are normal

The considerable decrease of organic carbon values is mainly due to the intensification of microbiological activity of the soil and vegetation installation. The constant value of the percentage of N in 2002 is the result of processes of leaching soluble compounds newly formed N.

#### **Analytical results of 2013**

The result of field observations: the soil is occupied by crops (corn) due to the change the category of use of pasture farmland, is an increase vegetative stronger crop plants located on the former surface pollution in 1997, in relation to the rest of culture, Ao horizon differentiation between the transitional horizon is not clear due to AE preparation of the soil (plowing 28-30 cm deep) and crop maintenance.

In table. 5 is shown the result of physical and chemical analyzes carried out to the polluted soil, after a period of 10 years from the start of the study

Table 5.  
*Result physicochemical analyzes carried out to the polluted soil in 2013*

Horizons	Ao	AE <sub>1</sub>
Depts(cm)	0 - 20	20 - 24
Structure	Structuriă grăunțoasă mediu dezvoltată	
In water ph	6,0	5,7
Organic carbon %	2,8	2,8
Humus %	4,87	4,87
Total nitrogen	0,4	0,4
C / N ratio	7	7
Apparent density	1,40	1,40

In Fig. no. 10, 11, 12 indicators are presented graphically organic carbon, total nitrogen percentage and C / N, soil polluted soil compared with control values for 2013.

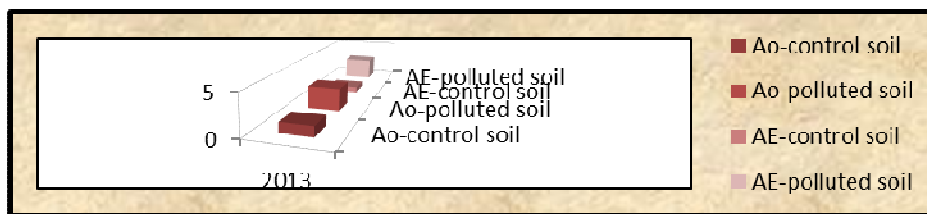


Fig.10. Comparative amounts of organic carbon between soil and soil pollution control (2013)

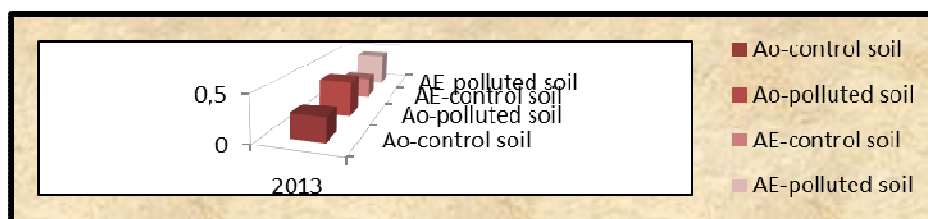


Fig. 11. The comparative values of total nitrogen, from polluted soil and ground control (2013)

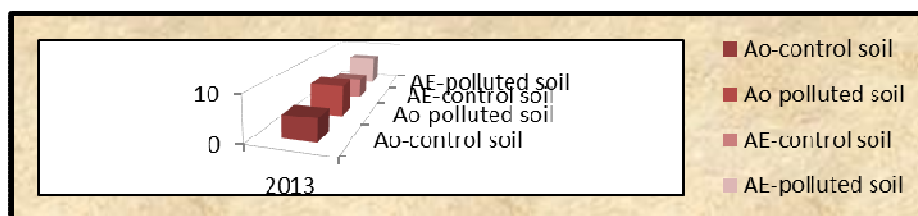


Fig. 12. Comparative values of C / N ratio between the polluted soil and ground control (2013)

Interpreting laboratory results and observations gained ground: the vegetative growth more pronounced registered plants due to organic carbon converted into humus over 15 years of evolution of the soil and the higher percentage of total nitrogen than the areas adjacent organic carbon content is equivalent to the contents of land of medium fertility, percentage of total N is low, but higher than the surrounding areas. The weakness is attributed to compounds N leaching accentuated newly formed, under a slightly acid pH and lack of ground bases.

Results on the development of indicators organic carbon, total nitrogen and C / N in the period 1997-2013

No dashboard. 6 shows the values of the indicators studied the entire study period, 1997-2013, the affected soil pollution.

Table 6.

Table summarizing the indicator values for the period 1997-2013

Year	1997		2002		2007		2013	
Soil horizon	Ao	AE <sub>1</sub>	Ao	AE <sub>1</sub>	Ao	AE <sub>1</sub>	Ao	AE <sub>1</sub>
Organic carbon content%	8,78	7,63	6,62	6,84	3,46	3,92	2,8	2,8
Total nitrogen content in %	0,26	0,24	0,37	0,31	0,37	0,31	0,4	0,4
C / N ratio	33,76	31,79	17,89	22,06	10,17	12,64	7	7

In Figs. 13-17, are the comparative test results on indicator values organic carbon, total nitrogen and C / N ratio between ground control and polluted soil, throughout the survey period, and the time evolution of values.



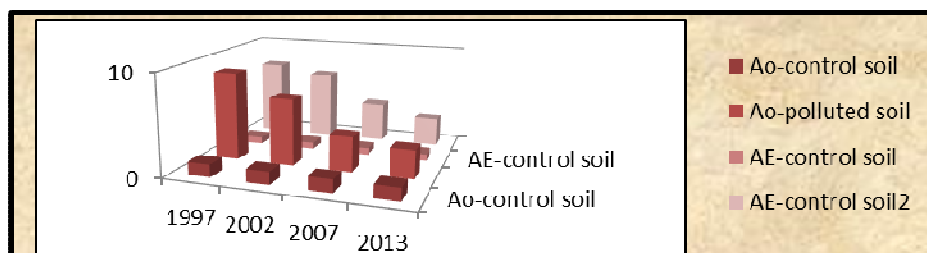


Fig.13. Comparative results on the evolution of organic carbon indicator in the study period 1997-2013

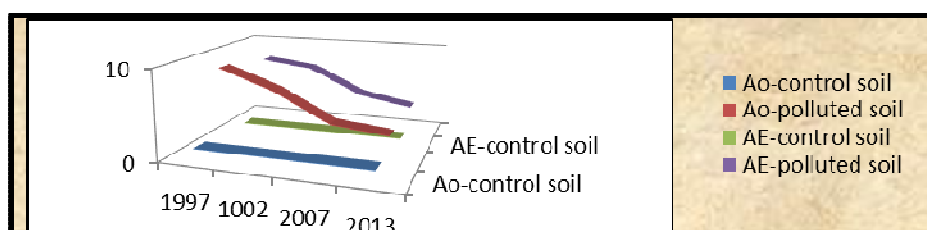


Fig. 14. Comparative results on the evolution of nitrates, total study period 1997-2013

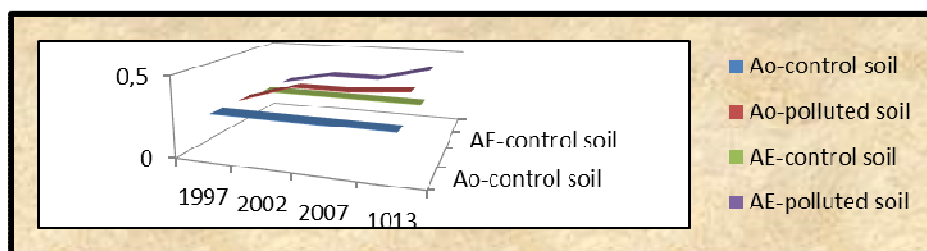


Fig. 15. Evolution of total nitrogen content in soil polluted 1997-2013 period compared with the control soil

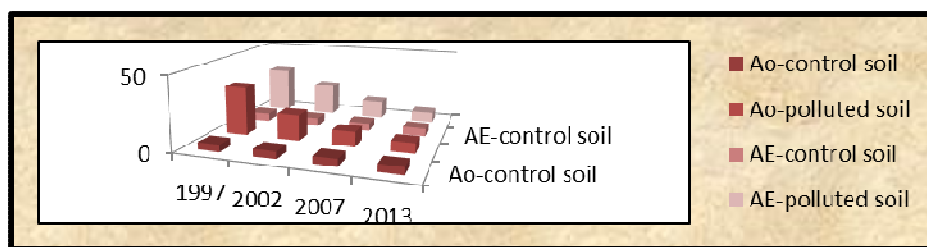


Fig. 16. Comparative results on the evolution of the indicator C / N in the study period 1997-2013

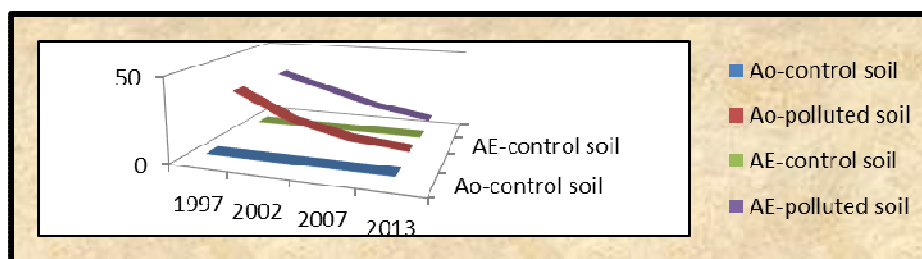


Fig. 17. The evolution of the ratio C / N during the period 1997-2013 of soil polluted soil compared to the control

During the study is a continuous decrease in the value of organic carbon, from 8.78% to 2.8%, the most significant being between 1997 and 2002. Declines continue due to microbiological activity in soil, which is becoming more active inensitate decreases the toxic effect of the pollutant is formed of organic compounds of different new properties that the total mineralization of simple inorganic compounds form accessible to plant growth, enabling the installation of vegetation.

With the decrease in the percentage of organic carbon, held increasing the percentage of total nitrogen, from 0.26 in 1997 to 0.4 in 2013 as a result of total mineralization simple organic compounds from the decomposition of oil. Increasing the percentage of value

total nitrogen and continuous decrease in the percentage of organic carbon, had as a consequence decline in the value C / N ratio of 33.76 7 Ao horizon.

The comparison study end parameter values in the study with control values can be seen that the properties were polluted soil trophicity were slightly higher, being comparable with a medium soil fertility

## CONCLUSIONS

The drop in soil organic carbon content without the intervention of human factor, due to the onset of self-regulating mechanisms in the soil, the soil through their own mechanisms having the ability climate conditions data, to return to its original state.

In the absence of permanent source of pollution in the first phase held oil degradation mechanisms triggering the action of heterotrophic aerobic bacteria, facultative anaerobic, anaerobic, sulfur-reducing bacteria, sulfur-oxidizing bacteria, bacteria and bacteria hydro-carbon-oxidant having resulting in decreased organic carbon content.

It is assumed that degradation occurs resins constituting the oil (oil extracted from Suplacu Barcău contains approximately 15.65% of resin) resulting in volatile organic acids, oxygen acids, unsaturated acids, carbohydrates etc., which formed the total mineralized ground aerobically  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,

H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, after the combination of bases or acids from the soil form salts of Ca, Mg, K, Na, NH<sub>4</sub>, etc., resulting feedback while the decrease in the percentage of carbon, increasing the nitrogen content soil, thus creating the minimum conditions for installation of vegetation. The decrease in organic carbon content and vegetation installation has the effect of lowering the value of secondary and bulk density, and increasing soil aeration. During the study is a continuous decrease in the value of organic carbon, from 8.78% to 2.8%, the most significant being between 1997 and 2002. Declines continue due to microbiological activity in soil, which is becoming more active intensity decreases the toxic effect of the pollutant is formed of organic compounds of different new properties that the total mineralization of simple inorganic compounds form accessible to plant growth, enabling the installation of vegetation.

With the decrease in the percentage of organic carbon, held increasing the percentage of total nitrogen, from 0.26 in 1997 to 0.4 in 2013 as a result of total mineralization simple organic compounds from the decomposition of oil. Increasing the percentage of total nitrogen value and continuous decrease in the percentage of organic carbon, it had as a consequence decline in the value C / N ratio of 33.76 7 A<sub>0</sub> horizon.

The comparison study end parameter values in the study with control values can be seen that the properties were polluted soil trophicity were slightly higher, being comparable with a medium soil fertility.

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