Study on the efficiency of depollution measures applied in a hydrocarbons-contaminated area

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Abstract. Soils that are heavily polluted with hydrocarbons due to accidental leaks are generally unusable for agricultural purposes, a fact that can have important economic implications if the affected surfaces are larger and located in an agriculturally significant area. The current paper intends to present and to assess the biological and pedological measures used for the depollution of an area accidentally polluted with hydrocarbons and located near Poarta Alba, Constanta county, Romania. The pollution is described by means of various analyses carried out in several points across the affected area and then the decontamination response solutions are also described and assessed. The authors intend to use this case for developing efficient depollution measures for similar cases of contamination with hydrocarbons.

Key Words: polluted soil, chemical analyses, decontamination, bioremediation.

Introduction. Soils polluted with hydrocarbons are a serious environmental problem, since the contaminants tends to affect the normal biological circuits, hampering the normal development of plants (Avram et al 2006; Kingston 2002).

This type of pollution can have several sources, the most common being (Avram et al 2006):

- accidental failures of hydrocarbons pipelines;
- exploitation of research and exploitation wells;
- leakage from hydrocarbons storages or losses during their transportation;
- road and railway accidents which involve oil tanks;
- marine pollution due to the activity of oil rigs;
- pollution of water courses and their shores by intentional or accidental spilling.

The accidental failures of pipelines alone have resulted in the loss of around 6.4 million liters of oil on land, in 2001 (Salanitro 2001).

Beneath several other approaches to this problem, bioremediation is an environmentally-friendly technique that is rapidly gaining acknowledgment due to its benefits. It uses live microorganisms to produce enzymes that attack and decompose the contaminants into less toxic forms. The microorganisms employed for this purpose can originate from the polluted environment itself, or they can be brought there from other areas (innoculation). The bioremediation process usually implies also a manipulation of the environmental parameters in order to promote the microbial growth and accelerate the degradation processes (Barbulescu 2014; Avram et al 2006).

Compared to other soil decontamination technologies, bioremediation offers several advantages. For example, its application is relatively cheap. As opposed the chemical methods that merely transfer the contaminant from one environmental factor to another one, bioremediation reduces the contaminating oils to mineral compounds. Furthermore, it is based on a natural depollution process, so it can be considered a „green" technology (Avram et al 2006; EPA 2006; Stoica et al 2014).

Bioremediation can be applied either in-situ, directly to the polluted soil without moving it, or ex-situ, on soil that has been excavated from the polluted area and then placed on an impermeable barrier (Boopathy 2000; EPA 2006).

The in-situ techniques are employed more often, because they lead to smaller costs and less disturbances to the environment. For example, oxygen can diffuse in sufficient amounts only to depths of at most 0.3 m, affecting the chances for the biodegrading microorganisms to develop properly. Also, in-situ techniques are successful only if the maximal pollutant concentration in the soil (TPH) does not exceed 8%.

On the other hand, ex-situ techniques require specialised equipment for airing the soil, equipment for providing nutrients and often a larger volume of work. Among the better known ex-situ treatment types there can be mentioned landfarming, composting and bio-stacking (Boopathy 2000; EPA 2006; Venosa et al 2016).

The success of depollution measures depends, however, also on a favourable structure of the soil. Therefore, any efficient depollution must comprise, beneath bioremediation measures, also pedological treatment methods (such as airing, scarification etc.).

In the current paper, the authors intend to present a scientific approach, based on the development of an assessment matrix, to depollution measures applied in the case of a hydrocarbons-polluted area near Poarta Alba, Constanta county, Romania and to assess the efficiency of these measures.

Material and Method. The authors have chosen for their studies an area located near Poarta Alba in Constanta county, Romania (Figure 1), that was heavily polluted due to an accidental oil leak from a pipeline.

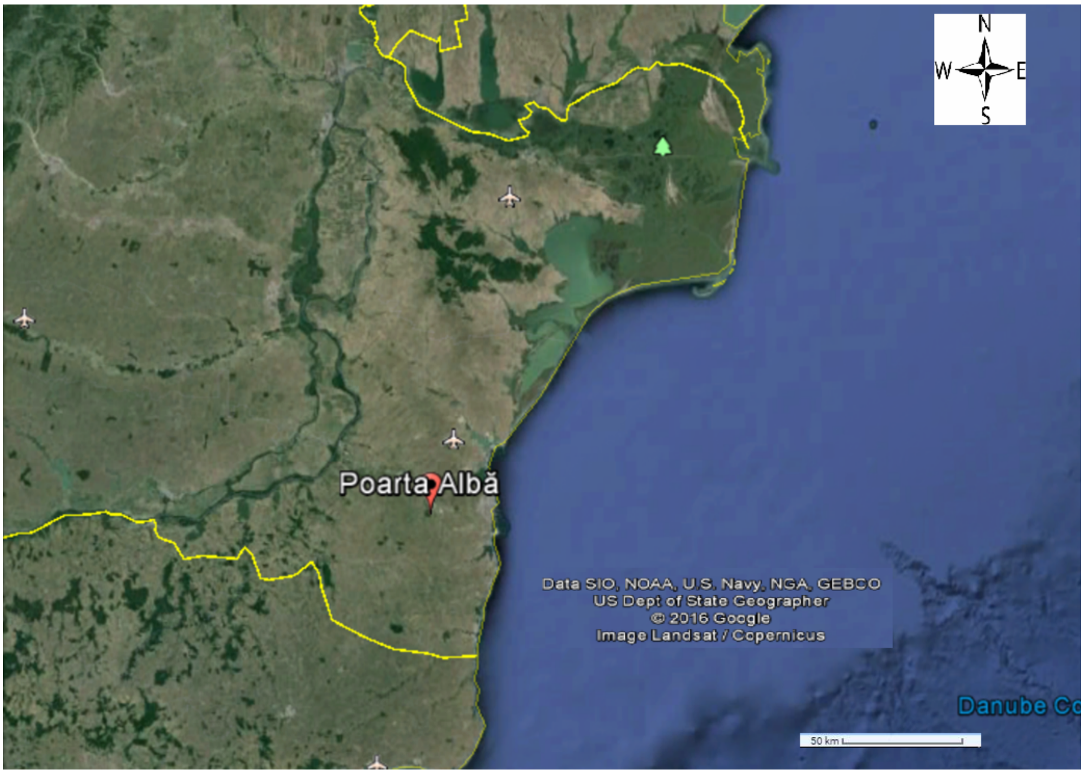

Figure 1. Location of the polluted area near Poarta Alba, Constanta county, Romania (Google Earth 2016).

In this area, there have been selected for closer analysis 12 different locations with various kinds of vegetation and original destination: agricultural areas, meadows or forested areas, that showed various degrees of pollution (Figure 2). The researches in this area were carried out starting in 2013, lasting for the durations indicated in Table 4 for the respective locations (and in the case of a few very polluted areas they continue to the present day with periodical chemical analyses documenting the actual progress of bioremediation).

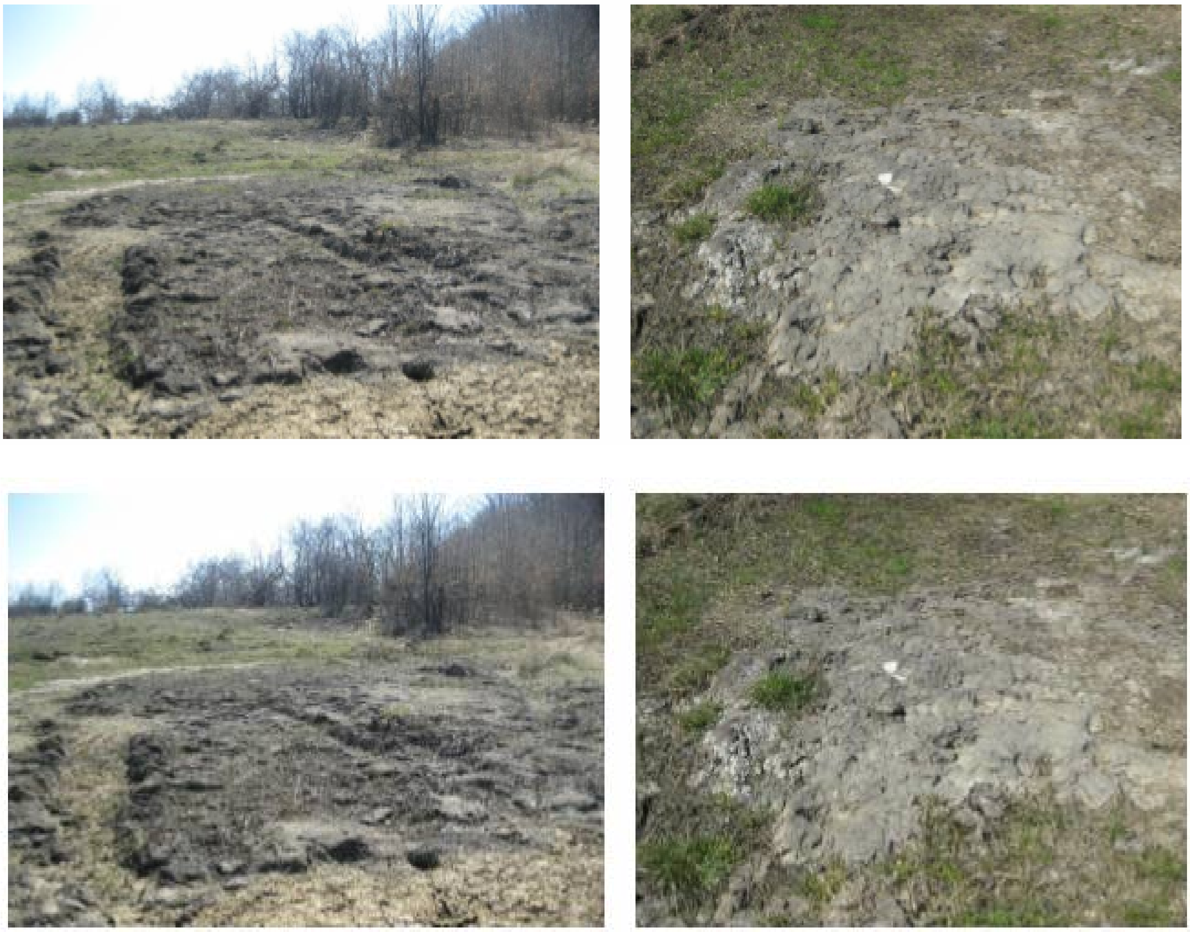

Figure 2. Aspects of surfaces polluted with oil in the studied area.

From these locations, there were extracted in a first phase contaminated soil samples that were subjected to a series of tests.

Firstly, there were determined the physical characteristics of the soil: texture, porosity, hydraulic conductivity, relative density.

The soil's structure controls the efficiency of the supply with air, water or nutrients. It can be improved by adding materials like straw or sawdust (Barbulescu 2014; Huesemann 2004).

The amount of available oxygen determines the aerobic or anaerobic character of the biodegradation of hydrocarbons. However, the most efficient biodegradation occurs in aerobic conditions. Therefore, it is highly recommended, even if applying on-site bioremediation, to carry out soil treatment measures such as airing or plowing to loosen the soil and make more oxygen available, but also to water the soil to provide a high enough level of humidity (Barbulescu 2014; EPA 2003).

Another important set of analyses consisted of chemical determinations for the soil: pH, content of organic matter, content of soluble salts, content of phosphorus, potassium and nitrogen, but also determinations on the nature and characteristics of the contaminant hydrocarbons (type of hydrocarbons, total petroleum hydrocarbon content, density, pollution age etc.).

Since most microorganisms have very specific requirements for their development, the pH, for example, is very important. In order to encourage the development of hydrocarbons-degrading microorganisms, the soil's pH must be comprised between 6 and 8. If the soil is too acid, its pH can be increased by adding lime, while if it is too alkaline, the pH can be decreased by adding elemental sulphur (Vidali 2001; Neag 2009).

Sometimes, the soil can be affected not only by the oil itself, but also by saltwater associated with the oil. An elevated level of salinity in the soil can be toxic for the microorganisms that are essential for revitalising the soil and for bioremediation. Salinity can be assessed by measuring the electrical conductivity (EC) and can be corrected by adding gypsum to the soil (Matei 2004; Brown et al 2016).

Furthermore, the content of nutrients such as nitrogen, phosphorus and potassium is very important for the development of the microorganisms, along with the presence of microelements such as copper, manganese, cobalt, zinc, selenium, tungsten and molybdenum (Barbulescu 2014).

The type of contaminating oil is also a very important factor. Generally, the heavier hydrocarbons (oils) are less biodegradable than lighter oils. The American Petroleum Institute (API) gravity of oils is often used as an indicator for their composition and for their biodegradability. Hydrocarbons with an API gravity larger than 30 can be considered easily biodegradable, while those with an API gravity of less than 20 (heavy oils) are difficultly biodegradable (McMillen et al 2002; Venosa et al 2016).

Equally important is the concentration of hydrocarbons in the contaminated soil, expressed through the so-called total petroleum hydrocarbons (TPH) content. The TPH can be determined either by gravimetric methods or using infrared spectrometry (IR) (Villalobos et al 2008; Levei et al 2014; Bezza & Chirwa 2016). For the study presented in this paper, the authors chose to rely on the infrared spectrometry method, since it is more sensitive than the gravimetric method.

The so-called pollution aging refers to the fact that over time, oils tend to change their composition due to processes such as chemical reactions, biotransformation, volatilization etc. Since some hydrocarbon molecules such as phytane or pristane are more resistant to the microbial degradation than C18-hydrocarbons, for example, the ratio between C18 hydrocarbons and phytane will decrease as the oil is biodegraded over time by the microorganisms (Macaulay 2015; Brown et al 2016).

Not least, there were carried out also microbiological analyses in order to determine what microorganisms were present and in what amounts, so as to be able to decide either on the stimulation of growth of already existing („indigeneous") bacteria or on extracting only specific strains that can be developed off-site and then reintroduced.

Based on all these analyses, on the importance of the various factors that can affect the biodegradation of soils on their specific ranges and also on previous researches (Barbulescu 2014), the authors have defined a biodegradability assessment matrix, presented in Table 1. Starting from a number of points allocated for the behaviour regarding the specific ranges of the parameters, this assessment matrix allows to define global biodegradability ranges using the total number of points for each of the cases mentioned above.

Table 1

Biodegradability assessment matrix

Parameter	*Very easily biodegradable (4 points)*	*Easily biodegradable (3 points)*	*Average biodegradability (2 points)*	*Difficultly biodegradable (1 point)*	*Very difficultly biodegradable (0 points)*
TPH (%)	1-3	3-5	5-10	10-15	> 15
EC, $\mu S\ cm^{-1}$	< 2000	2000-4000	4000-8000	8000-14000	> 14000
Microorganisms (MPN g^{-1} soil)	≥ 10^7	≥ 10^5	≥ 10^4	≥ 10^3	< 10^3
Clays (%)	< 10	10-20	20-40	40-60	> 60
API density	> 30	25-30	20-25	15-20	< 15
Pollution age	(C18/phytane) soil ≈ 100% (C18/phytane) oil	(C18/phytane) soil ≈ 75% (C18/phytane) oil	(C18/phytane) soil ≈ 50% (C18/phytane) oil	(C18/phytane) soil ≈ 25% (C18/phytane) oil	(C18/phytane) soil almost insignificant
pH	6.81-7.20	5.81-6.80 7.21-7.80	5.41-5.80 7.81-8.40	5.01-5.40 8.41-9.00	< 5.00 > 9.00
Global biodegradability	28 points	21-27 points	14-20 points	7-13 points	0-6 points

Based on all these elements, the authors were then able to define specific bioremediation recipes for each analysed location and to assess whether it is enough to apply only bioremediation measures or whether bioremediation should be combined with other types of depollution measures.

Results and Discussion. The results of the physical, chemical and microbiological analyses carried out in the 12 locations within the contaminated area targeted for this study are presented in Table 2.

Table 2

Results of the analyses carried out on the samples of contaminated soil

Soil sample no.	*Initial TPH (IR), mg kg^{-1}*	*TPH (IR) after 6 months, mg kg^{-1}*	*Bacteria, MPN g^{-1} soil*	*pH*	*Electrical conductivity µS cm^{-1}*	*Fe, mg kg^{-1}*	*Clays, %*	*API gravity of the oil*	*C18/ phytane oil*	*C18/ phytane soil*	*SAR*
A1	34600	31600	$\geq 10^6$	7.44	2690	1430	2.85	22.4	Heavy oil	-	14
A2	76000	52700	$\geq 10^6$	7.55	5140	2690	0.15	17.2	Heavy oil	-	26
A3	70300	44500	$\geq 10^6$	7.73	3680	3640	0.5	14.6	Heavy oil	-	19
A4	100800	74800	$\geq 10^6$	7.99	3420	2350	3.4	17.1	Heavy oil	-	19
A5	145000	100200	$\geq 10^6$	8.32	4310	3810	1.7	17.1	Heavy oil	-	20
A6	19200	10600	$\geq 10^6$	7.92	2230 dilution 1/10	4680	0.72	19.0	Heavy oil	-	23
A7	35600	28800	$\geq 10^6$	8.08	2370 dilution 1/10	2960	3.3	19.0	Heavy oil	-	24
A8	27900	17600	$\geq 10^6$	7.79	1700	1180	10.2	30.2	6.91	4.93	26
A9	8700	7400	$\geq 10^8$	7.20	10280	1010	4.6	36.9	7.4	2.95	45
A10	54800	47800	$\geq 10^8$	7.84	1570	2650	2.9	33.2	-	-	7
A11	15700	12200	$\geq 10^8$	7.75	850	2950	7.6	28.9	3.91	2.22	2
A12	18600	12700	$\geq 10^8$	7.56	8740	810	12.9	33.2	3.67	3.25	23

If applying the results of the analyses in the biodegradability assessment matrix (Table 1), it leads to the matrix presented in Table 3.

Table 3

Assessment matrix resulted for the analysed samples

Soil sample no.	*Score for TPH*	*Score for EC*	*Score for bacteria*	*Score for clays*	*Score for API density*	*Score for pollution age (C18/Phytane)*	*Score for pH*	*Total score*	*Assessment of biodegradability*
A1	3	3	3	4	2	0	3	18	Average
A2	2	2	3	4	1	0	3	15	Average
A3	2	3	3	4	0	0	3	15	Average
A4	1	3	3	4	1	0	2	14	Average
A5	1	2	3	4	1	0	2	13	Difficult
A6	4	0	3	4	1	0	2	14	Average
A7	3	0	3	4	1	0	2	13	Difficult
A8	4	0	3	3	4	3	3	20	Average
A9	4	1	4	4	4	1	4	22	Easy
A10	2	4	4	4	4	1	2	21	Easy
A11	4	4	4	4	3	2	3	24	Easy
A12	4	1	4	3	4	3	3	22	Easy

Based on the results of the individual analyses for the 12 locations but also on the overall assessment of the biodegradability of the contaminants in each location, there were determined specific treatment recipes and procedures for each location, presented in Table 4.

Table 4

The bioremediation treatments prescribed for each of the 12 locations in the targeted area

Sample no.	*Total treatment duration [months]*	*NPK treatment duration [months]*	*N [mg kg^{-1} soil]*	*P [mg kg^{-1} soil]*	*K [mgkg^{-1} soil]*	*Gypsum, stage I [g m^{-2}]*	*Gypsum, stage II [g m^{-2}]*	*Gypsum, stage III [g m^{-2}]*	*Straw [kg m^{-2}]*	*Surfactant [l m^{-2}]*
A1	24	15	1483	297	297	0	0	0	10	3
A2	24	32	3257	651	651	340	0	0	10	3
A3	84	30	3013	603	603	0	0	0	10	3
A4	96	43	4320	864	864	0	170	0	10	3
A5	72	62	6214	1243	1243	200	0	0	10	3
A6	108	8	823	165	165	1000	1000	900	10	3
A7	96	15	1526	305	305	1000	1000	1000	10	3
A8	72	12	1196	239	239	1000	950	0	10	3
A9	24	4	373	75	75	1000	250	900	10	3
A10	24	23	2349	470	470	0	0	0	10	3
A11	24	7	673	135	135	0	0	0	10	3
A12	24	8	796	159	159	730	0	0	10	3

For this, there have been taken into account several factors:

- nitrogen, phosphorus and potassium have to be added so as to reach an optimum ratio C:N:P:K of 100:10:1:1 (Barbulescu 2014; Chaîneau et al 2003);
- however, these elements cannot be added in too high amounts at once, because this could lead to the environment becoming toxic for the biodegrading microorganisms; the authors have decided to split the monthly additions of these elements as follows:
    - N: 30 g m^{-2};
    - P_2O_5: 12 g m^{-2};
    - K: 7 g m^{-2};
- gypsum is added in the case of soils that are contaminated also with brine. The amount of gypsum to be added depends on the content of sodium and of calcium, respectively:
    - TGR (Total Gypsum Requirement) = $Na^2/500 - Ca/15$, in t ha^{-1} (1);
    - however, gypsum should not be added in amounts larger than 10 t ha^{-1} (or 1000 g m^{-2}) every 6 months;
- the total necessary duration of the bioremediation treatment was determined based on the decrease of the TPH content over 6 months (as presented in Table 2) and on the duration of the treatment with nutrients. These considerations led to the values indicated in Table 5:
- straw is added to improve the consistency and structure of the soil;
- the surfactant has the role of facilitating the contact between the biodegrading microorganisms and the contaminant, in order to speed up the degradation process;
- the actual bioremediation treatment has to be accompanied by pedological measures such as soil airing, scarification or ploughing;
- once the TPH drops below 3000 mg kg^{-1}, the area can be treated through phytoremediation, by replanting it with certain plant species that are specific for the respective terrain usage.

Table 5

Duration of the bioremediation treatment function of the global biodegradability and of the initial TPH

Initial TPH [mg kg^{-1}]	*Treatment duration [months]*		
	Easily biodegradable	*Average biodegradability*	*Difficultly biodegradable*
< 5000	12-24	24-48	> 48
5000–10000	24-48	48-72	> 72
10000-15000	48-84	72-96	> 96

As can be seen, this scientific approach to bioremediation led to usable data and to success in depollution at the end of the treatment.

However, especially for the case of heavy pollution (and/or of difficultly biodegradable oils), the total time needed to achieve a satisfactory depollution level is very long and if this heavier pollution is restricted only to some smaller areas, this can lead either to long overal depollution times (as it would not be practical to have patches of land in different stages of remediation) or to an incomplete depollution, so in both cases the efficiency is lowered.

Therefore, in order to increase the efficiency of the depollution it would be recommendable, especially if off-site bioremediation is considered, to combine bioremediation (at least in the heavier polluted areas) with other depollution techniques, such as thermal methods (incineration).

Conclusions. In the current paper, the authors have presented a scientific, methodical approach to applying a bioremediation treatment in order to assess the efficiency of this method.

The presented case study has shown that the assessment matrix developed by the authors can, in correlation with other considerations and factors, be taken as a fundament for unfolding a successful bioremediation treatment.

Also, by using rigorous scientific considerations, the authors were able to determine precise recipes for bioremediating the targeted locations.

However, it has been shown that such a precise approach also exposes a low efficiency of the bioremediation method, if applied on its own. The authors therefore recommend to combine bioremediation, at least in heavily polluted areas, with other methods, such as thermal techniques.

In future, the authors intend to continue their researches and to improve their bioremediation approach.

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