ASSESSMENT ON THE PHYTOREMEDIATION OF CRUDE OIL POLLUTED SOILS, GROWTH PERFORMANCE OF *ACHILLEA MILLEFOLIUM* AND TPH REMOVAL EFFICIENCY

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Abstract. The study presents experimental data on phytostabilization/ phytoremediation of 5.57% total petroleum hydrocarbons contaminated soils, using plants of the *Achillea millefolium* species. Studies have been conducted on pots placed in outdoors in three experimental variants in the absence/presence of an additional treatment: 1.contaminated soil; 2. contaminated soil treated with fertilizer agent, stabilized sewage sludge; 3. contaminated soil treated with fertilizer and amendment based on indigenous volcanic tuff with clinoptilolite. After five months of growth the plant roots have formed a strong twinned network throughout the vegetation soils of volume pots. The content reduction of the total petroleum products in the contaminated soil was 45.4% and 65.4% for the variant of contaminated soil treated with fertilizer agents, anaerobically stabilized sewage sludge from the municipal treatment plant in the absence/presence of the amendment with indigenous volcanic tuff.

Introduction

Currently the concept of using plants to remedy soils contaminated with organic pollutants is based on observations regarding the faster reduction of pollution in vegetated areas than on polluted soils devoid of vegetation [1-3].

On the other hand the correlation between current agricultural technology and the phytoremediation potential of a contaminated soil is not well determined, the most advanced agricultural techniques can't increase the speed and extent of the phytoremediation processes. Plants are primarily affected by

the most persistent pollution compounds that can cause disturbances in the rhizosphere system, the acquisition of micro and macronutrients [4-6]. A number of components of crude oil i.e. aromatic hydrocarbons are the most dangerous and recalcitrant, all the while stimulating pathogenic microbial potential. Polycyclic aromatic hydrocarbons, however, have a tendency to adsorb on the soil particles and they remain non-biodegradable in these forms a large period of time [7-9].

From these soil particles the aromatic compounds may not be tranlocated in plants in bioavailability forms. Vegetation installed on total petroleum hydrocarbons (TPH) polluted soil can take over and carry pollutant compounds according to their physical-chemical characteristics [10-13].

It was found that a polluted soil can be invaded by certain plants, weeds, specific to a particular geographical location. Weeds are gradually replacing the selected cultivated crops because pollution is reduced. The efficiency of the phytoremediation process depends on the age of the polluted landfill and on the plant species selected to receive the phytoremediation strategy. The age of the pollutants and the pollution type are limiting factors for the biodegradability of these compounds [14-15].

The purpose of this study is to obtain data on the effect vegetation has on reducing TPH content in the soil. More the study includes relations between TPH pollution and different parts of the plant.

Experimental part

The studies were carried out in three experimental variants: polluted soil with an amount of 55.7 g/kg D.M. total petroleum hydrocarbons untreated and fertilized with sewage sludge anaerobically stabilized in the absence/presence of an amendment modified indigenous volcanic tuff.

The soil used in this experiment was taken from a collection point and the temporary storage of crude oil coming from several probe extraction operations from wells.

The soil poses recent and continuous crude oil pollution. Unpolluted soil, blank variant, was taken from an agricultural area located near the polluted site. Since the initial degree of soil pollution was high at 17%. For these studies the high polluted soil was mixed with unpolluted soil. The mixture contains two parts unpolluted soil and one part polluted soil. The mixture was prepared as follows: polluted and unpolluted soils were cleaned of plant debris, stones etc. Soils were dried and shredded. They were sieved through sieves with mesh the size of 10 mm for polluted soils and 1mm for unpolluted soils. The resulting mixture was used as such or fertilized with anaerobic stabilized sewage sludge [16] in an amount of 5 $t \cdot ha^{-1}$ in the absence/presence of an inorganic amendment [17-18], modified indigenous volcanic tuff name *Aln Tuf*. The amount of inorganic amendment used was 2.0 $t \cdot ha^{-1}$.

Soil physical-chemical characteristics

In Table 1 are shown the characteristics of unpolluted and polluted soil variants, untreated and treated which were used in the experimental study block.

Table 1

The characterization of polluted and unpolluted soil used in the experimental study

No.	Soil type	Physical-chemical characteristics					
		pH	Organic carbon [%]	Total petroleum hydrocarbon [%]	Total nitrogen [%]	C:N Ratio	C:N Ratio Recommended [19]
1	Blank (unpolluted soil)	6.8	1.3	-	0.06	22	10-15
2	Polluted soil	7.4	19.2	55.7	0.12	160	10-15

Nutrient characteristics

In Table 2 are shown the characteristics of the used fertilizer agent, sewage sludge.

Table 2

The content of nutrients in the used fertilizer agent

No.	Fertilizer agent	Physical-chemical characteristics				
		pH	Humidity [%]	Organic matter [%]	Total N [%]	Total P [mg/kg D.M.]
1	Sewage sludge	8.5	91,5	59.78	1.138	1107

The inorganic amendment based on indigenous modified tuff Tuf Aln was prepared in the ECOIND Laboratory according to the ECOIND [20]..

Plant characteristics

The plant selected for the phytoremediation study is part of the *Asteraceae* family, an herbaceous perennial plant with hairy leaves and white or rosy flowers. It grows in plains or in subalpine regions. It originates from Europe and West Asia. The plant was picked up together with a layer of unpolluted soil of 2 cm in which the rhizosphere was occupied with a dense network of root fibers.

Experimental variants

Experiments are carried out in vegetation pots equipped with 6.5 kg soil The experimental variants used were: blank normal soil (symbol M), soil polluted with TPH (symbol P), the variant with polluted soil fertilized with anaerobically stabilized sewage sludge (symbol P+B) and the variant with

polluted soil fertilized and treated with altered tuff (P+B+T symbol). For the experiments the plants are put together with a layer of the original soil of 2-3 cm in pots already prepared. Each variant was studied in three replicates.

The obtained cultures for the experimental variants were periodically watered and monitored. Soil sampling, preparing them for the analysis of TPH was performed as described in a personal paper [22].

Results and Discussion

In this study we followed the resilience of *Achillea millefolium* plant seedlings taken from a normal meadow, regarding the experimental soil variants and the degree of reduction of the TPH content in the soil for a study period of 4 months of growth. Furthermore, plant species probably gradually adapted to the presence of recalcitrant pollutants in the soil in the same way as in the other variants [7-9].

In Table 3 are presented the characteristics of plants cultivated on the experimental polluted soil variants respectively polluted soils fertilized in the absence of the modified indigenous volcanic tuff amendment.

Table 3

Height variation in the plants from the *Achillea millefolium* species grown in the experimental variations on polluted soils in the absence/presence of an modified indigenous tuff. Plant transplanting date: 05.03.2013

No	Date	Experimental variant/plant height [cm]			
		M	P*	P+B	P+B+T
Vegetative cycle 1					
1	05.03.2013	3-7	1-2	3-7	3-7
2	25.05.2013	8-12	3-4	6-14	6-16
3	25.06.2013	20-22	3-6	16-18	18-24
Vegetative cycle 2					
1	10.07.2013	3-7	3-7	3-7	3-7
2	30.07.2013	10-12	3-8	10-15	10-15

*Plants do not grow or bloom

In the first complete cycle of vegetation which was held in March-July, the plants placed on the polluted and treated soil developed through this cycle similarly to the plants on the unpolluted soil. From the data presented in Table 3 it is observed: an increase in the plant height from the first cycle than the ones grown on the second cycle of vegetation. The treatment of polluted soil with fertilizer agent and amendment determined a vegetative cycle of plants similarly with the one observed on the unpolluted soil. Also, from Table 3 it can be seen

that plants of *Achillea millefolium* grown in polluted soils presents signs of suffering in the upper parts of tissue. Plants do not grow or bloom.

In Table 4 are presented the characteristics of the flowers belonging to the plants grown on the experimental variations of polluted soils, respectively polluted soils fertilized in the presence/absence of an modified indigenous volcanic tuff amendment.

Table 4

The characteristics of plant inflorescence of the *Achillea millefolium* species cultivated on the experimental variants of polluted soils fertilized in the absence/presence of an amendment modified indigenous volcanic tuff

No	Date/ Stage	Experimental variants/inflorescence diameter [cm]			
		M	P	P+B	P+B+T
Vegetative cycle 1					
	15-25.05.2013 / The first flowering	2.0-4.0	*	1.5-2.0	1.8-4.0
Vegetative cycle 2					
	30.07.2013/The second flowering	2.0	1-1.5	1.0-1.5	1.0-2.5

*Plants do not bloom

It is noted that plants grown on polluted soils, untreated in the first vegetative cycle did not produce flowers but the plants grown in the second cycle develop on their own. The inflorescences that are harvested by the first growth cycle of the fertilized and amended soils have the size in the range of 1.8-4.0 cm.. These flowers were smaller than those collected from the blank experimental variants. From the data presented in Table 4 it is observed: an increase in the inflorescences from the first cycle than the ones grown on the second cycle of vegetation.

In Table 5 it is shown the quantity of TPH determined periodically in the cultivated soil of the studied experimental variants and the efficiency of the pollution reduction.

Table 5

The quantities of TPH determined in the cultivated soil of the studied experimental variants, and the efficiencies reduction in the treated soil

No	Experiment Variants	TPH content in the soils				
		Iniţial	After two months of vegetation		After five months of vegetation	
			[g/kg D.M.]	[%]	[g/kg D.M.]	[%]
1	P	55.71±1.53	53.30±1.48	4.3	51.65±1.22	7.3
2	P+B	55.31±1.53	46.57±1.43	15.8	30.16±1.13	45.4
3	P+B+T	55.21±1.53	40.89±1.41	26.0	19.07±0.76	65.4

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Depth of soil sampling for the analysis of petroleum products was 2-5 cm. From the table 5 it is observed the gradual reduction of TPH in the

cultivated soils treated with organic fertilizer in the absence/presence of an amendment as modified indigenous tuff. Crops of the *Achillea millefolium* species consumed through its own metabolic processes or induced in the soil derivate compounds of TPH. So after two months of growing, the oil content in the top layers of fertilized soil decreased by 15.8% and 26.1% after five months of growing plants of *Achillea millefolium* species. Furthermore after two months of growing, the TPH content in the top layers of treated with sewage sludge mixed with modified indigenous volcanic tuff decreased by 45.4-% respectively 65.4%. after five months of phytoremediation process.

Conclusions

The *Achillea millefolium* culture used for phytoremediation strategy TPH polluted soil requires minimal agricultural works so that this technology becomes accessible and economical. Installing a ground cover with species of plants of *Achillea millefolium* species on soils polluted with 5.57% TPH has been achieved by prior treatment with fertilizer based on anaerobically stabilized sewage sludge in the absence/presence of inorganic amendments as modified indigenous volcanic tuff. Plants grown in the treated experimental variants were developed similarly to plants grown on normal soils. These plants have vegetative cycles similar to those grown on blank normal soils. The efficiencies reduction of the total petroleum hydrocarbons over a five-month growing season that went through two cycles vegetative plants was up to 45.4% for the phytoremediation of polluted and fertilized topsoil and to 65.4% for the phytoremediation of polluted, fertilized and amendment with modified volcanic indigenous tuff.

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