EVOLUTION IN TIME OF SOME CHEMICAL AND MICROBIOLOGICAL SOIL CHARACTERISTICS UNDER THE IMPACT OF OIL AND PETROLEUM PRODUCTS POLLUTED SOILS ELECTRO REMEDIATION TECHNOLOGIES

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Abstract. Soil chemical and microbiological characteristics variations in time were studied in the frame of a project aiming to elaborate a platform for oil pollution risk assessment, during an electro remediation process. On the background of very slight variations of the soil macro-elements contents different organic carbon and total nitrogen contents accumulation are registered at the electrodes, under the influence of potential difference and other factors as well. Nitrates contents register a great leap in the last stage of the experiment due to weather conditions but remain within the normal agricultural soils limits. Mobile phosphorus and potassium contents vary insignificantly within the limits of a good agricultural soils supply. The reaction remained slightly alkaline all along the experiment with a slight pH increasing tendency. All the samples have a chloride salinisation with slight and moderate intensities and sodium chloride is predominant in their composition. The bacteria numbers increased in some of the collecting pits and decreased in the others.

Introduction

Larger and larger areas contaminated with different polluting substances proceeded from industrial activities occur both in Europe and in the World. Therefore there is an increasing interest in the last years for their monitoring and especially for their ecologic remediation by developing and applying various *ex situ* or *in situ* technologies which rely on different degradation processes and mechanisms. Choosing one or another decontamination technique of polluted soils

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is decided by a series of factors such as risk management, technical feasibility, cost/benefit ratio, as well as the environment, social, and economic impact.

In situ treatments do not significantly expose the workers and the environment to further contamination and the costs are much lower as compared to the *ex situ* techniques (Ana, 2010).

In a previous experiment the electro kinetic remediation process registered a 45-55% organic contaminant removal efficiency in the cathodes area after 200 treatment hours (Anicai, 2010).

1. Matherial and method

A dellocated technologic park was chosen for the experiment, at Răzvad – Valea Voievozilor, Dâmboviţa County, near Târgovişte (fig. 1). The lot was contaminated with a significant oil quantity proceeded from accidental pollution: tanks leaking and cracked pipes.

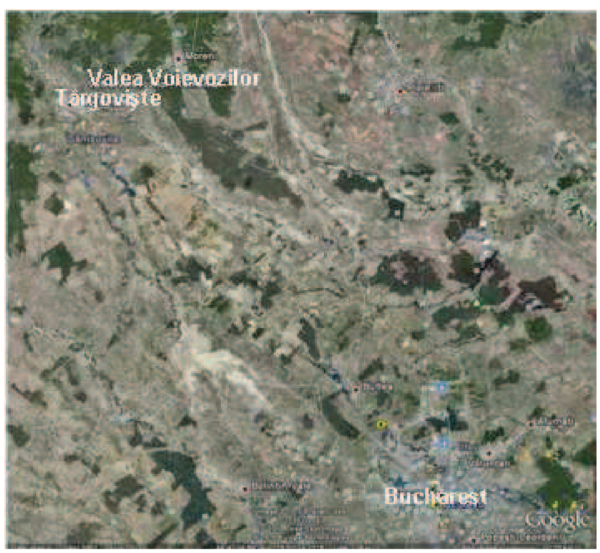

Fig. 1 – The localization of the experimental field

Three cathodes and three anodes were inserted in the experimental field, in 2 m deep pits, following the chart presented in Figure 2. The F1-F4 electrodes were inserted in porous ceramics tubes and Pj and C electrodes in PVC (polymerized vinyl chloride) ones. The cathodes are made out of stainless steel and the anodes out of graphite.

The experiment was carried out during September 4 and 11 2009.

A variable electric voltage was applied between the electrodes of 50; 100; 10; 20; 30 V and 10-12; 26; 1-2; 5; 8; 4 A.

The soil was sampled at the electrodes, on the 0-25 cm depth, two days before the beginning of the experiment, four days (96 hours) after its beginning, and 7 days (168 hours) after, when the electro kinetic treatment ceased.

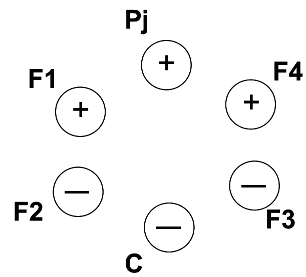

Fig. 2 – The electrodes emplacement chart in the experimental field

Bacteria were applied on September 9th, at each sampling point.

Laboratory analyses were performed as follows: organic carbon, total nitrogen, mobile phosphorus and potassium contents; soluble salts contents; microbiological analyses. Standard methodology was used as currently practiced in the laboratories of RISSA Bucharest and County pedological and agrochemical studies offices. The analytical data were graphically processed to highlight the modifications occurred during the remediation process.

2. Results and disscussions

The organic carbon contents distribution in the sampling points of the perimeter submitted to the electro kinetic bioremediation process is very scattered (fig. 2), which is natural taking into account the patchy character of oil pollution, the weather variations (especially rain) and the groundwater small and fluctuating depth. The values range from 2.16 to 7.55%, with a 4.81% average, within the medium and high contents classes for a medium textured soil (Florea et al., 1987). The average values (fig. 3) suggest an accented accumulation of organic carbon at the F2 and F4 (negative, positive respectively) electrodes and substantially lower at the F3, C, and Pj electrodes (the first two negative, the last positive). The conclusion is that not only the electric voltage determines the organic carbon accumulation at the electrodes but also other factors, especially the groundwater level and flow direction.

The total nitrogen contents range from 0.122 to 0.288%, in the low to big contents domains, and is non-uniform just like the organic carbon one (fig. 4). The average values for each sampling point (fig. 5) have a different distribution as compared to the organic carbon ones proving the lack of any relation between the soil organic matter and its total nitrogen content which would be normal in unpolluted soils. The C negative electrode and the Pj positive electrode stand out, with medium contents, the lowest amongst all average values, respectively the highest among all average values.

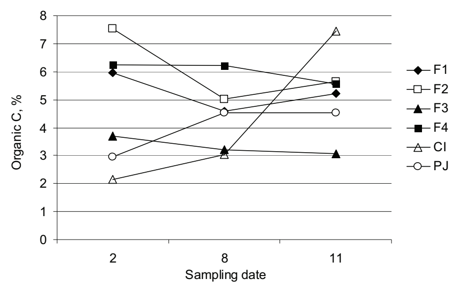

Fig. 2 – The organic carbon contents evolution at the electrodes during the electro kinetic remediation process

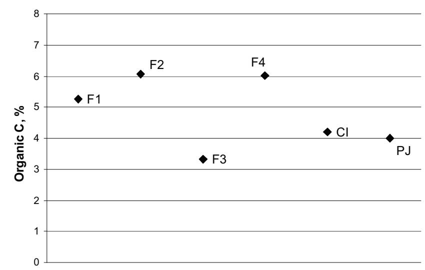

Fig. 3 – The average organic carbon contents in the six sampling points

The nitrate nitrogen contents in the soil samples collected in the first two series are very close and range between 2.3 and 6.8 mg/kg which is very low for agricultural soils. A great increase is noticed at the last sampled series (fig. 6) due to temperature decrease and rain occurred a few days earlier. Along with the sudden increase differences appear at the electrodes (fig. 7).

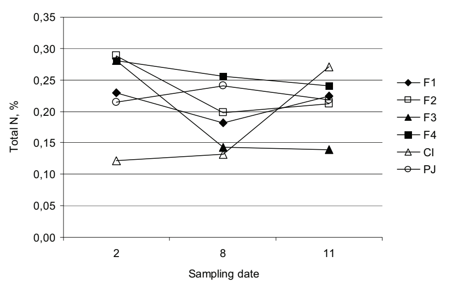

Fig. 4 – The total nitrogen contents evolution at the electrodes during the electro kinetic remediation process

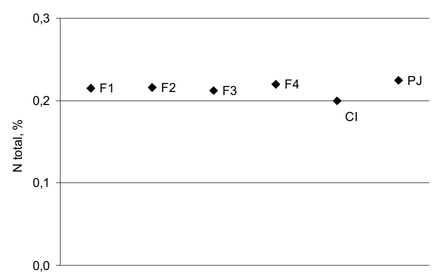

Fig. 5 – The average total nitrogen contents in the six sampling points

The mobile phosphorus contents soluble in ammonium acetate lactate at pH = 3.75 ranges between 12 and 41 mg/kg in the first two stages and suddenly increases to 62 mg/kg in the last due to bacteria application two days before.

Except for the F3 negative electrode where a decrease of the mobile phosphorus content is registered in the last stage.

The mobile potassium contents soluble in ammonium acetate lactate at pH = 3.75 range between 164 and 358 mg/kg, in the medium up to very high content classes and has insignificant variations from one sampling stage to the next (Figure 10). There are, though, great variations between the sampling points (Figure 11) due to the land irregularities and which change de wage-class from one electrode to the other.

The soil reaction remained slightly alkaline all along the experiment with a slight pH value increasing tendency (tab. 1).

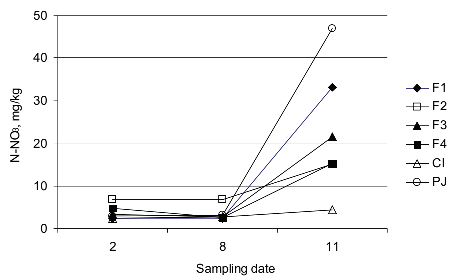

Fig. 6 – The nitrate nitrogen contents evolution at the electrodes during the electro kinetic remediation process

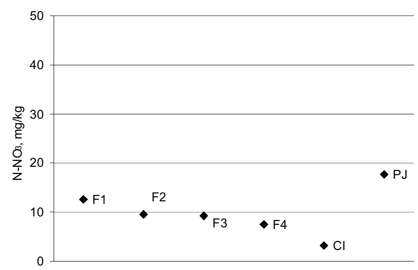

Fig. 7 – The average nitrate nitrogen contents in the six sampling points

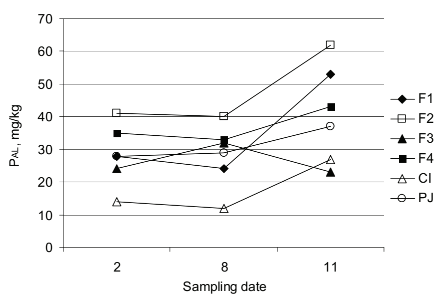

Fig. 8 – The mobile phosphorus contents evolution at the electrodes during the electro kinetic remediation process

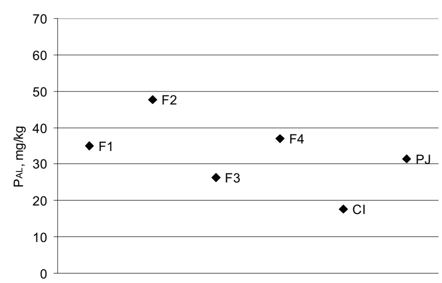

Fig. 9 – The average mobile phosphorus contents in the six sampling points

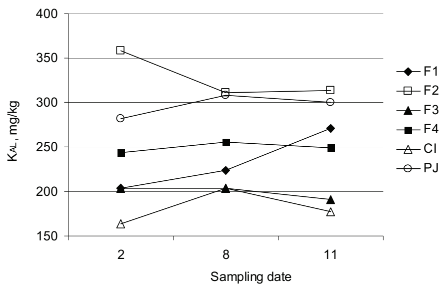

Fig. 10 – The mobile potassium contents evolution at the electrodes during the electro kinetic remediation process

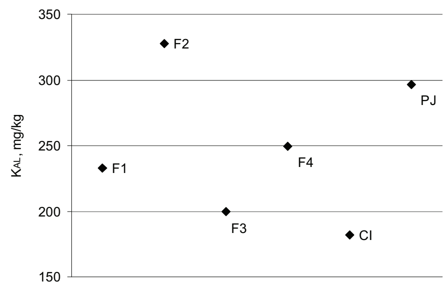

Fig. 11 – The average mobile potassium contents in the six sampling points

For a medium texture soil all samples have a slight up to moderate chloride salinisation. Slight increasing or decreasing tendencies were registered at the electrodes. Small amounts of other salts were also determined: calcium bicarbonate (8.0-13.2%), sodium bicarbonate (0-16.4%), sodium sulphate (0-7.4%), magnesium bicarbonate (0-7.4%), and potassium chloride (1.0-3.0%).

Table 2 presents the microbiological analysis results. The bacteria numbers vary but there is no regularity in this variation. Increases were registered at the C and F1 electrodes and decreases at the other ones. The bacteria number variation is linked to the organic carbon content but a regularity can't be established; there are other factors too which influence it, the weather amongst them and the irregular soil distribution of nutritional macro-elements: nitrogen phosphorus, potassium.

Conclusions

In the framework of an electro-kinetic bio-remediation depollution experiment soil chemical and microbiological properties were studied in order to asses the environmental impact of the depollution process.

On the background of a very slight variation of macro-elements contents of the soils differentiated organic carbon and total nitrogen accumulations stand out at the electrodes influenced by the potential difference and by weather conditions. The nitrate nitrogen contents register a great increase in the final stage due to weather conditions but remain in the normal content interval for agricultural soils. The mobile phosphorus and potassium contents variations are not significant and in the limits of a good supply with these nutritional elements.

The soil reaction remained slightly alkaline all along the experiment with a slight pH value increasing tendency.

Sampling data	Electrode	pH	HCO_3^-		SO_4^{2-}		Cl^-		Ca^{2+}		Mg^{2+}		Na^+		K^+		Cond. rez.	Min. rez.
		H_2O	mg	me	mg	me	mg	me	mg	me	mg	me	mg	me	mg	me	mg	mg
02.09.2009	F1	7,85	59	0,98	10	0,20	69	1,93	6	0,28	2,3	0,19	47	2,06	2	0,04	185	195
	F2	7,42	46	0,75	5	0,10	304	8,57	16	0,80	1,1	0,09	159	6,90	5	0,14	707	536
	F3	7,88	61	1,00	10	0,20	137	3,87	8	0,38	1,1	0,09	93	4,05	2	0,05	326	312
	F4	7,75	61	1,00	10	0,20	188	5,29	13	0,66	1,7	0,14	115	5,00	3	0,07	447	391
	C1	7,96	47	0,78	7	0,15	126	3,55	9	0,47	1,1	0,09	80	3,48	2	0,05	289	273
	PJ	8,00	73	1,20	14	0,30	106	2,99	7	0,33	1,1	0,09	82	3,58	3	0,07	282	286
08.09.2009	F1	7,65	66	1,08	10	0,20	90	2,52	8	0,38	1,1	0,09	66	2,87	2	0,05	230	241
	F2	7,63	37	0,60	10	0,20	278	7,83	14	0,71	1,1	0,09	146	6,33	4	0,11	646	489
	F3	7,97	53	0,88	7	0,15	122	3,43	8	0,42	0,6	0,05	82	3,58	2	0,04	296	275
	F4	7,86	59	0,98	12	0,25	111	3,13	9	0,47	1,7	0,14	77	3,34	2	0,06	271	273
	C1	7,75	47	0,78	14	0,30	174	4,90	11	0,56	2,3	0,19	91	3,96	2	0,05	351	342
	PJ	8,01	47	0,78	12	0,25	121	3,40	8	0,42	1,7	0,14	80	3,48	3	0,07	286	273
11.09.2009	F1	7,98	53	0,88	10	0,20	70	1,96	8	0,42	1,1	0,09	47	2,06	3	0,08	216	193
	F2	7,77	58	0,95	14	0,30	304	8,57	14	0,71	1,1	0,09	146	6,33	5	0,13	690	542
	F3	8,09	52	0,85	12	0,25	81	2,28	8	0,38	0,6	0,05	55	2,39	2	0,05	220	209
	F4	7,95	58	0,95	14	0,30	116	3,26	8	0,38	1,1	0,09	71	3,10	3	0,07	273	270
	C1	7,81	47	0,78	12	0,25	155	4,36	12	0,61	1,1	0,09	95	4,15	2	0,05	384	324
	PJ	8,14	84	1,38	12	0,25	129	3,62	8	0,38	1,1	0,09	91	3,96	4	0,10	326	328

Tab. 1 – The reaction and soluble salts contents of the soil samples collected from the lot submitted to electro kinetic

Electrode	R1		R2		R3	
	Identified bacterial species and genera (in their frequency order)	TBN×10^6 cfu/g dry soil	Identified bacterial species and genera (in their frequency order)	TBN×10^6 cfu/g dry soil	Identified bacterial species and genera (in their frequency order)	TBN×10^6 cfu/g dry soil
C	Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis, Bacillus megaterium	36,99	Arthrobacter citreus, Bacillus megaterium, Pseudomonas	43,93	Pseudomonas, Bacillus megaterium, Arthrobacter globiformis,	28,90
F1	Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis, Mycobacterium roseum, Bacillus megaterium, Bacillu sphaericus	45,45	Bacillus megaterium, Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis	40,25	Pseudomonas, Mycobacterium roseum, Arthrobacter globiformis, Arthrobacter citreus	25,97
F2	Arthrobacter citreus, Pseudomonas, Bacillus megaterium, Arthrobacter globiformis, Mycobacterium roseum	77,66	Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis	45,76	Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis, Bacillus megaterium, Mycobacterium roseum	85,99
F3	Pseudomonas, Bacillus megaterium, Arthrobacter globiformis, Arthrobacter citreus	47,10	Pseudomonas, Bacillus megaterium, Arthrobacter citreus	56,52	Bacillus megaterium, Arthrobacter citreus Pseudomonas, Arthrobacter globiformis	53,83
F4	Arthrobacter globiformis, Arthrobacter citreus, Pseudomonas, Bacillus megaterium	60,81	Pseudomonas, Arthrobacter globiformis, Arthrobacter citreus, Bacillus megaterium	52,70	Pseudomonas, Bacillus megaterium Arthrobacter globiformis	51,35
PJ	Pseudomonas, Bacillus megaterium, Arthrobacter globiformis, Arthrobacter citreus, Mycobacterium roseum	91,13	Pseudomonas, Bacillus megaterium Arthrobacter globiformis, Arthrobacter citreus	39,24	Bacillus megaterium, Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis	77,21

Tab. 2 – Quantitative determinations and taxonomic variety of the soil samples collected from the electrodes (2.09.2009)

Electrode	R1		R2		R3	
	Identified bacterial species and genera (in their frequency order)	TBN×10^6 cfu/g dry soil	Identified bacterial species and genera (in their frequency order)	TBN×10^6 cfu/g dry soil	Identified bacterial species and genera (in their frequency order)	TBN×10^6 cfu/g dry soil
C	Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis, Bacillus megaterium, Actinomicete	62,05	Pseudomonas, Arthrobacter globiformis, Arthrobacter citreus, Bacillus megaterium	34,60	Pseudomonas, Bacillus megaterium, Arthrobacter globiformis	22,67
F1	Pseudomonas, Arthrobacter globiformis, Arthrobacter citreus, Mycobacterium roseum	45,45	Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis, Bacillus megaterium	19,28	Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis, Mycobacterium roseum, Bacillus megaterium	53,71
F2	Bacillus megaterium, Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis, Bacillus circulans	48,12	Pseudomonas, Arthrobacter globiformis, Arthrobacter citreus, Bacillus megaterium, Bacillus circulans	24,06	Pseudomonas, Bacillus megaterium, Arthrobacter citreus, Arthrobacter globiformis, Mycobacterium roseum	32,08
F3	Pseudomonas, Bacillus megaterium, Arthrobacter globiformis, Arthrobacter citreus	61,45	Pseudomonas, Arthrobacter globiformis, Bacillus megaterium, Arthrobacter citreus	39,69	Pseudomonas, Bacillus megaterium, Arthrobacter globiformis	19,20
F4	Pseudomonas, Bacillus megaterium Arthrobacter citreus,Bacillus sphaericus	46,41	Pseudomonas, Arthrobacter globiformis, Arthrobacter citreus, Bacillus megaterium	60,47	Pseudomonas, Bacillus megaterium Arthrobacter globiformis	16,87
PJ	Pseudomonas, Bacillus megaterium Arthrobacter globiformis, Arthrobacter citreus	42,06	Pseudomonas, Bacillus megaterium, Bacillus cereus, Arthrobacter globiformis, Arthrobacter citreus, Mycobacterium roseum,Bacillus sphaericus	58,34	Bacillus megaterium, Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis	28,49

Tab. 2 – Quantitative determinations and taxonomic variety of the soil samples collected from the electrodes (8.09.2009)

Electrode	R1		R2		R3	
	Identified bacterial species and genera (in their frequency order)	TBN×10^6 cfu/g dry soil	Identified bacterial species and genera (in their frequency order)	TBN×10^6 cfu/g dry soil	Identified bacterial species and genera (in their frequency order)	TBN×10^6 cfu/g dry soil
C	Pseudomonas, Arthrobacter globiformis, Arthrobacter citreus, Bacillus megaterium, Bacillus cereus, Mycobacterium roseum	113,63	Bacillus megaterium, Pseudomonas, Arthrobacter citreus, Bacillus megaterium, Bacillus cereus	90,90	Pseudomonas, Bacillus megaterium, Arthrobacter globiformis, Arthrobacter citreus, Mycobacterium roseum	98,48
F1	Bacillus megaterium, Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis	30,26	Pseudomonas, Bacillus megaterium, Arthrobacter citreus, Mycobacterium roseum, Arthrobacter globiformis	53,64	Pseudomonas, Arthrobacter globiformis, Arthrobacter citreus, Mycobacterium roseum	35,76
F2	Arthrobacter citreus, Pseudomonas, Arthrobacter globiformis, Mycobacterium roseum, Bacillus megaterium	39,03	Pseudomonas, Bacillus megaterium, Arthrobacter citreus, Arthrobacter globiformis	31,53	Arthrobacter citreus, Arthrobacter globiformis, Bacillus megaterium	19,51
F3	Pseudomonas, Arthrobacter citreus, Bacillus circulans, Bacillus megaterium, Actinomicete	22,58	Pseudomonas, Bacillus megaterium, Arthrobacter citreus, Bacillus circulans, Arthrobacter globiformis	36,38	Pseudomonas, Bacillus megaterium, Arthrobacter citreus Arthrobacter globiformis, Actinomicete	28,85
F4	Arthrobacter citreus, Pseudomonas, Arthrobacter globiformis, Bacillus megaterium, Bacillus sphaericus	74,17	Pseudomonas, Bacillus megaterium, Arthrobacter citreus, Arthrobacter globiformis	48,07	Pseudomonas, Arthrobacter globiformis, Arthrobacter citreus, Bacillus megaterium	63,18
PJ	Arthrobacter globiformis, Pseudomonas, Arthrobacter citreus, Bacillus megaterium	30,26	Bacillus megaterium, Pseudomonas, Arthrobacter citreus, Arthrobacter globiformis	17,88	Pseudomonas, Bacillus megaterium, Arthrobacter globiformis	26,13

Tab. 2 – Quantitative determinations and taxonomic variety of the soil samples collected from the electrodes (11.09.2009)

All the samples have a chloride salinisation with slight and moderate intensities.

The bacteria numbers vary at the electrodes but, as there are many factors influencing this variation a regularity could not be established.

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