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Pollution and amelioration methods of the polluted soils

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Abstract: This paper aims to determine the degree of pollution with oil and salt water and a methodology to amelioration the polluted soil. Pollution came from oil extraction and transport, from the settlement and change of the upper soil horizons following the activities of oil transport by pipeline or by drawing roads of wells and by the contamination of the upper horizon with gravel, concrete, etc.

Keywords: pollution, hydrocarbons, salt water, soil amelioration

1. INTRODUCTION

Land area investigated is a 30 ha pasture. The investigated area was identified several soil types and subtypes that are part of the following classes: luvisols, cambisols and protisols.

In case of luvisols, precipitation water or coming from technological accidents infiltrates through the upper soil profile, accumulate in the Bt horizon which produces a sharp wetting or even the appearance of stagnant groundwater that can be loaded with oil or soluble salts. In summer evapotranspiration is high and rising capillary water laden with pollutants can re-wet the transition horizon or even eluvial horizon. In the rainy periods water that infiltrates joins with the stagnant water blade producing a uniform soil wetting and therefore recontamination.

Bt horizon riches in clay over 50% are subject to crack processes. In dry periods at level of that horizon can cause cracks in the soil material derived from transition or El (laden with pollutants) entering in the Bt contaminating it. Thus pollution with oil and soluble salts can reach depths of 100 cm soil depth. In the same time through the movements of crack at the soil surface forms a layer of mulch that brings pollutants from depth to surface.

In case of eutric cambisols infiltrating rainwater or from accidents is much easier since these soils have medium texture (clay-sand with varying proportions of skeleton), however due to colluvial material which give some of the soil surface impermeabilization in these areas are founded stagnant water, too.

Protisols represented by fluviosols doesn't have developed profiles having a medium, loamy and clayey- sandy texture with lenses of medium-coarse sands, or some quantity of skeletal material, or near the valley, or in extended gulfs in areas of confluence where secondary valleys have dejection cones out of the hills.

In the meadow area because coarser texture and presence of skeletal the infiltration of rain water or from accidents is greater and therefore the circulation to the profile of water laden with pollutants is greater.

2. MATERIAL AND METHOD

For chemical characterization and identification of the degree of loading with pollutants of the surface waters and groundwater were collected from the field a series of 10 samples from the brook in the area, from wells located near the next village and from a series of stagnant water existing on the land taken into the study.

Sampling locations for surface waters was based on the following considerations:

- surface water sampling from the brook was conducted upstream of the searched area - A5- (to have a blank for the salts level), in the searched land- A2, A3, A4 - (to evaluate the evacuated salts content of the area following surface washings, discharges into the brook, intentional or accidental and the groundwater supply) and downstream of the area (approximately 1 km) to evaluate brook water salinity outside the study area.

The classification of chemical elements determined in water samples collected as quality indicators, was performed according to the order no. 161/16.02.2006 issued by the MMGA. Element considered for system acidification was pH value and for salinity were the mineral residue and for conductivity at 105°C, chlorides, sulfates, calcium, magnesium and sodium (Table 2, Table 3).

To fit the contents of hydrocarbons in water samples using the STAS 4706/1974 stating is imperative that any groundwater or surface water that contains more than 0.1 mg/dm3 hydrocarbon oil is considered polluted (Table 1).

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3. RESULTS AND DISCUSSIONS

Table 1 Hydrocarbon content from oil

No. crt.	Point of harvest	Content of hydrocarbons mg/dm^3	Class of pollution
1	A1	2,33	II
2	A2	0	I
3	A3	0	I
4	A4	0	I
5	A5	0	I
6	A6	1,67	II
7	A7	1,33	II
8	A8	1,33	II
9	A9	0	I
10	A10	1,67	II

In terms of total hydrocarbon content in water samples collected shows that stagnant water and surface water samples from the area and upstream (A2, A3, A4, A5) and some ground water in the village (A9) are not polluted. They fall within the range 0.0-0.1 mg/ dm^3, I-a grade, unpolluted waters.

Water source under the slope (A1) and surface water from downstream area (A8) has a content of 2.33 mg/l respectively 1.33 mg/l which indicating that the plateau groundwater are low contaminated with hydrocarbons, them reaching in the studied territory by a spring. Water from this spring, some seeps into the ground and some flows to the brook through torrential organisms.

The water that stagnates on the plateau (A6, A7) is loaded with hydrocarbons over allowed limit (1.67 respectively 1.33 mg/l), with the risk of infiltration into the soil or its evaporation resulting in deposition of pollutants at the soil surface.

Ground water in the village is partly polluted with hydrocarbons over permissible limit (A10 - 1.67mg/l).

Acidification regime of the collected waterfalls mostly in the normal range of 6.5-8.5 except for A2 sample harvested from a grid of probe where the pH is lower (6.18). pH of spring water and brook varies between 7 and 7.38 and that from the village has a range between 6.87-6.94.

Harvested water salinity regime situates them in the quality classes from I (very good) to V (poor) according to different chemicals elements and mineral residue. Table 3 shows the classification of these waters in quality classes.

According to the residual mineral content (mg/l) water from source/spring under the slope and the surface water from the brook downstream area will fall in quality class V (poor) due to the high content of salts (9882, respectively 2852 mg/l). There is extremely high content of sodium and chloride, which is evidence that pollution is likely chloro-sodium, sulfur content is very low. In the stagnant water is also observed high sodium content (A6, A7) which however does not significantly affect water quality (Class II - good)

Stagnant waters from the wells area or their immediate vicinity have also high contents of sodium and chlorine, such as being assigned to Class IV - poor (A2) or only sodium (A6), will falls in class V (bad).

Table 2 Chemical properties of water samples

Elements analyzed	Point of harvest									
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
HCO_3^- mg/l	311	119	143	195	189	119	119	201	351	366
HCO_3^- me	5.10	1.95	2.35	3.20	3.10	1.95	1.95	3.30	5.75	6.00
Cl^- mg/l	6083	530	82	61	23	217	271	1564	50	52
Cl^- me	171	14.93	2.30	1.71	0.64	6.12	7.64	44.06	1.42	1.47
SO_4^{2-} mg/l	48	33	10	10	5	14	19	38	14	10
SO_4^{2-} me	0.99	0.69	0.20	0.20	0.10	0.30	0.40	0.79	0.30	0.20
Ca^{2+} mg/l	768	51	19	56	45	0	23	307	115	113
Ca^{2+} me	38.3	2.54	0.94	2.82	2.26	0	1.13	15.34	5.74	5.65
Mg^{2+} mg/l	162	5	1	8	6	26	3	42	19	19
Mg^{2+} me	13.3	0.38	0.09	0.66	0.47	2.16	0.28	3.47	1.60	1.60
Na^+ mg/l	2484	286	79	34	17	144	186	690	41	28
Na^+ me	108	12.44	3.42	1.49	0.76	6.26	8.08	30.01	1.77	1.21
K^+ mg/l	27	27	14	5	5	9	9	9	19	5
K^+ me	0.68	0.70	0.37	0.13	0.13	0.22	0.23	0.24	0.50	0.13
Mineral residue mg/l	9882	1051	348	369	290	529	630	2852	610	593

Table 3 Classification in quality classes of water samples according to OM 161/2006 MMGA

Point of harvest	Cl^- mg/l	SO_4^{2-} mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l	Na^+ mg/l	Mineral residue mg/l
A1	V	I	V	IV	V	V
A2	V	I	II	I	V	IV
A3	III	I	I	I	III	I
A4	III	I	II	I	II	I
A5	I	I	I	I	I	I
A6	III	I	I	II	IV	II
A7	IV	I	I	I	IV	II
A8	V	I	V	II	V	V
A9	II	I	III	II	II	II
A10	III	I	III	II	II	II

Quality classes: I – very good; II – good; III – moderate; IV – weak; V – poor/ bad.

For physical and chemical characterization of soils and their degree of pollution have been made two main profiles and 6 surveys. Profile P1 was located on an eutric stagnic fluvisol, P2 and S6 on vertic hipostagnic luvisol and surveys S1 and S3 on calcaric fluvisol, S2 on eutric luvisol and S4 and S6 on hipostagnic luvisol.

Table 4 Chemical characteristics of soil samples

Area	Depth (cm)	pH	Humus %	Nt	C/N
P1	0-2	5.99	3.42	0.209	11
	2-18	6.69	2.40	0.126	13
	20-40	7.00	1.62	0.069	16
	50-70	7.00	2.28	0.090	17
	75-90	7.15	1.02	0.045	15
	90-110	6.83	0.48	0.034	10
P2	4-14	6.88	3.18	0.131	16
	22-39	6.15	2.82	0.107	18
	39-49	5.66	1.62	0.056	20
	55-75	5.55	0.90	0.040	15
	90-110	5.90	0.72	0.037	13
S1	0-20	6.49	3.06	0.099	21
	20-40	6.57	1.32	0.034	26
	40-50	7.09	0.66	0.020	22
	50-60	7.00	0.18	0.008	15
S2	0-20	6.05	2.34	0.068	23
	20-40	6.57	1.44	0.053	18
	40-60	6.69	1.32	0.035	26
S3	0-20	7.95	2.10	0.070	20
	20-40	8.51	1.68	0.051	22
	40-60	8.04	0.96	0.021	31
	60-80	7.58	0.78	0.023	23
	80-100	7.24	0.36	0.019	13
S4	0-20	5.95	2.64	0.075	24
	20-30	5.38	1.02	0.036	19
	50-70	4.88	0.84	0.039	15
	80-100	5.42	0.72	0.018	27
S5	0-20	7.47	3.06	0.106	20
	20-40	8.24	3.00	0.086	24
	50-70	7.85	1.20	0.026	31
	80-100	5.51	0.90	0.016	38
S6	0-20	4.87	1.44	0.046	21
	20-40	4.31	1.26	0.026	33
	50-70	4.23	1.08	0.015	49
	80-100	5.11	0.90	0.011	55

Table 4 shows that, due to salt water pollution, has been an anthropogenic acidification or alkalization, pH values being higher or lower than those characteristic of existing soil types.

Large variation of pH is due to salt water pollution and physical pollution.

For the determination of humus content, soil samples were located generally in areas devoid of vegetation affected by pollution. It was found that the humus content is correlated with the content of residual oil and while some of it was mineralized.

In terms of total nitrogen content was found that soils have very low nitrogen content, except grassy surface layer.

In case of soils polluted with oil ratio carbon/ nitrogen is very important because it indicates imbalance of organic matter and total nitrogen content. If the ratio carbon/nitrogen exceeds the limit of variation for soils in the area, oil pollution and amelioration over time under natural conditions acted. Values above 20 indicate that soil disturbances due to mineralization of organic carbon derived from oil. At surveys S5 and S6, oil content found in the deep was totally mineralized, microorganisms degrade soil and consume nitrogen.

Cationic exchange properties are presented in Table 5.

Table 5 Cationic exchange properties

Area	Depth (cm)	SB	T	Na_{sch}	V_{Na}
		me/100 g sol			
P1	0-2	25.28	29.37	0.19	0.7
	2-18	20.41	21.85	0.23	1.0
	20-40	20.82	22.41	0.17	0.7
	50-70	22.44	24.51	0.61	2.5
	75-90	19.60	21.36	0.32	1.5
	90-110	18.18	19.89	0.85	4.3
P2	4-14	19.00	22.51	3.03	13.5
	22-39	18.79	23.37	4.66	19.9
	39-49	24.47	29.05	4.26	14.7
	55-75	25.68	29.29	3.29	11.2
	90-110	25.88	28.86	0.74	2.6
S1	0-20	16.77	18.68	0.14	0.7
	20-40	17.98	20.38	0.24	1.2
	40-50	15.96	17.23	0.20	1.2
	50-60	17.37	19.40	0.51	2.6
S2	0-20	12.92	16.05	0.09	0.6
	20-40	13.32	15.08	0.11	0.7
	40-60	13.12	14.40	0.09	0.6
S3	0-20			1.30	7.1
	20-40			4.96	19.8
	40-60			2.29	11.8
	60-80			1.57	9.9
	80-100	19.40	20.46	1.68	8.2
S4	0-20	12.92	17.55	0.15	0.8
	20-30	10.28	16.91	0.17	1.0
	50-70	19.00	32.01	0.35	1.1
	80-100	21.22	30.68	0.55	1.8
S5	0-20			2.01	6.1
	20-40			1.49	5.4
	50-70			2.23	6.5
	80-100	24.87	29.75	0.29	1.0
S6	0-20	13.52	19.47	0.05	0.3
	20-40	15.15	24.90	0.06	0.2
	50-70	20.82	31.64	0.08	0.3
	80-100	25.88	30.81	0.07	0.2

Table 5 shows that the base sum is usually middle – and only in S4 and S6 appear values below 16 me/100g soil. As a result the total cationic exchange capacity is generally middle, only in S2 appear a value of 14.40 me/100g soil.

In profile P1 and surveys S1, S2, S4 and S6 exchangeable sodium content is very low, below 1 me/100g soil, in profile P2 has the highest values and the other has medium values.

Depending on the degree of saturation in sodium resulting alkalization intensity.

CONCLUSIONS

Studies have shown that the analyzed surface appeared from exploitation and transportation of oil, chemical pollution - with oil and salt water - and physical pollution through the activities of drilling, mining and transportation of oil.

Physical pollution occurs through soil compaction, excavation and arable land decreased, pollution produced by the machines that arranged the wells area and drilling and maintenance equipment. Decreasing agricultural area due to employment areas by road networks, electric and telephone lines, over and underground pipes, storage of materials, construction, etc. Also, abandoned work sites of concrete, different buildings, machinery, mud pits, drilling or oil waste, different materials, parts or subassemblies metal pollute the environment and especially soil. Measures to amelioration physical pollution refers to the removal of all remains of human activity from the improved territory and to perform specific work to restore the top layer of soil.

For this is recommended the following:

- Maintaining strict operating road routes past the site plans;
- Uncovering illegal roads, to a depth of 25-30 cm;
-Uncovering surfaces with saline vegetationless soils produced by salinity and oil residues to a depth of 30 cm;
- Collecting debris of gravel, concrete, scaffoldings;
- Elimination of underground pipes that are not used or degraded;
- Materials uncovered, if not affected by chemical pollution (without saline vegetationless soils), can be used to fill gullies to a depth of 20 cm, the rest to the land surface being loose soil material. Filling material may come from material excavated for building canals or drainage ditches or other structures;
- Soil with large gravel, crusts of oil residue, soil material on the saline vegetationless soils surface uncovered of 20-25 cm that cannot be used to fill gullies should be stored in a landfill located in an area surrounded by a channel to collect water from rainfall fallen to the landfill and that infiltrates through the overburden washing the soluble salts and oil residue.

Channel is outside proofed with clay or PVC materials. Water collected in the channel to be carried outside the perimeter, treated or reinjected.

- Dump will be located so as not to allow neighboring land pollution.

In terms of chemical pollution, is found that oil pollution is insignificant and does not affect soil fertility.

The pollution of concern is salt water, pollution that affects soil properties and fertility.

Pedo-ameliorative measures to be taken to remove chemical pollution are:

- Deep loosening of soil;
- Amendment of the chalk;
- Homogenization the soil profile;
- Leveling;
- Disposal of excess water;
- Fertility improvement;
- Restoring the vegetation cover.

This works must be done, without any stop work so complex to function properly. Works must be performed without reverse order.

Mixed polluted soils can be improved in a technological cycle of 2 years.

Moderately polluted soils can be improved in 2-3 technological cycle taking into account the rainfall and soil treatment internal possibilities. After each technological cycle are needed soil analyzes to see the state in which the improvement process is and its possible improvement or extension of time of application.

Following the study has results the conclusions:

- The territory suffered a saltwater and oil pollution, salt water being the dominant;
- Pollution by oil is within the class very weak, and the pollution with soluble salts is from low at the surface to moderate and strong in depth;
- Depth of penetration of the pollutant in the soil depends on soil texture;
- High content of exchangeable sodium lead to increased soil alkalization process;
- Soil salinisation is the most important limiting factor in reducing soil fertility;
- For the less polluted area is recommended keeping with the use of pasture improvement overseeding and organic and mineral fertilization;
- For moderately and heavily polluted areas is recommended to change pasture with reforestation after the amelioration works.

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