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Effects of hydrocarbons on temporal changes in soil and crops

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Changes in soil chemical properties, plant density and crops yield (maize, winter wheat, winter barley, soybean and oilseed rape) grown in soil contaminated by different degrees of crude oil and drilling fluids were monitored for three years. Drilling fluids had a stronger impact on chemical properties of the studied soil, while plant density and yield were strongly affected by crude oil. The influence of crude oil contamination on changes in soil chemical characteristics, plant density and yield was significant only during the first year of investigation. The problem of soil contamination by TPH and PAH may be solved through soil bioremediation or aeration by any kind of tillage practice. The common agricultural management practices (inter-row cultivation for spring row crops; management of stubble and autumn ploughing for winter crops) and mineral fertilization reduced the soil TPH and PAHs levels to a tolerable level for production of field crops as early as the second year of investigation.

Key words: Soil, crops, crude oil, drilling fluids.

INTRODUCTION

The exposure of terrestrial environments to crude oil can come from a number of sources, but pipeline leaks are a major contributor (Mendelsohn et al., 1990; Timmerman, 1999). Although the state-of-the-art technical solutions and modern materials used in all phases of the process warrant a high level of safety, the possibility of different incidents is not fully excluded (Issoufi et al., 2006). Such incidents endanger natural resources, primarily soil (Miller and Pesaran, 1980; Bauder et al., 2005), water (Asia et al., 2007) and plants (Kyung-Hwa et al., 2004). Depending on their severity, they may for a certain period of time jeopardize the intended use of land on which the incident has occurred (Callahan et al., 2002; De Jong, 1980). One of the outcomes of drilling process is waste, oil contaminated solid consisting of cuttings and a number of waste fluids used in the drilling process (Veil and Dusseault, 2003). The research objective was to

investigate the possibility of:

1. Changes in soil reactions (soil pH), organic matter (soil organic matter), carbon, nitrogen and sulphur at different concentrations of crude oil and drilling fluids in soil.
2. Changes in concentration of total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAHs) in soil due to its contamination by crude oil and drilling fluids.
3. Effect of soil tillage as a form of bioremediation on the reduction of TPH and PAHs concentrations.
4. Effects of different concentration of crude oil and drilling fluids on emergence, plant density and crops yield.

MATERIALS AND METHODS

The trial was set up on Stagnic Luvisol and located near Struzec collection-transport station and Central waste pit (N 45°31'49" – E 16°34'48") in Panonian agricultural part of Croatia. The total trial field covered 1.25 ha; the size of each trial plot was 96 m² (6.0 m x 4.0 m x 4 replications). The soil was contaminated with crude oil

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Table 1. Methods used in investigations.

Analysis	Method
Soil sampling	ISO 10381; 1-8 (2001-2006)
Preparation of soil samples for physical and chemical analyses	ISO 11464:2004
Determination of particle size distribution in mineral soil material – Method by sieving and sedimentation	ISO 11277:2004
Determination of organic (TOC/OM) and total carbon (TC) after dry combustion (elemental analysis)	ISO 10694:2004
Determination of total nitrogen by dry combustion (elemental analysis)	ISO 13878:2004
Determination of pH (CaCl ₂)	ISO 10390:2004
Extraction of trace elements soluble in aqua regia	ISO 11466:2004
Determination of content of hydrocarbons in the range C ₁₀ to C ₄₀ by gas chromatography	ISO 16703:2004
Determination of polycyclic aromatic hydrocarbons	ISO 18287:2005, EPA 550

Table 2. Particle size distribution of Stagnic Luvisols.

Depth (cm)	Soil horizon	Particle size distribution (%)					Texture
		Coarse sand (2 - 0.2 mm)	Fine sand (0.2 - 0.05 mm)	Coarse silt (0.05 - 0.02 mm)	Fine silt (0.02 - 0.002 mm)	Clay (<0.002 mm)	
0 - 15	Ap + Eg	2.0	5.40	46.25	27.75	18.60	Silty loam
15 - 30	Eg + Btg	1.5	6.40	41.80	30.00	20.30	Silty loam

and drilling fluids only once, at the beginning of investigation in May 2006. Before preparing a seedbed layer on the soil surface, crude oil and drilling fluids were added. For all crops, the seedbed was prepared using a tractor-mounted rototiller to a depth of 25 cm. The experiment was set up as randomized complete block design with four replications of each of the following treatments:

- I - Control (unamended soil);
- II - Soil contaminated by crude oil - 8 L m⁻²;
- III - Soil contaminated by crude oil - 4 L m⁻²;
- IV - Soil contaminated by crude oil - 2 L m⁻²;
- V - Soil contaminated by drilling fluids - 30 kg m⁻²;
- VI - Soil contaminated by drilling fluids - 20 kg m⁻²;
- VII - Soil contaminated by drilling fluids - 10 kg m⁻².

The following crops were grown on trial field:

- First year - 2006: Maize (*Zea mays* L.) and Soybean (*Lysine max* L.);
- Second year - 2006/07: Oilseed rape (*Brassica napus* L.) - Winter wheat (*Triticum aestivum* L.) – Winter barley (*Hordeum vulgare* L.), and;
- Third year - 2007/08: Winter wheat – Soybean – Maize.

Composite soil samples, in four replications, were taken for soil chemical analyses for each treatment from two depths: 0 - 15 cm and 15 - 30 cm. Soil chemical analyses: soil pH, soil organic matter (SOM); total carbon, total nitrogen, total sulphur, total petroleum hydrocarbons; total polycyclic aromatic hydrocarbons (PAH), were determined once a year. The first sampling took place just before maize and soybean were sown in May 2006. The following sampling was done after harvest in July 2007, and the last sampling was carried out after harvest in October 2008.

Observed data were subjected to analysis of variance (ANOVA)

using SAS Institute 9.1.3 and mean values were separated by Fisher's LSD test at $P \leq 0.05$. Methods used to determine the studied parameters are given in Table 1.

RESULTS

Texture of the studied soil was determined solely at the beginning of the investigation and is shown in Table 2. Surface and subsurface layers are characterized by silty loam, while silty-clay-loam texture is found in deeper layers. Major physical and chemical characteristics of crude oil and water-based drilling fluids (muds) applied in the trial are given in Table 3.

Changes in soil pH, soil organic matter, carbon, nitrogen, C/N ratio and sulphur

Research results show marked and expected heterogeneity of the studied parameters. In trial treatments where drilling fluids were applied (V, VI and VII) soil pH was significantly higher compared to other treatments (Table 4). During the second year of investigation the greatest changes in soil pH were recorded in the first layer (0 – 15 cm). Compared to the other investigated treatments significantly higher soil pH values were also recorded in subsurface layer (15 - 30 cm) in treatments V, VI, and VII for 2006 and 2008.

Significantly higher values of SOM were determined in

Table 3. Some characteristics of applied materials (crude oil and drilling fluids) in the trial.

Crude oil									
		Total volume (%)	Density at 15°C (g cm ⁻³)		Viscosity at 37.8°C (mm ² s ⁻¹)				
Light gasoline		6.53	0.69						
Light gasoline + heavy gasoline		32.00	0.75						
Kerosene		10.40	0.82						
Gas oil		17.57	0.85						
Low viscosity lubricant oil		12.08	0.86 - 0.89						
Medium viscosity lubricant oil		6.75	0.89 - 0.90		7.5 - 20.6				
High viscosity lubricant oil					20.6 - 43				
Residue		20.51			> 43				
Loss		0.69	0.96						

Water (%)	Total sulphur (%)	Viscosity at 30°C (mPa)	Viscosity at 30°C (mm ²)	Pour point (°C)	Coke (%)	Ash (%)	Paraffins (%)	Asphaltenes (%)	Total nitrogen (%)
0.08	0.43	5.56	6.65	- 8	2.19	0.004	5.57	0.68	0.44

Drilling fluids					
g kg ⁻¹	Calcium	Barium	Carbon	Nitrogen	Sulphur
Minimum	10	0.16	116	1.10	2.60
Maximum	156	2.33	141	1.40	5.80
Average	103	1.60	127	1.30	4.50

Table 4. Changes in soil pH and soil organic matter (SOM).

Treatment (Year)		I	II	III	IV	V	VI	VII
Soil pH 0 - 15 cm	2006	5.64 b*	5.76 b	5.50 b	5.71 b	6.79 a	7.23 a	7.23 a
	2007	5.88 b	5.34 c	5.16 c	5.31 c	7.04 a	7.15 a	7.26 a
	2008	5.74 b	5.40 b	5.20 b	5.51 b	6.82 a	7.02 a	7.02 a
Soil pH 15 - 30 cm	2006	5.34 b	5.41 b	5.23 b	5.26 b	6.58 a	6.59 a	6.92 a
	2007	5.56 bc	4.95 c	4.91 c	5.05 c	6.48 ba	6.47 ba	6.91 ba
	2008	5.72 b	5.39 b	5.28 b	5.40 b	7.07 a	7.08 a	7.05 a
SOM (%) 0 - 15 cm	2006	2.68 d	5.71 a	3.92 b	3.45 bc	3.50 bc	2.78 d	2.94 cd
	2007	2.87 b	4.90 a	4.03 ba	2.92 b	3.02 b	3.02 b	2.92 b
	2008	3.05 ba	3.90 a	3.63 a	2.80 ba	3.47 a	2.87 ba	2.03 b
SOM (%) 15 - 30 cm	2006	1.83 cb	4.07 a	2.07 cb	1.30 c	2.07 cb	1.83 cb	2.53 b
	2007	2.17 a	2.22 a	2.40 a	1.83 a	2.18 a	1.82 a	1.87 a
	2008	2.33 a	3.53 a	3.63 a	3.07 a	3.10 a	2.57 a	2.77 a

* Values are means of 4 replicates. For each parameter, values in the same row followed by an identical letter are not significantly different according to Fisher's LSD test ($P \leq 0.05$).

treatments II, III, IV and V for the first year of investigation than in control treatment (Table 4). This difference in SOM content gradually diminished with depth, from the first to the last year of investigation. The SOM content in the last year of investigation, in treatments involving crude oil, was not significantly higher compared to other

treatments.

Changes in total carbon follow trends and statistical differences that are almost identical to SOM (Table 5). Compared to the control treatment, significantly higher carbon content was recorded in the first year of investigation in treatments where crude oil was applied

Table 5. Changes in total carbon, total nitrogen, C/N ratio and total sulphur in soil.

	Treatment (Year)	I	II	III	IV	V	VI	VII
Carbon (%) 0 - 15 cm	2006	1.70 c*	2.78 a	2.57 a	2.40 ba	2.42 ba	2.03 bc	1.99 bc
	2007	1.79 c	2.84 a	2.52 ba	1.90 c	2.21 bc	2.15 bc	1.81 c
	2008	1.71 a	2.06 a	1.87 a	1.36 a	1.49 a	1.67 a	1.70 a
Carbon (%) 15 - 30 cm	2006	1.09 a	1.37 a	1.30 a	1.08 a	1.44 a	1.24 a	1.67 a
	2007	1.22 a	1.48 a	1.43 a	1.16 a	1.37 a	1.16 a	1.17 a
	2008	1.33 a	1.71 a	1.81 a	1.53 a	1.72 a	1.51 a	1.40 a
Nitrogen (%) 0-15 cm	2006	0.184 c	0.200 bac	0.212 ba	0.230 a	0.222 a	0.182 bc	0.197 bac
	2007	0.203 a	0.206 a	0.232 a	0.187 a	0.200 a	0.184 a	0.188 a
	2008	0.181 a	0.184 a	0.185 a	0.137 a	0.149 a	0.161 a	0.168 a
Nitrogen (%) 15-30 cm	2006	0.123 a	0.112 a	0.118 a	0.120 a	0.146 a	0.125 a	0.169 a
	2007	0.143 a	0.138 a	0.151 a	0.145 a	0.142 a	0.135 a	0.133 a
	2008	0.136 a	0.153 a	0.170 a	0.154 a	0.150 a	0.143 a	0.141 a
C / N ratio 0 - 15 cm	2006	9.24 f	13.90 a	12.12 b	10.43 de	10.90 dc	11.15 c	10.10 fe
	2007	8.82 a	13.79 a	10.86 a	10.16 a	11.05 a	11.68 a	9.63 a
	2008	9.45 c	11.20 a	10.11 cb	9.93 cb	9.99 cb	10.37 b	10.12 cb
C / N ratio 15 - 30 cm	2006	8.86 c	12.23 a	11.02 ba	9.00 bc	9.86 bc	9.92 bc	9.88 bc
	2007	8.59 a	10.48 a	8.94 a	7.35 a	9.08 a	8.39 a	8.32 a
	2008	9.76 a	11.33 a	10.60 a	9.96 a	11.49 a	10.53 a	9.86 a
Sulphur (%) 0 - 15 cm	2006	0.042 c	0.057 ba	0.053 bac	0.047 bc	0.063 a	0.063 a	0.062 a
	2007	0.111 a	0.084 a	0.081 a	0.084 a	0.123 a	0.111 a	0.082 a
	2008	0.076 a	0.107 a	0.071 a	0.058 a	0.056 a	0.069 a	0.064 a
Sulphur (%) 15 - 30 cm	2006	0.029 c	0.037 b	0.032 cb	0.047 a	0.037 b	.034 cb	0.038 b
	2007	0.066 a	0.079 a	0.062 a	0.056 a	0.067 a	0.078 a	0.059 a
	2008	0.066 a	0.062 a	0.106 a	0.054 a	0.062 a	0.061 a	0.058 a

*Values are means of 4 replicates. For each parameter, values in the same row followed by an identical letter are not significantly different according to Fisher's LSD test ($P \leq 0.05$).

(treatments II, III and IV) as well as in treatment with the highest dose of drilling fluids (treatment V). But, in the last year of investigation, the level of total carbon in surface layer in all treatments showed no significant difference. In surface layer, carbon content was reduced through the investigated period, while in subsurface layer it was increased through the investigated period. This is attributed to enhanced leaching of carbon from surface towards deeper layers.

Significantly higher nitrogen content in the surface layer in the first year, compared to the control treatment, was determined in treatments IV and V. No significant differences in nitrogen content were determined in other treatments and depths during the three years of investigation (Table 6).

Regarding the sulphur content, it was only during the

first year of investigation that a significantly higher sulphur content compared to the control treatment was recorded in the first soil layer (treatments: II, V, VI and VII) and in the second soil layer (treatments: II, IV, V and VII). In all other measurements during the investigated period, there were no statistical differences in sulphur content.

Total petroleum hydrocarbons (TPH)

Soil contamination by TPH is shown in Table 6. In comparison with the control treatment, a statistically higher TPH content was recorded in the first year of investigation in treatments II, III, IV, V and VI (depth 0 – 15 cm). Reduction of TPH content was observed in

Table 6. Changes in total petroleum hydrocarbons and polycyclic aromatic hydrocarbons.

Treatment (Year)		I	II	III	IV	V	VI	VII
TPH (g kg ⁻¹) 0 - 15 cm	2006	0.15 d*	12.29 a	6.50 b	2.33 c	2.51 c	2.09 c	0.86 dc
	2007	0.14 c	4.59 a	2.78 b	1.47 cb	1.24 cb	0.89 b	0.40 b
	2008	0.11 b	1.06 a	0.40 ba	0.13 b	0.38 b	0.43 ba	0.21 b
TPH (g kg ⁻¹) 15 - 30 cm	2006	0.09 b	3.28 a	3.03 a	0.34 b	1.01 b	0.58 b	0.39 b
	2007	0.07 b	2.34 a	0.91 b	0.58 b	0.62 b	0.64 b	0.29 b
	2008	0.08 b	1.67 a	0.59 b	0.39 b	0.75 b	0.45 b	0.16 b
PAH (mg kg ⁻¹)** 0 - 15 cm	2006	0.07	47	17	10	13	12	13
	2007	0.04	0.01	0.05	0.01	0.10	0.14	0.07
PAH (mg kg ⁻¹) 15 - 30 cm	2006	0.08	14	13	10	22	0.74	16
	2007	0.05	0.05	0.02	0.02	0.03	0.05	0.25

*Values are means of 4 replicates. For each parameter, values in the same row followed by an identical letter are not significantly different according to Fisher's LSD test ($P \leq 0.05$).

**PAH content was also investigated in 2008 for both depths and it was less than 0.001 mg kg⁻¹.

surface layer in the second and third year, compared to the first year of investigation. During the whole period of investigation, a significantly higher TPH content was recorded in surface layer in treatment II than in control treatment. In subsurface layer, treatment with 8 L m⁻² of crude oil significantly influenced TPH content during all three years of investigation.

Polycyclic aromatic hydrocarbons (PAHs)

The sum of PAH are shown in Table 6, and individual components of PAH are presented in Table 7 (depth 0 – 15 cm) and Table 8 (depth 15 – 30 cm). The highest PAH content in the first year of investigation was determined in the surface layer in treatment where the highest crude oil doses were applied. During the first year of investigation PAH content was reduced with depth in treatments II, III and VI. Differences in PAH content between treatments were not as pronounced in the second year. During the second year, relatively higher PAH content was determined in treatments where drilling fluids were applied compared to the treatments with crude oil (Table 6).

Differences in individual PAH between treatments are shown in Tables 7 and 8. PAH with less benzene rings prevail in treatments with crude oil whereas less degradable PAH with more benzene rings predominate in treatments with drilling fluids. During the first year of investigation, phenanthrene, composed of three benzene rings, prevailed among individual PAH both in crude oil and in drilling fluids down to 0 - 15 cm depth (Table 7) and 15 - 30 cm depth (Table 8). In the second year of investigation, fluoranthene and pyrene (four benzene rings PAHs) were determined in surface layer in treatments where drilling fluids were applied. However,

besides the mentioned PAH, benzo(a)anthracene and chrysene, also composed of four benzene rings, and benzo(b)fluoranthene (five or six benzene rings PAHs) were found in the second year in surface and subsurface layers in treatments involving drilling fluids.

Changes in plant density and yield of crops

During the first year of investigation, depending on the different TPH contents in soil, differences in crop emergence were observed as early as at the germination and emergence stages of maize and soybean (Table 9). Maize and soybean growth and emergence were inversely proportional to soil TPH content. In treatment where the highest dose of crude oil was applied, plant density and yield were about one-fifth of the yield achieved in the control treatment. In treatments where drilling fluids were applied, plant density and yields of grown crops were significantly lower compared to the control treatment, but this difference was not as marked as in treatments with higher doses of crude oil. During the first year, soybean responded more strongly to soil TPH content than maize. Lower plant density and yield were recorded in all treatments of soybean compared to treatments in which maize was grown.

During the second year of investigation, in the late summer and autumn of 2006, the following winter crops were sown on the trial field after maize and soybean harvests: oilseed rape, wheat and barley. Although significant differences in oilseed rape density were recorded (the highest density was recorded in treatment with the highest dose of drilling fluids), there were no statistical differences in yield between the trial treatments. The highest plant density and barley grain yield were

Table 7. Soil contamination by polycyclic aromatic hydrocarbons, mg kg⁻¹, 0-15 cm.

		Treatment (Year) *	I	II	III	IV	V	VI	VII	
Three Carbon (benzene) rings	Fluorene	2006	<0.001	4.5	<0.001	0.9	0.5	0.3	0.5	
		2007	<0.001	<0.001	<0.001	<0.001	0.005	0.003	<0.001	
	Phenanthrene	2006	0.002	41.0	8.0	5.6	3.0	2.6	3.0	
		2007	<0.001	0.01	0.05	0.01	0.04	0.03	0.001	
	Anthracene	2006	<0.001	1.5	<0.001	1.7	1.0	1.0	1.0	
		2007	<0.001	<0.001	<0.001	<0.001	0.005	0.01	0.005	
Four Carbon (benzene) rings	Fluoranthene	2006	0.02	<0.001	6.0	1.8	2.0	1.0	2.0	
		2007	0.02	<0.001	<0.001	<0.001	0.02	0.004	0.04	
	Pyrene	2006	0.02	<0.001	3.0	<0.001	2.0	2.0	2.0	
		2007	0.01	<0.001	<0.001	<0.001	0.03	0.04	0.02	
	Benzo(a) Anthracene	2006	0.003	<0.001	<0.001	<0.001	1.0	1.0	1.0	
		2007	<0.001	<0.001	<0.001	<0.001	0.001	0.02	0.001	
Chrysene	2006	0.01	<0.001	<0.001	<0.001	2.0	2.0	2.0		
	2007	<0.001	<0.001	<0.001	<0.001	<0.001	0.03	0.004		
Five or six Carbon (benzene) rings	Benzo(b) Fluoranthene	2006	0.001	<0.001	<0.001	<0.001	0.75	0.55	0.30	
		2007	<0.001	<0.001	<0.001	<0.001	<0.001	0.02	<0.001	
	Benzo(k) fluoranthene**	2006	0.001	<0.001	<0.001	<0.001	<0.001	1.0	1.0	
		2006	0.01	<0.001	<0.001	<0.001	0.75	0.55	0.20	
	pyrene	2007	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
		2006	0.003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

* Listed individual PAH content was investigated in 2008 and it was less than 0.001 mg kg⁻¹. ** Contents of Benzo(k)fluoranthene and Indeno(1,2,3-c,d)pyrene in 2007 were also less than 0.001 mg kg⁻¹.

achieved in treatment with 20 kg m⁻² of drilling fluids. As regards plant density in winter wheat production, the best results were achieved in treatment involving the highest dose of drilling fluids.

During the third year of investigation, in trial treatment maize and soybean were grown again. Significantly higher plant density of maize compared to all other treatments was determined in treatment with the highest dose of drilling fluids, while the highest yield of maize grain was obtained in control treatment and treatment with the lowest dose of drilling fluids. Treatment with the highest dose of drilling fluids gave the best results in soybean production as well. Better crop response in treatments where drilling fluids were applied is attributed to their chemical composition. As an increased content of calcium was found in the chemical composition of drilling fluids (Table 3), this material acted as liming material.

DISCUSSION

In treatments where crude oil was applied, soil pH remained almost identical over the whole trial period and both depths. These findings indicate that crude oil had no influence on changes in soil pH during the three-year

investigation period. Similar results were obtained by Miller and Pesaran (1980) and Bauder et al. (2005). In treatments where drilling fluids were applied, soil pH was significantly higher compared to other treatments. Certain amounts of calcium and barium sulphate are used as additives to increase drilling fluid density and as additives for corrosion inhibition of oil and gas pipes. This is why drilling fluids contain larger amounts of calcium and barium. Also, material with increased calcium content is usually added to bind fluids when repairing a pipe breakage or other incidents (Veil and Dusseault, 2003). Due to increased carbon and lower nitrogen contents in treatments where higher doses of crude oil (treatments II and III) and larger amounts of drilling fluids (treatments V and VI) were applied, significant changes in C/N ratios occurred, notably in the surface layer. De Jong (1980) reported on unfavourable carbon to nitrogen ratios in his investigations as well. Nitrogen addition with mineral fertilizers (Kirkpatrick et al., 2006) or organic soil improvers (Aerogun and Ataga, 2007; Rojas-Avelizapa et al., 2007) may enhance the development of microbiological processes in soil and thereby improve the C/N ratio.

Regarding the sulphur content, volatile fraction influenced sulphur reduction. Severin et al. (1983) reported that highly volatile sulphur compounds prevail in

Table 8. Soil contamination by polycyclic aromatic hydrocarbons, mg kg⁻¹, 15-30 cm.

		Treatment (Year) *	I	II	III	IV	V	VI	VII	
Three carbon (benzene) rings	Fluorene	2006	<0.001	<0.001	1.0	0.8	0.8	0.03	0.6	
		2007	<0.001	<0.001	<0.001	<0.001	0.005	<0.001	0.002	
	Phenanthrene	2006	0.004	8.0	12.0	9.0	8.0	0.3	5.2	
		2007	<0.001	0.03	0.01	0.01	0.01	0.02	0.05	
		Anthracene	2006	0.008	<0.001	<0.001	0.2	1.4	0.06	1.0
			2007	<0.001	<0.001	<0.001	<0.001	<0.001	0.004	0.001
Four carbon (benzene) rings	Fluoranthene	2006	0.002	<0.001	<0.001	<0.001	2.3	0.14	2.0	
		2007	0.02	0.01	0.01	0.1	0.01	0.001	0.07	
	Pyrene	2006	0.01	<0.001	<0.001	<0.001	2.7	0.14	2.0	
		2007	0.01	<0.001	<0.001	0.1	0.005	0.025	0.05	
		Benzo(a) Anthracene	2006	0.02	6.0	<0.001	<0.001	1.0	<0.001	1.0
			2007	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Chrysene	2006	0.01	<0.001	<0.001	<0.001	3.0	<0.001	2.0		
	2007	<0.001	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	0.02	
Five or six carbon (benzene) rings	Benzo(b) Fluoranthene	2006	0.007	<0.001	<0.001	<0.001	0.9	0.05	0.6	
		2007	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	0.01	
	Benzo(k) Fluoranthene	2006	0.003	<0.001	<0.001	<0.001	1.0	<0.001	1.0	
		2007	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	0.002	
	Benzo(a) pyrene	2006	0.009	<0.001	<0.001	<0.001	0.9	<0.001	0.6	
		2007	0.01	<0.001	<0.001	<0.001	0.001	0.001	0.025	
		Benzo(ghi)perylene**	2006	0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
			2007	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Indeno(1,2,3-c,d)	2006	0.005	<0.001	<0.001	<0.001	<0.001	0.02	<0.001		
	2007	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	0.02		

* Listed individual PAH content was investigated in 2008 and it was less than 0.001 mg kg⁻¹.

** Content of Benzo(ghi)perylene in 2007 was also less than 0.001 mg kg⁻¹.

crude oil.

Research results have indicated that the usual tillage procedures, such as plowing, disc harrowing, harrowing and preparing seeding layer can reduce the concentration of TPH to a tolerant level. In this case, after only one year of investigation and the agro-technical interventions that were carried out, vertical mixing of contaminated soil from the surface with deeper layers where the soil is clean occurs. Due to the predominance of the volatile aromatic fraction in their structure, most TPH evaporate into the air or are degraded by microbiological processes (Ogboghodo et al., 2004) or by soil tillage practices (Chaineau et al., 2003). TPH remaining in the soil in concentrations below 5 g kg⁻¹ are degraded very slowly and bind strongly to the soil adsorption complex. According to these investigations, the mentioned TPH concentration is not harmful to the plant density and yield of crops grown. More precisely, the studied crops can be produced, without greater limitations to plant density and yield, on soil containing less than 5 g kg⁻¹ of TPH. Kyung-Hwa et al. (2004) report that 10 g kg⁻¹ of TPH was toxic in the production of studied crops, but they also say that phytotoxicity was not

determined in soil containing not more than 1 g kg⁻¹ TPH. Some authors (Timermann, 1999; Kisic et al., 2009) maintain that the rate of TPH degradation in soil is primarily associated with the quantity and type of crude oil or drilling fluids, organic matter content and soil mechanical composition, soil moisture status and soil use as well as with the season in which increased TPH content was detected in soil.

Individual PAH with more benzene rings are the reason why higher PAH contents were determined in treatments with drilling fluids during the second year of investigation. The PAH containing more benzene rings are present in treatments with drilling fluids and have not yet been degraded by physical (Hund and Traunspurger, 1994), chemical (Riser-Roberts, 1998) or microbiological processes (Liste and Felgentreu, 2006). The above indicates that the number of benzene rings is a decisive indicator of the rate of PAHs degradation. The less benzene rings, the faster degradation; the more benzene rings, the slower degradation.

During the first year of investigation crude oil had a much stronger influence on plant density and yield than drilling fluids. TPH form a thin film around the seed germ

Table 9. Number of plants and yield.

Treatment	I	II	III	IV	V	VI	VII
1st investigation year							
Maize							
Plants hectare ⁻¹	56.667 a*	10.000 f	23.333 e	36.667 d	43.333 d	36.667 c	46.667 b
Yield, t ha ⁻¹	9.80 a	2.07 d	4.97 c	9.50 a	8.43 b	7.70 b	7.93 b
Soybean							
Plants hectare ⁻¹	3.513.333 a	580.000 g	843.333 f	1.190.000 e	1.826.667 d	2.156.667 c	2.530.000 b
Yield, t ha ⁻¹	1.98 a	0.41 e	0.59 ed	0.66 d	1.08 c	1.40 b	1.43 b
2nd investigation year							
Oil seed rape							
Plants hectare ⁻¹	2.900.000 c	2.850.000 d	2.950.000 b	2.950.000 b	3.050.000 a	2.950.000 b	2.850.000 d
Yield, t ha ⁻¹	1.51 a	1.39 a	1.40 a	1.47 a	1.48 a	1.47 a	1.48 a
Winter Barley							
Plants hectare ⁻¹	6.300.000 c	5.600.000 g	5.733.333 f	5.933.333 e	6.233.333 d	6.366.667 a	6.333.333 b
Yield, t ha ⁻¹	4.17 a	3.62 c	3.84 c	3.72 c	4.13 a	4.18 a	4.01 ba
Winter wheat							
Plants hectare ⁻¹	6.833.333 b	6.166.666 d	6.500.000 c	6.500.000 c	7.000.000 a	6.833.333 b	6.500.000 c
Yield, t ha ⁻¹	4.50 a	4.07 a	4.27 a	4.27 a	4.60 a	4.50 a	4.27 a
3rd investigation year							
Maize							
Plants hectare ⁻¹	63.333 c	60.000 d	60.000 d	66.667 b	70.000 a	60.000 d	63.333 c
Yield, t ha ⁻¹	10.17 a	9.93 a	9.87 a	10.03 a	9.50 a	9.87 a	10.17 a
Soybean							
Plants hectare ⁻¹	4.180.000 b	3.960.000 e	3.920.000 f	4.080.000 c	4.240.000 a	4.180.000 b	4.000.000 d
Yield, t ha ⁻¹	2.56 a	2.48 a	2.46 a	2.50 a	2.58 a	2.52 a	2.50 a
Winter wheat							
Plants hectare ⁻¹	6.798.000 c	6.475.000 f	6.329.333 g	6.840.000 b	7.104.000 a	6.580.000 d	6.489.000 e
Yield, t ha ⁻¹	4.80 a	4.40 a	4.63 a	4.60 a	4.73 a	4.63 a	4.60 a

* Values are means of 4 replicates. For each parameter, values in the same row followed by an identical letter are not significantly different according to Fisher's LSD test ($P \leq 0.05$).

and thereby prevent oxygen penetration, creating dry conditions around the seed. This situation prevents water uptake and leads to embryo death. Another reason for poorer emergence is that the TPH contaminated soil is more compacted and of poorer structure with an increased content of toxic TPH substances. In the following years of investigation the influence of crude oil and drilling fluids on plant density and yield was negligible. Shahriari et al. (2007) and Adedokun and Ataga (2007) reported that oil pollution inhibits seed germination and plant growth. This can be explained by the chemical properties of TPH in soil. The most toxic crude oil components are highly volatile fractions (Udo and Fayemi, 1975), which obviously preponderated in the initial phases of

the trial treatment. After disappearance of such crude oil fractions due to biodegradation, volatilization or land-farming, the expected crop growth occurs.

Conclusions

Drilling fluids had a stronger influence on the studied soil chemical properties while crude oil affected plant density and crop yield more strongly in the first trial year. The level of soil contamination by TPH and PAH in the first trial year had a crucial role for the achieved plant density and yield of crops grown.

TPH levels below 5 g kg⁻¹ in soil or 5 mg kg⁻¹ PAH in

soil had no significant effect on plant density of grown crops. Consequently, the value of 5 g kg⁻¹ TPH and 5 mg kg⁻¹ PAH in soil could be recommended as an alerting or emergency value for remediation of TPH contaminated soil.

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