Possibilities for the Use of Oil Contaminated Solids for Agricultural Purposes

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Summary

All phases of oil exploitation, from the start of oil-drilling works to construction of the transport system (underground pipeline network) are accompanied by interventions and procedures hazardous to the environment. Although the state-of-the-art technical solutions and modern materials used by INA in all exploitation phases warrant a high level of safety, the possibility of different incidents is unfortunately not fully excluded.

Incidents endanger natural resources, primarily soil and water, and may, depending on their severity, jeopardize for a certain length of time the intended use of the land on which the incident occurred, that is, rule out the possibility of its use for plant or livestock production.

In the last two decades, the staff members of the Faculty of Agriculture Department of General Agronomy participated in the number of studies dealing with the evaluation of the extent of contamination of soil on which an oil incident occurred and drew up studies and plans for remediation of such soils. The paper presents the results of three-year-long research on growing winter wheat (*Triticum aestivum* L.), winter barley (*Hordeum vulgare* L.) and soybean (*Glycine hyspida* L.) in pots under different degrees of soil contamination by oil. Research involved monitoring of changes in the soil chemical complex (pH, changes in plant available phosphorus and potassium, content of organic matter); also monitoring of number of plants, achieved yields and studying chemical changes in plant material caused by different degrees of soil contamination.

Key words

crops; oil contaminated solid; soil changes; yield

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Received: September 6, 2006 | Accepted: February 17, 2007

Introduction

During the last decade of the 20th century and at the beginning of the 21st century, among other agriculture related issues, two interconnected issues have come into focus: food security issue on one hand and food safety issue on the other hand. This has resulted in a number of projects launched within EU countries which could all have one common heading: from the producer to the consumer or from the field to the table; so called food route. This way we always have information where raw material, food item or product are produced, in what way and in what soil it has been grown, what was used for its fertilization, and where it was stored. Special attention has been given to the soil and its quality, in particular to soil contamination by various pollutants. As we know, some metals (Fe, Mn, Zn and Co) are biogenic elements which are phytotoxic in high concentrations, and their presence in the food chain in quantities above allowed levels may cause acute or chronic diseases. The foregoing and some other microelements (Cu and S) tend to accumulate unlimitedly in living organisms – plant tissue, which is particularly dangerous in contaminated sites which were included in these investigations.

Materials and methods

For the purpose of identifying potential changes in: the chemical composition of soil, mineral and total oil content; polycyclic aromatic hydrocarbon (PAH) content, and heavy metals, yield achieved, and changes in the plant material, in the greenhouse of the Department for General Agronomy of the Faculty of Agriculture in autumn 2003 a plant growth experiment was set up with four repetitions and the following treatments:

1. Check treatment (clean soil not affected by oil well operations), soil taken in the vicinity of the Števkovica – Beničanci (oil-hole Števkovica-4) pipeline rupture location (Muvrin and Benčić, 1992; Kisić et al., 2003; Kisić et al., 2005),
2. Completely contaminated soil – soil taken from the contaminated soil disposal site at the Števkovica 4 central landfill,
3. 1/2 clean soil + 1/2 contaminated soil,
4. 2/3 clean soil + 1/3 contaminated soil,
5. 3/4 clean soil + 1/4 contaminated soil,
6. Soil delivered to the pipeline rupture location,
7. 2/3 clean soil + 1/3 crude "fresh" oil,
8. 3/4 clean soil + 1/4 crude "fresh" oil.

The experiment was set up in pots with 4 repetitions, and the experimental area (pot) is 0.05 m^2. During crops growth usual agrotechnical measures (chemical treatment and mineral fertilization) were applied. Fundamental chemical analyses of the soil (soil reaction, organic matter content, available phosphorus and potassium, and mineral or organic oil content) were made twice a year: prior to setting up the experiment and after the "harvest".

The main purpose of the research is to identify possibility for growing crops in soils contaminated by hydrocarbons (Van-Camp et al., 2004; ISO 10381, 2005), and the effect the said contamination might have on crop yield by determining:

1. The influence of varying quantity of contaminated soil on the crop emergence time, establishment and yield achievment.
2. Changes in chemical composition of the soil: soil reaction, plant available phosphorus and potassium, and organic matter content.

Results and discussion

According to the above described method after site preparation (delivery of clean and contaminated soils from the area in the vicinity of the pipeline rupture location) the plant growth experiment was set up. Those treatments were were included where the changes were expected, both, in the soil (basic chemical properties, metals, oils, PAHs), and in the crops grown (chemical composition of plant material, crop establishment and yield achievment).

The data presented in this paper show slight, barely present chemical heterogeneity of the soil (Table 1). Soil reaction is low acid to neutral in all samples, and varies in the range from pH 6.42 to pH 7.13. These values indicate that soil reaction values are not significantly affected by varying quantities of hydrocarbons in the soil. However, this is not the case with the organic matter content in the soil. The soil taken from the site outside of the rupture location, the one which was not affected by oil well operations has lower organic matter content (treatments 1; 7 and 8). In all other treatments the organic matter content is higher, or it was increased consistent with the increase in the content of oil i.e. hydrocarbons in the soil. For that reason, we find it not surprising that the highest organic matter content has been found in completely contaminated soil taken from the contaminated soil disposal site at the Števkovica-4. The presence of available phosphorus and potassium in the soil is high, which can be attributed to fertilization carried out in plant growth experiment.

The crops being investigated include: winter wheat (*Triticum aestivum* L.) which was sown on 14 October 2003 and 26 October 2005 respectively, winter barley (*Hordeum vulgare* L.) sown on 21 October 2004 and soybean (*Glycine hyspida* L.) sown on 29 June 2005 and 3 July 2006 respectively. Sowing standards applied in these investigations

Table 1. Basic chemical properties of the soil

Time (date)	Soil reaction, pH		Organic matter		Plant available nutrition - mg 100g^{-1} of soil			
Sample of soil	n KCl	Valuation	%	Valuation	P_2O_5	Valuation	K_2O	Valuation
Teratment 1. Check treatment (clean soil not affected by oil well operations)								
Autumn 2003	6.51	neutral	2.1	low humic	24.4	rich	14.0	moderately rich
Summer 2005	6.47	low acid	2.4	low humic	>40.0	extremely rich	>40.0	extremely rich
Treatment 2. Completely contaminated soil – soil taken from the contaminated soil disposal site at Štv – 4								
Autumn 2003	6.67	neutral	5.6	high humic	>40.0	extremely rich	>40.0	extremely rich
Summer 2005	6.93	neutral	5.4	high humic	>40.0	extremely rich	>40.0	extremely rich
Treatment 3. 1/2 clean soil + 1/2 contaminated soil								
Autumn 2003	6.82	neutral	4.2	medium humic	>40.0	extremely rich	>40.0	extremely rich
Summer 2005	6.89	neutral	4.0	medium humic	>40.0	extremely rich	>40.0	extremely rich
Treatment 4. 2/3 clean soil + 1/3 contaminated soil								
Autumn 2003	6.78	neutral	3.2	medium humic	>40.0	extremely rich	>40.0	extremely rich
Summer 2005	6.89	neutral	3.4	medium humic	>40.0	extremely rich	>40.0	extremely rich
Treatment 5. 3/4 clean soil + 1/4 contaminated soil								
Autumn 2003	6.43	low acid	3.6	medium humic	>40.0	extremely rich	>40.0	extremely rich
Summer 2005	6.64	neutral	3.5	medium humic	>40.0	extremely rich	>40.0	extremely rich
Treatment 6. Soil delivered to the pipeline rupture location MS Števkovica OS Beničanci								
Autumn 2003	7.13	neutral	3.5	medium humic	35.9	extremely rich	>40.0	extremely rich
Summer 2005	7.07	neutral	3.4	medium humic	>40.0	extremely rich	>40.0	extremely rich
Treatment 7. 2/3 clean soil + 1/3 crude «fresh» oil								
Autumn 2003	6.51	neutral	1.9	low humic	>40.0	extremely rich	>40.0	extremely rich
Summer 2005	6.54	neutral	1.8	low humic	>40.0	extremely rich	>40.0	extremely rich
Treatment 8. 3/4 clean soil + 1/4 crude «fresh» oil								
Autumn 2003	6.42	low acid	2.2	low humic	>40.0	extremely rich	>40.0	extremely rich
Summer 2005	6.44	low acid	2.3	low humic	>40.0	extremely rich	>40.0	extremely rich

comply with standards for these crops sown in natural field conditions.

Crop establishment recorded, which will be probably be confirmed by yield achieved, indicates that oil contaminated soil was crucial factor in the decrease of crop establishment, and consequently number of plants and yield reduction. By the similar results in their research reached: Gogoi et al., 2003; Maliszewska-Kordybach and Smreczak 2003; River-Espinoza and Dendooven 2004. Judging by recorded crop establishment, the differences in yield achieved are expected, as shown in the tables 2, 3, 4 and 5.

During the first year of research, in winter wheat crops (variety - *Zlatni dukat*), in the very stages of germination and emergence, differences in crop emergence were observed depending on the different content of hydrocarbons in the soil. Emergence of plants being investigated was inversely proportional to the crude oil content of soil. In the treatments with significantly more contaminated soil (treatments 2, 4, 7 and 8) emergence recorded was lower relative to the treatments with less hydrocarbon or oil contaminated soil (Table 2). It is clear that a thin oil coating is formed around the germ thus preventing oxygen influx and causing death of the seed and/or slower emergence of the future plant. If an optimum number of plants would have been the one recorded in the check treatment(100%), then in contaminated soil 74% plants crop establishment was recorded; in treatment 3: almost 100%; in treatment 4: 60%; in treatment 5: 88% plants; while in treatment 6, crop establishment was only 50% plants. On the two remaining treatments crop establishment were 57% and 37% plants respectively. Yield achieved on check treatment was statistically higher relative to the other treatments, but no statistically significant differences were found between the other treatments.

During the second year of investigation winter barley (variety – *Rex*) was sown in pots. In the very beginning of crop emergence differences were observed relative to the first year of research when the wheat was sown. In the second year crop emergence was rather uniform and that which trend continued throughout the growth process. The number of plants recorded and crop establishment achieved show no differences that were observed during the first year. Based on the established number of plants no statistically significant differences were noticed. However, yield achieved indicates statistical differences, but less striking than in the first year. The greatest difference was recorded between the check (treatment 1) and contaminated soil (treatment 2), while other treatments had more or less uniform yield (Table 3).

After barley was removed from the pots, soybean was sown (cultivar *Sabina*: 00-000 maturity group). Crop establishment and yield show very interesting changes relative to the previous year. As usual, sowing standard for all treatments and all pots was the same. However, in the early

Table 2. Some parameters in the growing of winter wheat (2003/04)

Treatment. Parametar	Number of plants with spike	Number of plants without spike	Total number of plants	Length of spike, cm	Yield, g pot^{-1}
1. Check – clean soil	72	35	107	5.2	44.5
2. Contaminated soil	64	15**	79	4.5	22.3
3. 1/2 clean+1/2 contaminated soil	74	31	105	4.2	31.7
4. 2/3 clean+1/3 contamin. soil	47**	16**	63**	5.0	26.9
5. 3/4 clean+1/4 contamin. soil	60	33	93	4.4	28.0
6. Soil deliv. to pipeline rupture	43**	10**	53**	5.0	26.9
7. 2/3 clean+1/4 crude «fresh» oil	48**	12**	60**	5.1	22.4
8. 3/4 clean+1/4 crude «fresh» oil	37**	2**	39**	5.0	23.6
$t_{5\%}$*	18.0	17.4	29.3	n.s.	8.3
$t_{1\%}$**	25.1	24.2	40.8		11.6

Table 3. Some parameters in the growing of winter barley (2004/05)

Treatment. Parametar	Number of plants with spike	Number of plants without spike	Total number of plants	Length of spike, cm	Yield, g pot^{-1}
1. Check – clean soil	106	25	131	5.0	61.2
2. Contaminated soil	91	22	112	3.5**	51.2**
3. 1/2 clean+1/2 contaminated soil	102	30	133	3.5**	55.4*
4. 2/3 clean+1/3 contamin. soil	98	30	128	3.5**	54.7*
5. 3/4 clean+1/4 contamin. soil	95	30	125	4.1**	57.4
6. Soil deliv. to pipeline rupture	110	29	139	3.5**	56.2*
7. 2/3 clean+1/4 crude «fresh» oil	97	26	122	3.9**	54.1*
8. 3/4 clean+1/4 crude «fresh» oil	96	31	128	3.5**	54.2*
$t_{5\%}$*	n.s.	n.s.	n.s.	0.7	8.0
$t_{1\%}$**				1.0	12.0

Table 4. Some parameters in the growing of winter wheat (2005/06)

Treatment. Parametar	Number of plants with spike	Number of plants without spike	Total number of plants	Length of spike, cm	Yield, g pot^{-1}
1. Check – clean soil	108	21	129	3.5	46.6
2. Contaminated soil	81*	5**	86*	3.5	42.6
3. 1/2 clean+1/2 contaminated soil	96	18**	114	3.4	48.9
4. 2/3 clean+1/3 contamin. soil	103	20*	123	3.3	45.5
5. 3/4 clean+1/4 contamin. soil	95	18**	113	3.5	41.6
6. Soil deliv. to pipeline rupture	94	18**	112	3.5	48.0
7. 2/3 clean+1/4 crude «fresh» oil	96	19**	115	3.5	36.3**
8. 3/4 clean+1/4 crude «fresh» oil	97	18**	115	3.5	37.8**
$t_{5\%}$*	20.3	3.9	24.1		9.7
$t_{1\%}$**		5.4			13.6

Table 5. Some parameters in the growing of soybean (2005 and 2006)

Treatment. Parametar	Number of plants, 2005	Number of beans, 2005	Yield, g pot^{-1} 2005	Number of plants, 2006	Number of beans, 2006	Yield, g pot^{-1} 2006
1. Check – clean soil	14	105	32.8	8	38	15
2. Contaminated soil	8**	54**	18.0**	8	35	11
3. 1/2 clean+1/2 contaminated soil	6**	52**	19.3**	9	39	14
4. 2/3 clean+1/3 contamin. soil	5**	44**	17.9**	8	34	13
5. 3/4 clean+1/4 contamin. soil	9**	73	20.3*	8	40	12
6. Soil deliv. to pipeline rupture	2**	14**	6.5**	8	46**	16
7. 2/3 clean+1/4 crude «fresh» oil	8**	77	23.2*	8	47**	17
8. 3/4 clean+1/4 crude «fresh» oil	8**	72	22.4*	9	53**	16
$t_{5\%}$*	5.5	32.6	9.8	n.s.	10.5	n.s.
$t_{1\%}$**	7.6	45.4	13.7		14.6	

emergence stage and also during the growth cycle significant differences were observed in crop establishment and yield achieved. Throughout the growth cycle the largest number of plants was recorded with the check treatment, while with other treatments the established number of plants varied (Table 5). By far the worst crop establishment was found with treatment 6, and with other treatments it was significantly lower than with the check treatment. The highest yield was recorded with the check treatment; while with others, yield was significantly lower. Although the experiment was commenced three years ago, it can be noticed that oil contamination even then had significant effect on the number of emerged plants and, accordingly, crop establishment of soya.

In order to make a comparison with the first year of research when winter wheat was sown in pots, this crop (the same variety – *Zlatni dukat*) was sown again in 2005. In the early emerging stage significant changes could be noticed in crop establishment achieved relative to the first investigation (Table 4). As in the first year, around 200 viable seeds per pot were sown and wheat establishment varied from 70% with the check treatment to 50% with the soil completely contaminated with oil. During the earing up stage almost similar percentages were recorded. If establishment achieved with the check treatment is taken as optimum establishment in the earing up stage then 70% establishment achieved could be noticed with contaminated soil (treatment 2), 95% establishment with treatment 4, and with all other treatments crop establishment was around 90% of the optimum establishment achieved with the check treatment.

Knowing that in the first year of research when the same crop of the same type was in the pots, the establishment with some treatments was only 30% of the optimum establishment, the differences recorded this year are not considered to be statistically significant, except treatment 2 where was recorded lower number of plants. In correlation with check treatment the treatment where crude fresh oil was used yield was significantly smaller (Table 4).

In the latest year of research presented in this paper (in autumn 2006 barley variety *Rex* was sown again in pots), in July 2006 the soybean was sown again, but this time another cultivar – *Dora*: 0-00 maturity group. In relation to 2005 when soybean type *Sabina* was sown in pots, this year, crop establishment (the number of emerged plants) was significantly different. This requires clarification of the difference in the number of emerging plants with the check treatment in these two years when in both cases the soybean was sown in the pots. *Sabina* is a type of soybean which is sown with higher target plant population: 1.400.000 plants per hectare, while *Dora* is a type which is sown in the target plant population of 650.000 plants per hectare. This accounts for the difference in the number of emerged plants. However, based on recorded crop establishment, it can be assumed with a great degree of probability that these differences will not be great or statistically significant (Table 5).

The presented results of three-year research and growth of five crops indicate that incidents caused by various oil well operations result in soil changes and changes in the plant material or yield. Similar conclusion results in their research bring forth: Riser, 1998; Rhykerd et al., 1999; Maila and Cloete, 2005; King et al., 2006; Osuji and Onojake, 2006. The changes are particularly noticeable during the first year followed by the obvious decrease in changes in the following years. Similarly, the differences in yield and crop establishment between stubble crops and spring crops were observed. Since these are investigations of plant growth in pots, all doubts arising out of such research will be addressed in the three-year field research yet.

Thanks to financial contribution of INA Exploration and Production and to an international European project "Development of Programme for Constant Monitoring of Croatian Soils Including the Pilot Project – LIFE05 TCY/CRO/000105" a field project (near Nature Park Lonjsko polje) was set up using very similar methodology.

Conclusions

In the first year of research the degree of oil contamination of soil was crucial for yields achieved and all other investigated parameters. The largest number of plants was recorded with the check treatment; a significantly smaller number of plants was recorded with treatments 4; 6; 7 and 8. This only confirms the presumption that the effect of increased soil contaminant is the most adverse in the emerging stage, which is when crops are established. The plants which emerged with delay will go through all stages of growth, but due to poorer establishment, yield shall be lower. During the second and the third year of research when winter barley and winter wheat respectively were sown in the pots no such significant differences in crop establishment and yield achieved were recorded. Expectedly, the best results were recorded with the check soil treatment; crop establishment and yield achieved with others, oil contaminated treatments were barely statistically significant.

When soybean (cultivar: Sabina) was planted, the best results were with check soil treatment, while crop establishment and yield achieved with other treatments were statistically lower than with the check treatment. The next year (cultivar Dora) crop establishment with all treatments was uniform and did not differ statistically. These investigations have been planned as a five-year research and its continuation shall help to clarify certain doubts.

It is not our intention to name any institution in particular; however, we think that all those that wish and those that should have as a goal to protect natural resources of Croatia could consider joining this research to help preserve our environment for generations to come.

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