

**SOME PROPERTIES OF SOIL CONTAMINATED
WITH FUEL OIL AFTER APPLICATION
OF DIFFERENT SUBSTANCES**

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Key words: heating oil contamination, nitrogen, compost, bentonite, zeolite, calcium oxide, soil properties.

A b s t r a c t

The study has been undertaken in order to determine the influence of different substances (nitrogen, compost, bentonite, zeolite and calcium oxide) on selected properties of soil contaminated with fuel oil. The analyzed properties of soil proved to be dependent on the fuel oil contamination and application of different substances. The experiment was set up on acid soil which was contaminated with fuel oil in the following amounts: 0, 5, 10, 15 and 20 g kg⁻¹ d.m. of soil. Fuel oil raised the soil's pH but depressed its hydrolytic acidity, total exchangeable bases and cation exchange capacity. Among the substances applied to soil in order to neutralize the effect of contamination with fuel oil, bentonite and calcium oxide had the strongest influence on the soil's properties. They raised the soil's pH, total exchangeable bases and cation exchange capacity but lowered its hydrolytic acidity. The influence produced by the remaining tested substances, and nitrogen or compost in particular, on the examined characteristics of soil was relatively weak.

**WYBRANE WŁAŚCIWOŚCI GLEBY ZANIECZYSZCZONEJ OLEJEM OPAŁOWYM
PO APLIKACJI RÓŻNYCH SUBSTANCJI**

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Słowa kluczowe: zanieczyszczenie olejem opałowym, azot, kompost, bentonit, zeolit, tlenek wapnia, właściwości gleb.

A b s t r a k t

Celem badań było określenie wpływu różnych substancji (azotu, kompostu, bentonitu, zeolitu i tlenku wapnia) na wybrane właściwości gleby zanieczyszczonej olejem opałowym. Doświadczenia przeprowadzono na glebie kwaśnej zanieczyszczonej rosnącymi dawkami oleju opałowego: 5, 10, 15 i 20 g kg⁻¹ gleby. Badane właściwości gleby wykazywały uzależnienie od zanieczyszczenia olejem opałowym i aplikacji do gleby różnych substancji. Olej opałowy spowodował zwiększenie pH gleby, a zmniejszenie kwasowości hydrolitycznej, sumy wymiennych kationów zasadowych i całkowitej pojemności wymiennej. Spośród substancji zastosowanych w celu łagodzenia wpływu zanieczyszczenia gleby olejem opałowym najsilniej na właściwości gleby działały bentonit i tlenek wapnia, które spowodowały wzrost pH gleby, sumy wymiennych kationów zasadowych i całkowitej pojemności wymiennej oraz obniżenie kwasowości hydrolitycznej gleby. Wpływ pozostałych substancji, a zwłaszcza azotu i kompostu, na badane właściwości gleby był stosunkowo niewielki.

Introduction

Intensive growth of industry and agriculture necessities constant use of large quantities of fuels, which must be transported and stored to be used for different purposes (WYSZKOWSKI et al. 2004). Fuel transport and storage may cause contamination of the natural environment, including soils and the ground. Petroleum substances are responsible for extensive changes in soil properties, both biological (WYSZKOWSKA and WYSZKOWSKI 2010, XU et al. 1996) and physicochemical ones (CARAVACA and RODÁN 2003), often inhibiting (WYSZKOWSKI et al. 2004) or – when the contamination is very heavy – halting the growth and development of plants (MCGRATH 1992, OGBOGHODO et al. 2004). Such contaminated soils must be submitted to neutralization. Heavy soil pollution resulting from some breakdowns during fuel transport means that contaminated soils must be *ex-situ* reclaimed, which requires high financial outlays. When small quantities of petroleum substances permeate into soils, much less expensive *in-situ* reclamation technologies are applicable. Unfortunately, they are less effective (ZIÓŁKOWSKA and WYSZKOWSKI 2010), although can be successful when small-scale soil contamination is treated.

Therefore, a study has been undertaken in order to determine the influence of different substances on selected properties of soil contaminated with fuel oil.

Material and Methods

Experiment design. The experiment was set up in a greenhouse at the University of Warmia and Mazury in Olsztyn, on acid soil which was contaminated with fuel oil in the following amounts: 0, 5, 10, 15 and 20 g kg⁻¹ d.m. of soil. The soil tested in the experiment had the following characteristics: pH in 1 mol KCl dm⁻³ – 4.52; hydrolytic acidity (HAC) – 25.4 mmol(+) kg⁻¹; total exchangeable bases (TEB) – 85.3 mmol(+) kg⁻¹; cation exchange capacity

(CEC) – 110,7 mmol(+) kg⁻¹; base saturation (BS) – 77.1%; C_{org.} content – 11.3 g kg⁻¹; content of available forms of phosphorus – 71.9 mg P kg⁻¹; potassium – 118.6 mg K kg⁻¹ and magnesium – 104.2 mg Mg kg⁻¹. The experiment was run in five series: without any soil amending substances and with the application of nitrogen (200 mg N kg⁻¹ of soil), compost (270 g kg⁻¹ of soil), bentonite and zeolite (180 g kg⁻¹ of soil) and 50% of calcium oxide in a rate corresponding to one full hydrolytic acidity (11.7 g kg⁻¹ of soil). In addition, all the pots were enriched with macro- and micronutrients in the following quantities [in mg kg⁻¹ of soil]: N – 100 CO(NH₂)₂, P – 30 (KH₂PO₄); K – 100 (KH₂PO₄ + KCl); Mg – 50 (MgSO₄ · 7H₂O); Mn – 5 (MnCl₂ · 4H₂O); Mo – 5 [(NH₄)₆Mo₇O₂₄ · 4H₂O]; B – 0.33 (H₃BO₃). The petroleum substances, compost, bentonite and lime as well as the macro- and micronutrients in the form of aqueous solutions were mixed with 9 kg of soil when the experiment was set up and placed in polyethylene pots. Next, maize (*Zea mays* L.) cv. Reduta was sown. During the experiment, the soil relative moisture was maintained at 60% of capillary water capacity. Soil samples for analyses were taken during the harvest of maize in the intensive stem elongation phase.

Analysis of samples. The sampled soil was dried and passed through a 1 mm mesh sieve. The following determination were made: soil reaction (pH) with the potentiometric method in an aqueous solution of KCl in the concentration of 1 mol dm⁻³, hydrolytic acidity (HAC) and total exchangeable bases (TEB) – by Kappen's method (LITYŃSKI et al. 1976). From the hydrolytic acidity (HAC) and total exchangeable bases (TEB), the cation exchange capacity (CEC) and base saturation (BS) were computed according to the following formulas: CEC = TEB + HAC; BS = TEB · CEC⁻¹ · 100. Additionally, before the experiment was set up, the soil was tested for its content of organic carbon (C_{org.}) with Tiurin's method (LITYŃSKI et al. 1976), as well as the content of available phosphorus and potassium with Egner-Riehm's method (LITYŃSKI et al. 1976) and available magnesium with Schachtschabel's method (LITYŃSKI et al. 1976). The results underwent statistical processing with the two-factorial analysis of variance tests, using for that purpose the software Statistica (StatSoft, Inc. 2014). Dependences between oil contamination with fuel oil and the analyzed soil's attributes were also tested with Pearson's simple correlation tests.

Results and Discussion

Fuel oil contamination of soil and its amendment with different substances had significant influence on the analyzed soil properties. Fuel oil raised the soil's pH (to 10 g of fuel oil per 1 kg of soil) but depressed its hydrolytic acidity

(Table 1). In the series without any substances added to soil, the range of soil's pH increase ($r = 0.738$) and decrease in its hydrolytic acidity ($r = -0.904$) were comparable. In the series without soil amending substances, fuel oil depressed the total exchangeable bases ($r = -0.932$) and the cation exchange capacity ($r = -0.937$) but did not cause any large changes in the base saturation (Table 2). The biggest changes of the total exchangeable bases and the cation exchange capacity were caused by the rate of 15 g of fuel oil per 1 kg of soil. Both the total exchangeable bases and cation exchange capacity declined by the same percentage (11%) under the influence of this rate of the contaminant.

Table 1
pH and hydrolytic activity (HAC) in soil after maize harvest

Dose of fuel oil in [g kg ⁻¹ of soil]	Kind of substance neutralizing effect of heating oil						
	without additions	nitrogen	compost	bentonite	zeolite	CaO	average
pH in KCl							
0	4.62	4.57	5.02	6.71	5.33	6.59	
5	4.91	5.33	5.06	6.96	5.63	7.00	
10	5.32	5.10	5.25	7.00	5.58	7.24	
15	5.26	5.02	5.51	6.91	5.44	7.20	
20	5.11	5.05	5.37	6.94	5.67	7.02	
<i>r</i>	0.738**	0.372	0.880**	0.572	0.547	0.650*	
LSD	a - 0.02**, b - 0.02 **, a · b - 0.04**						
Hydrolytic activity (HAC), [mmol(+) kg ⁻¹ of soil]							
0	22.9	25.2	23.4	12.2	22.7	16.5	20.5
5	22.8	19.4	23.1	14.4	25.3	15.0	20.0
10	21.7	21.0	20.8	16.9	27.4	15.6	20.6
15	20.0	22.2	19.4	15.0	30.4	13.0	20.0
20	20.6	24.3	20.6	11.4	27.5	15.1	19.9
Average	21.6	22.4	21.5	14.0	26.7	15.0	20.2
<i>r</i>	-0.904**	0.067	-0.854**	-0.071	0.812**	-0.590	-0.585
LSD	a - n.s., b - 0.9**, a · b - 2.1**						

LSD for: *a* - heating oil dose, *b* - kind of neutralizing substance, *a · b* - interaction; significant for: ** - $p = 0.01$, * - $p = 0.05$, n.s. non-significant; *r* - correlation coefficient

Soil pollution with petroleum substances causes many changes in soil quality (OGBOGHODO et al. 2004, WYSZKOWSKA and WYSZKOWSKI 2010, ZIÓŁKOWSKA and WYSZKOWSKI 2010). Their actual effect on soil attributes depends on the type and degree of contamination with petroleum substances. Diesel oil generally causes larger changes than other petroleum products, e.g. petrol. BARAN et al. (2002) determined elevated pH, total base cations and cation exchange capacity near point sources of contamination with petroleum substances on the premises of a military airfield in Dęblin, compared to less

Table 2
Total exchangeable bases (TEB), cation exchange capacity (CEC) and base saturation (BS) in soil after maize harvest

Dose of fuel oil in [g kg ⁻¹ of soil]	Kind of substance neutralizing effect of heating oil						
	without additions	nitrogen	compost	bentonite	zeolite	CaO	average
Total exchangeable bases (TEB), [mmol(+) kg ⁻¹ of soil]							
0	104.9	95.3	100.0	125.8	88.7	108.7	103.9
5	100.0	99.8	93.3	136.4	99.9	107.7	106.2
10	99.4	95.4	93.9	140.3	90.9	122.2	107.0
15	93.3	103.5	95.3	132.1	92.3	127.0	107.2
20	94.5	104.7	99.8	130.7	100.7	112.1	107.1
Average	98.4	99.7	96.5	133.0	94.5	115.5	106.3
<i>r</i>	-0.932**	0.809**	0.078	0.157	0.475	0.480	0.843**
LSD	<i>a</i> -1.7**, <i>b</i> -1.8**, <i>a</i> · <i>b</i> - 4.1**						
Cation exchange capacity (CEC), [mmol(+) kg ⁻¹ of soil]							
0	127.8	120.5	123.4	138.0	111.4	125.2	124.4
5	122.8	119.2	116.4	150.8	125.2	122.7	126.2
10	121.1	116.4	114.7	157.2	118.3	137.8	127.6
15	113.3	125.7	114.7	147.1	122.7	140.0	127.2
20	115.1	129.0	120.4	142.1	128.2	127.2	127.0
Average	120.0	122.2	117.9	147.0	121.2	130.6	126.5
<i>r</i>	-0.937**	0.729*	-0.316	0.095	0.750**	0.432	0.781**
LSD	<i>a</i> - 1.9**, <i>b</i> - 2.1**, <i>a</i> · <i>b</i> - 4.6**						
Base saturation (BS), [%]							
0	82.1	79.1	81.0	91.2	79.6	86.8	83.3
5	81.4	83.7	80.2	90.4	79.8	87.8	83.9
10	82.1	82.0	81.9	89.2	76.8	88.7	83.4
15	82.3	82.3	83.1	89.8	75.2	90.7	83.9
20	82.1	81.2	82.9	92.0	78.5	88.1	84.1
Average	82.0	81.7	81.8	90.5	78.0	88.4	83.7
<i>r</i>	0.450	0.256	0.847**	0.145	-0.544	0.607*	0.766**
LSD	<i>a</i> - 0.6**, <i>b</i> - 0.6**, <i>a</i> · <i>b</i> - 1.4**						

LSD for: *a* - heating oil dose, *b* - kind of neutralizing substance, *a* · *b* - interaction; significant for: ** - *p*=0.01, * - *p*=0.05, n.s. non-significant; *r* - correlation coefficient

polluted soils. In contrast, KUCHARSKI and JASTRZEBSKA (2005) observed depressed pH, total exchangeable bases, cation exchange capacity and base saturation, a finding which is largely confirmed by the present study.

Application of the tested substances to soil, except nitrogen, favoured higher soil pH, with the strongest and comparable effects produced by bentonite and calcium oxide (Table 1). Bentonite and calcium oxide also caused highly significant decrease in the hydrolytic acidity, reaching 35 and 31%, respectively, in comparison to the series with no soil amendments. Zeolite produced a much weaker (24%) and reverse effect. The application of compost and

nitrogen as urea to soil did not result in any significant alterations of the soil's hydrolytic acidity.

Bentonite and calcium oxide had the strongest effect on the total exchangeable bases and cation exchange capacity of all the substances applied in order to alleviate the impact of soil contamination with fuel oil (Tables 1–2). They caused an increase in the total exchange bases, cation exchange capacity and – to a much smaller degree – the base saturation. Compared to the non-amended series, the total exchangeable bases and cation exchange capacity in soil rose by 35 and 23% under the influence of bentonite and by 17 and 9% when soil was neutralized with calcium oxide. Bentonite and calcium oxide also raised the base saturation by 9 and 6%, respectively. The other substances, and nitrogen (urea) or compost, had a much weaker neutralizing effect. Lime have positively effect on many soil properties (KACZOR et al. 2009). In research by WYSZKOWSKI and SIVITSKAYA (2015) and WYSZKOWSKI and ZIÓŁKOWSKA (2013), bentonite and calcium oxide had the strongest and most positive effect on the analyzed soil properties, especially hydrolytic acidity.

The application of neutralizing substances to soil may prove to be an effective measure in alleviating the effects of soil contamination with fuel oil. Studies completed by other researchers (BARAN et al. 2004, RIFFALDI et al. 2006, QUINTERN et al. 2006) suggest that organic substances, including compost, may have a beneficial effect on properties of soil contaminated with small amounts of fuel oil or petrol. They not only positively affect soil characteristics (BARAN et al. 2004, CZEKAŁA 1997) but also improve the growth and development of crops growing on such soil (KMEŤOVÁ and KOVÁČIK 2014, WYSZKOWSKI and ZIÓŁKOWSKA 2009). However, the above is true only when the soil contamination degree is small. More severe soil pollution with petroleum substances eliminates any possibility of crop cultivation (MCGRATH 1992, OGBOGHODO et al. 2004). Compost and other organic substances improve oxygenation of soil, thus accelerating the microbial decomposition of petroleum substances, besides, by producing a beneficial effect on the soil's sorptive properties, they improve the cycling of elements in the soil environment (ZIÓŁKOWSKA and WYSZKOWSKI 2010).

Conclusions

1. The analyzed properties of soil proved to be dependent on the fuel oil contamination and application of different substances.
2. Fuel oil raised the soil's pH but depressed its hydrolytic acidity, total exchangeable bases and cation exchange capacity.

3. Among the substances applied to soil in order to neutralize the effect of contamination with fuel oil, bentonite and calcium oxide had the strongest influence on the soil's properties. They raised the soil's pH, total exchangeable bases and cation exchange capacity but lowered its hydrolytic acidity.

4. The influence produced by the remaining tested substances, and nitrogen or compost in particular, on the examined characteristics of soil was relatively weak.

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